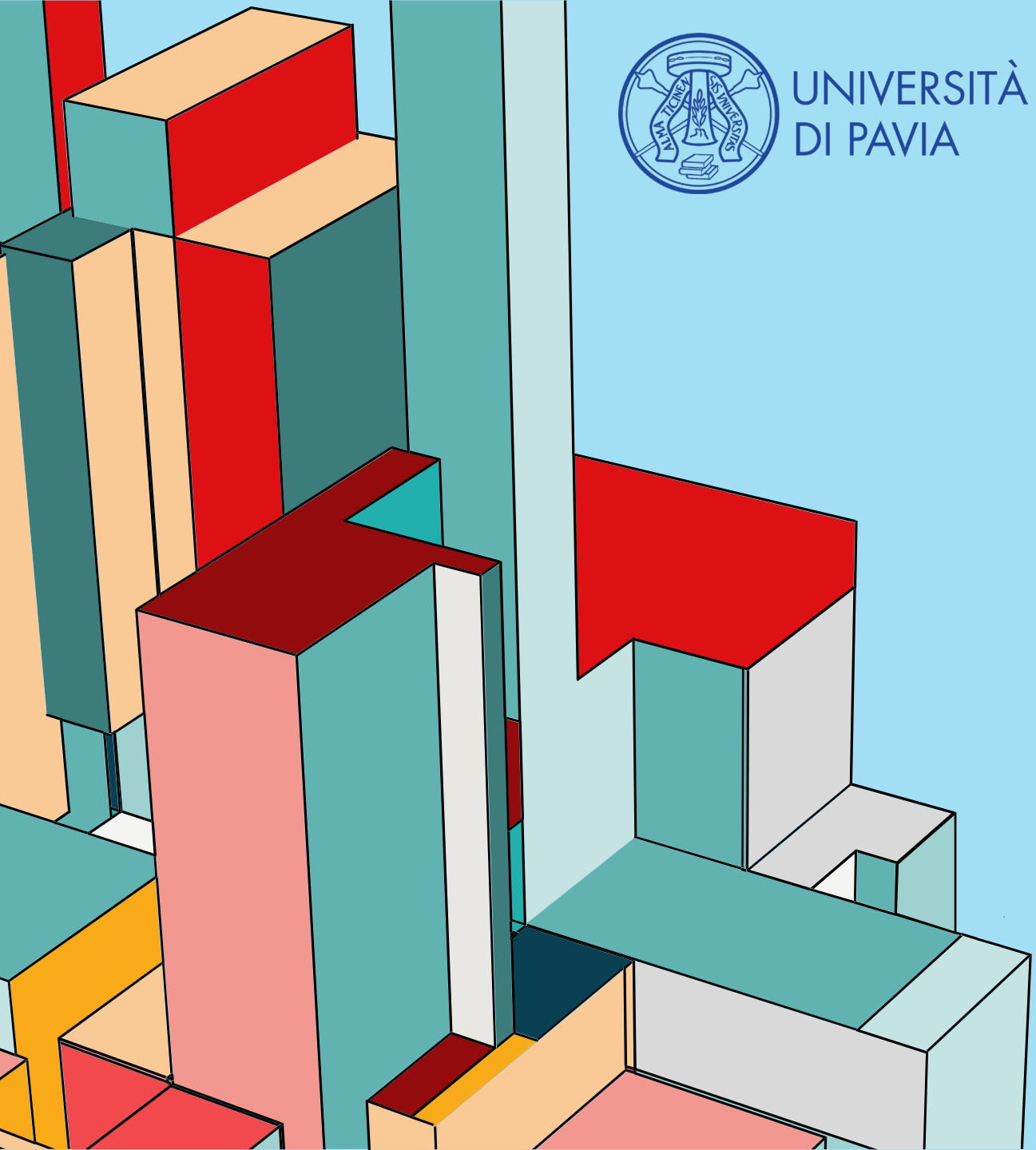


UNIVERSITÀ DI PAVIA

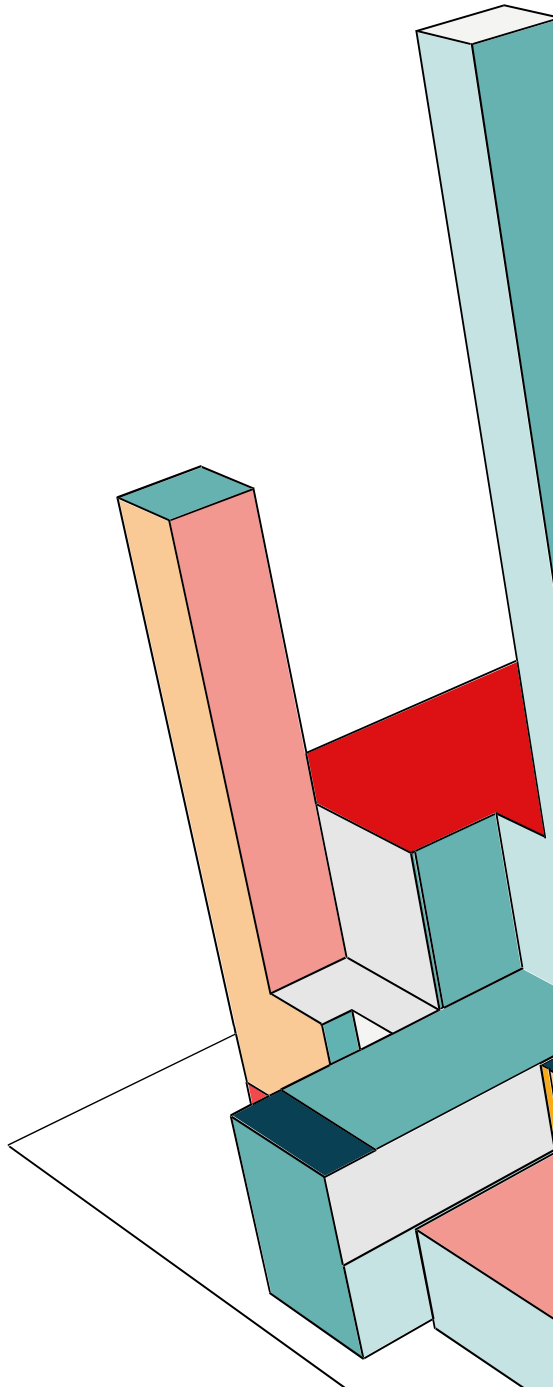
MODELING METHANE ABSORPTION IN CARTRIDGE

INFN
Istituto Nazionale di Fisica Nucleare

Paolo Vitulo

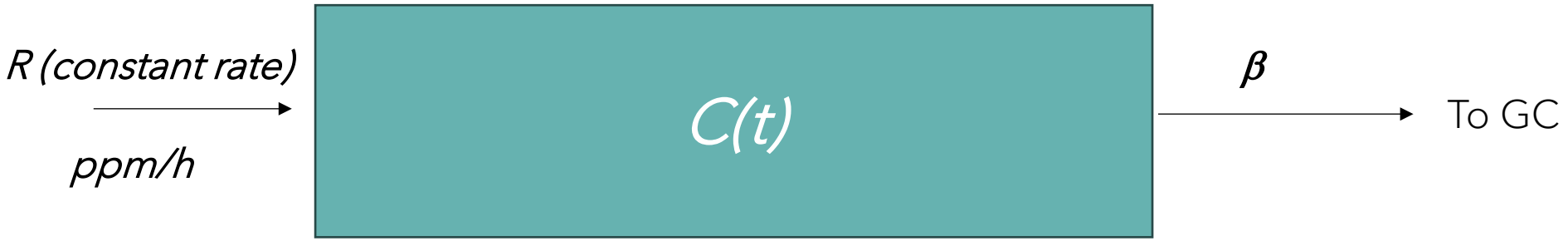
CH4rLiE Annual Meeting
Pavia 28 Jan, 2025

- The basic model
- Traffic island model
- CH4 absorbing curve
- Absorbed CH4: comparison with data
- Characteristic time of the process
- CH4 Leakage
- CH4 content in the gas mixture



THE BASIC MODEL

$$\frac{dC(t)}{dt} = R - \beta C(t)$$



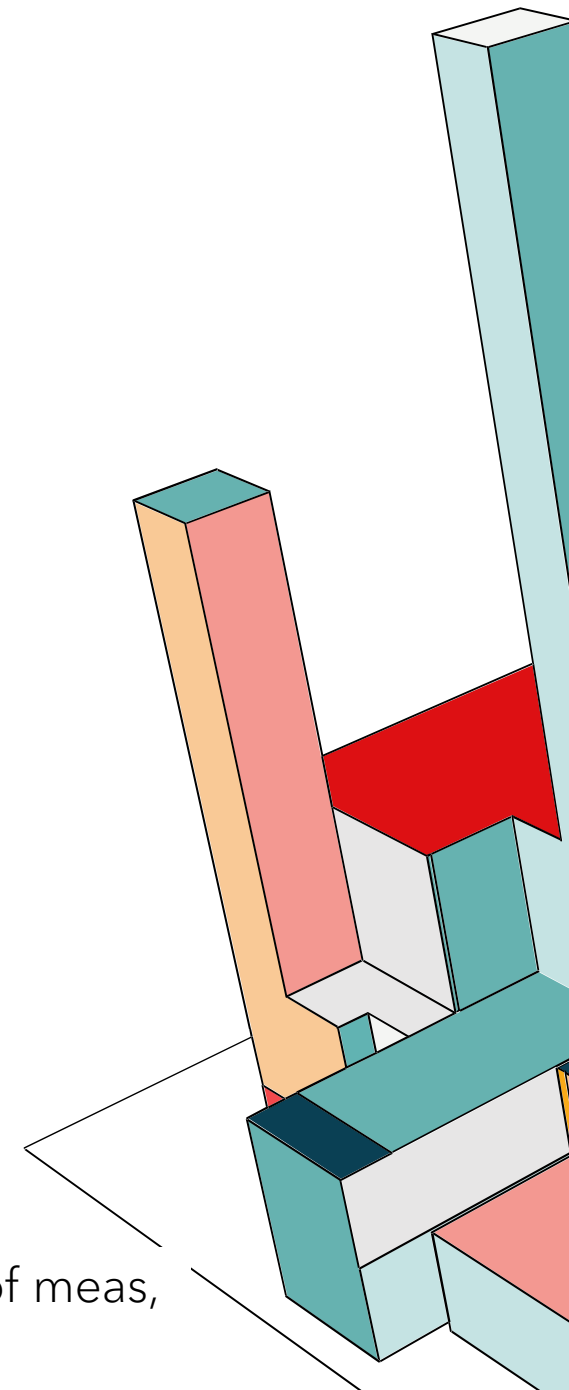
$$C(t) = \frac{R}{\beta} - \left(\frac{R}{\beta} - C_0\right) e^{-\beta t}$$

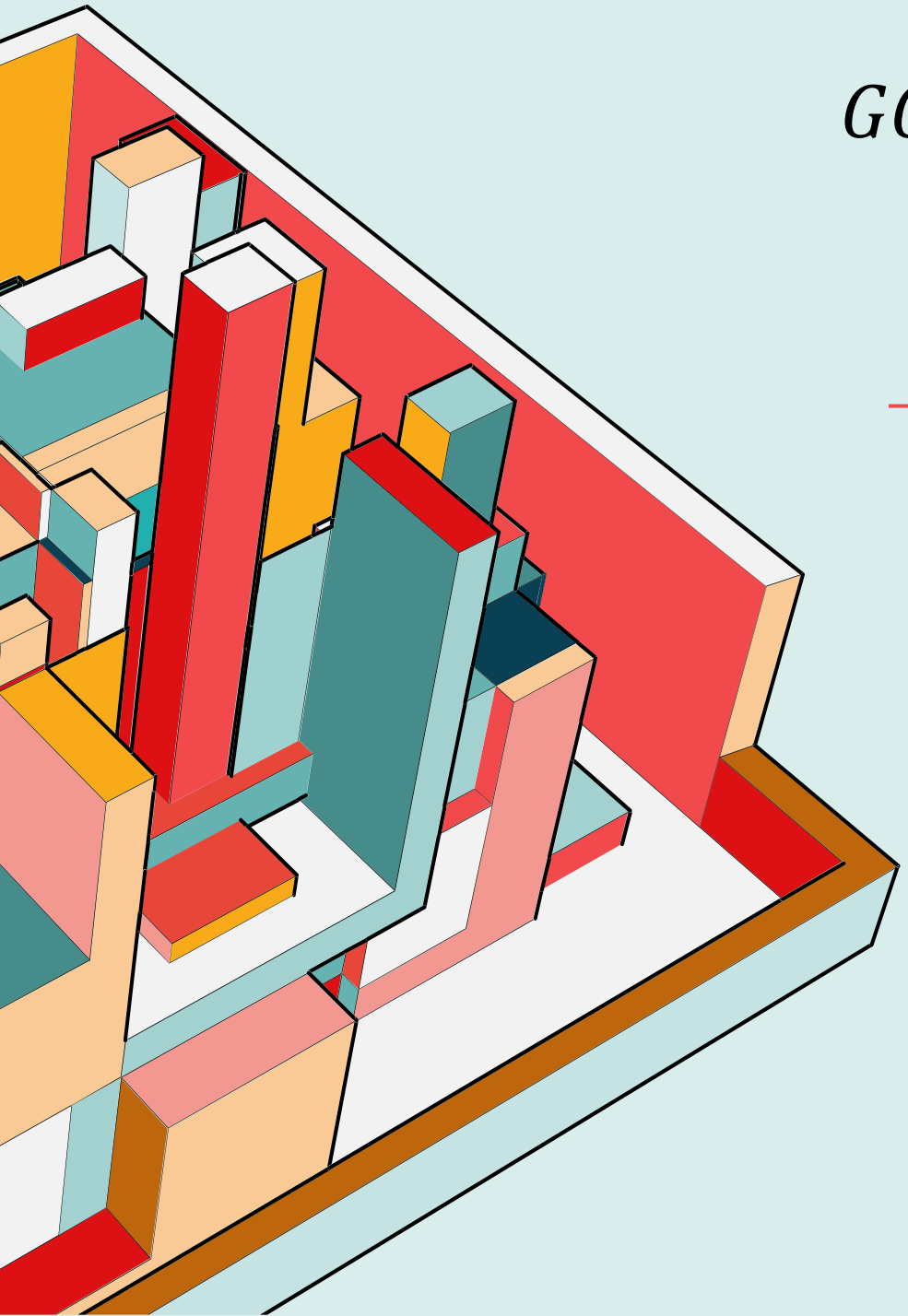
Methane concentration

The measurement at GC is taken into account through a time shift

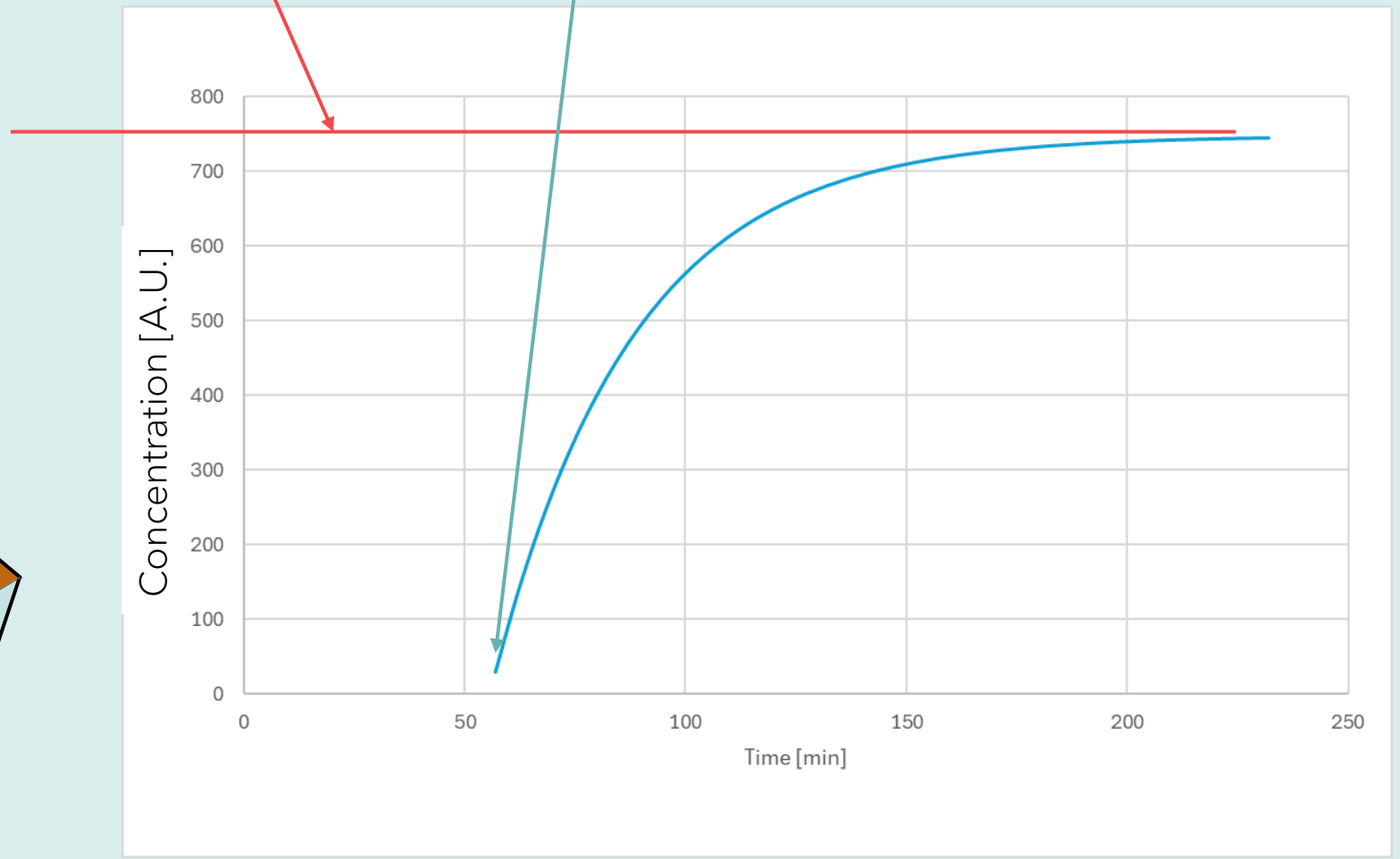
$$GC(t) = \frac{R}{\beta} - \left(\frac{R}{\beta} - C_0\right) e^{-\beta (t - t_m)}$$

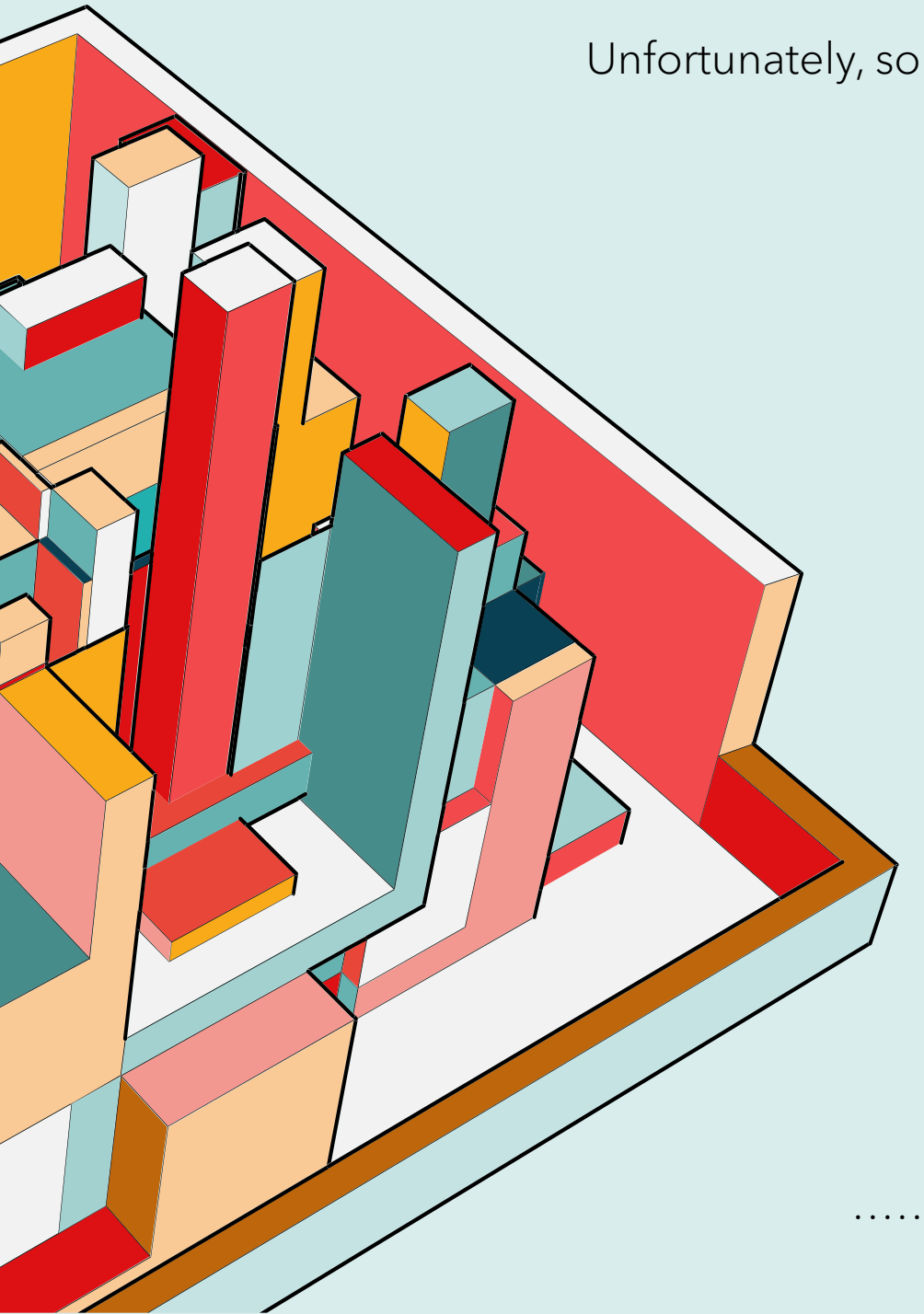
Residual concentration at the beginning of meas, or minimum detectable concentration



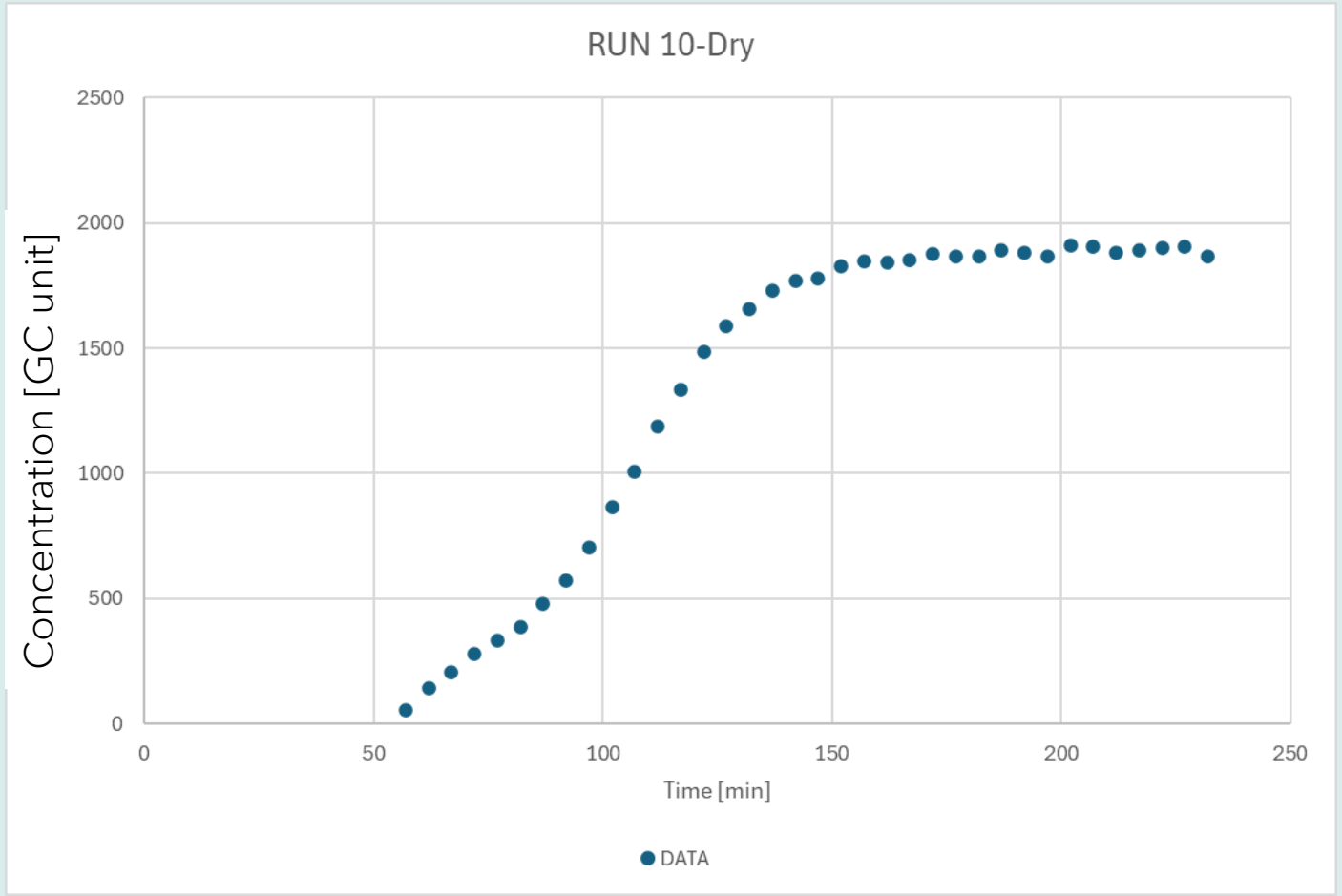


$$GC(t) = \frac{R}{\beta} - \left(\frac{R}{\beta} - C_0\right) e^{-\beta(t-t_m)}$$





Unfortunately, some data looks like this:

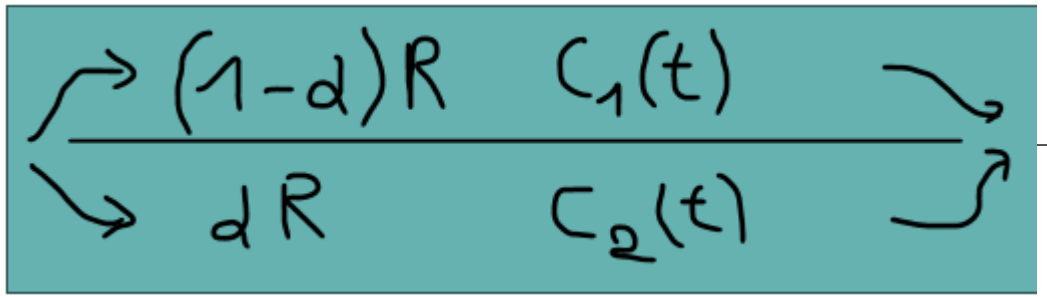


……back to the model…

TRAFFIC ISLAND MODEL

R (constant rate)

ppm/h



$\boldsymbol{\beta}$ → To GC

$$\begin{cases} \dfrac{dC_1(t)}{dt} = F_1 - \beta C_1(t) \\ \dfrac{dC_2(t)}{dt} = F_2 - \beta C_2(t) \end{cases}$$

Plus constraint: $F_1 + F_2 = R$

Dry runs had a leakage, so we left F1 and F2 unbound and later we extract the leakage from the fit.

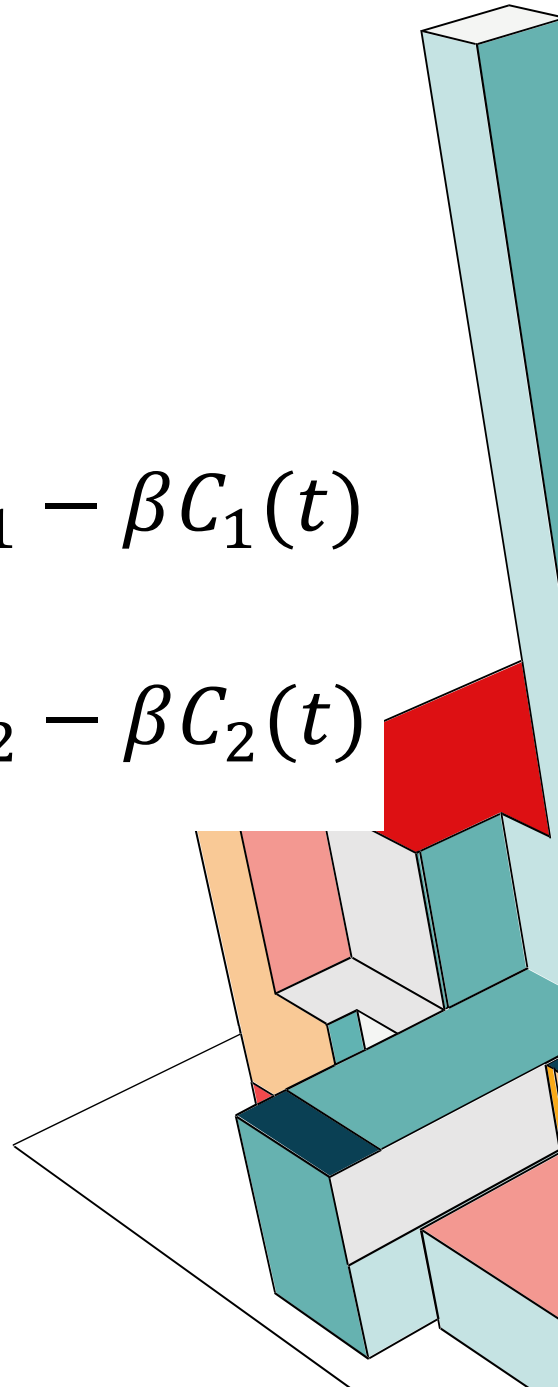
$$C_{1GC}(t) = (V_1 - Be^{-\beta(t-t_1)})\,\theta(t-t_1)$$

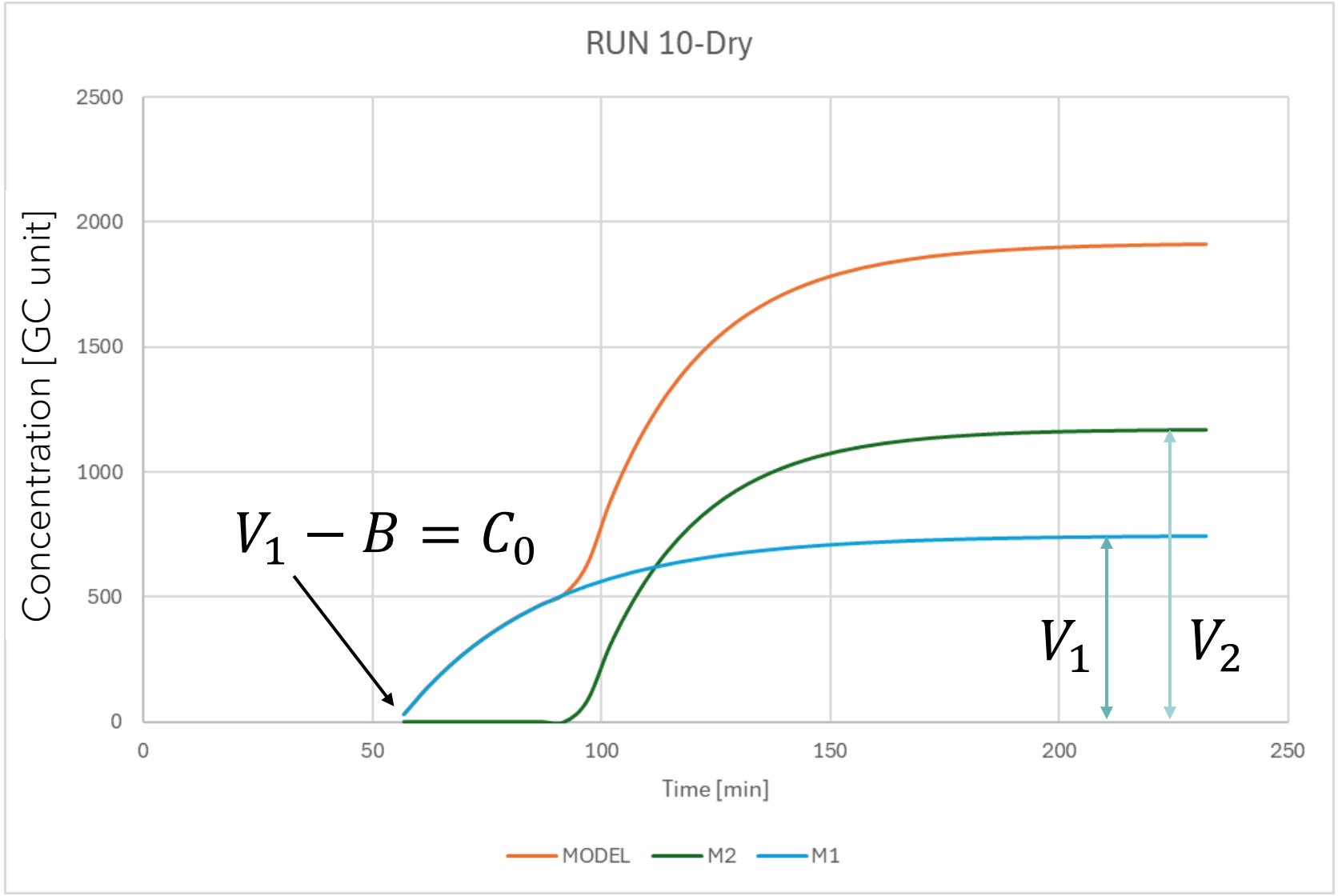
Early component

$$C_{2GC}(t) = V_2\left(1 - e^{-\beta(t-t_2)}\right)\theta(t-t_2)$$

Late component

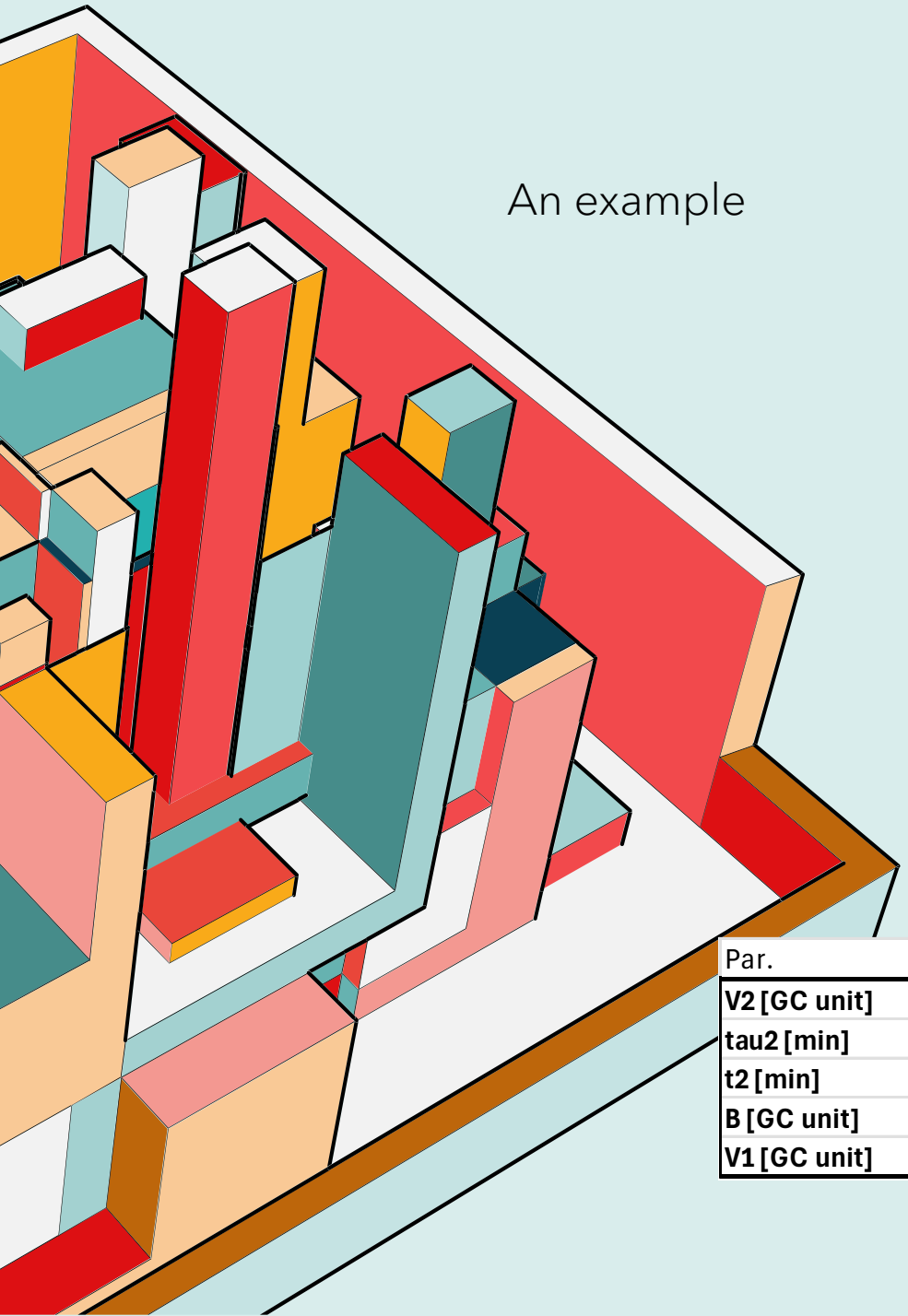
Heaviside



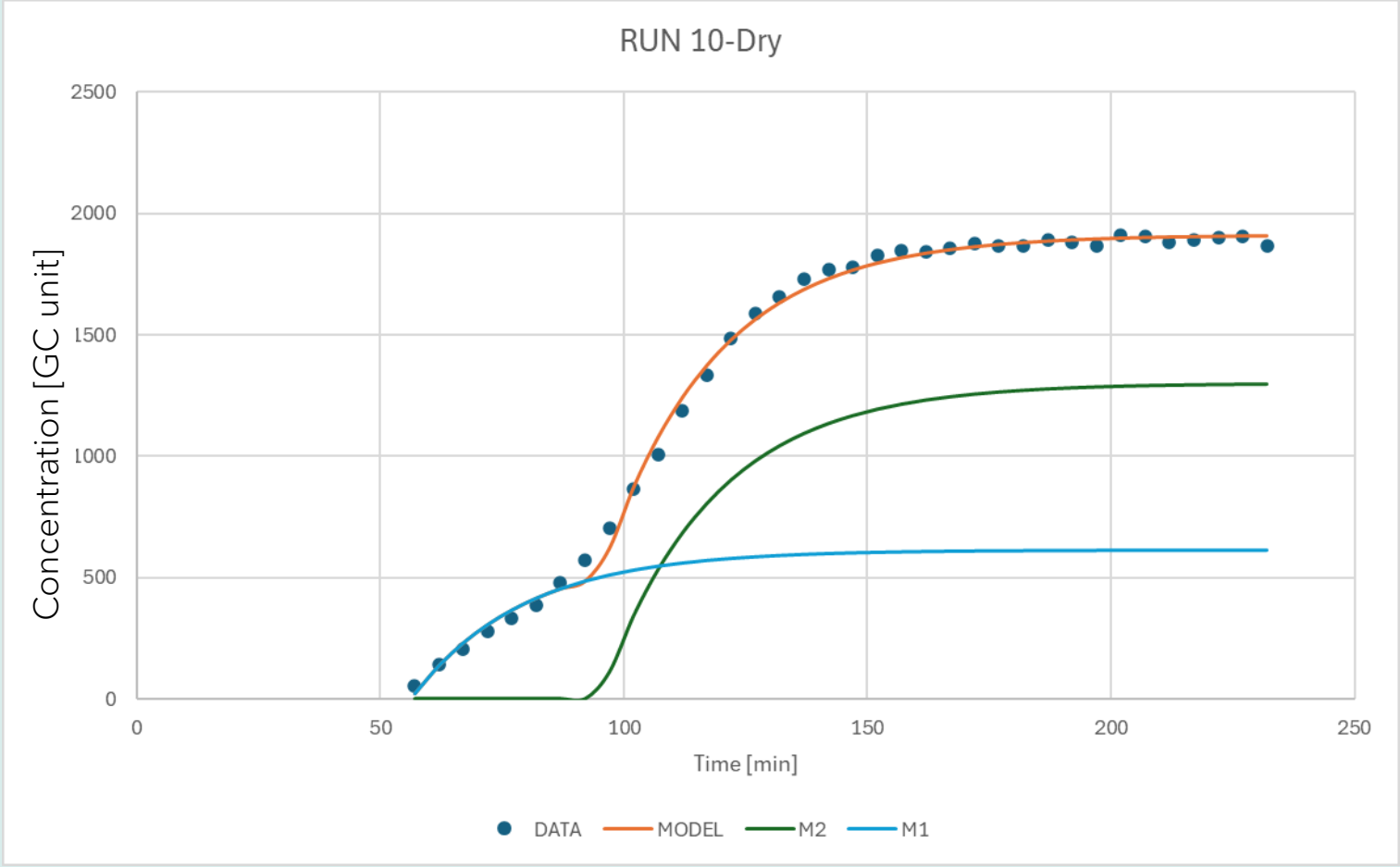


$$C_{1GC}(t) = (V_1 - Be^{-\beta_1(t-t_1)})\,\theta(t-t_1)$$

$$C_{2GC}(t) = V_2\left(1 - e^{-\beta_2(t-t_2)}\right)\theta(t-t_2)$$



An example



Par.	Value	Std. Err.	t calc.	Crit. t(.05)	Low. CI(.95)	Up. CI(.95)	Passed Prob.	Check	CV%
V2 [GC unit]	1299.0	29.2	44.4	2.0	1239.4	1358.6	1.22E-29	Ok	2.25
tau2 [min]	22.8	1.0	23.4	2.0	20.8	24.8	2.96E-21	Ok	4.28
t2 [min]	95.0	0.7	139.9	2.0	93.6	96.3	5.50E-45	Ok	0.71
B [GC unit]	591.4	47.6	12.4	2.0	494.3	688.4	1.40E-13	Ok	8.04
V1 [GC unit]	613.4	30.5	20.1	2.0	551.2	675.6	2.36E-19	Ok	4.97

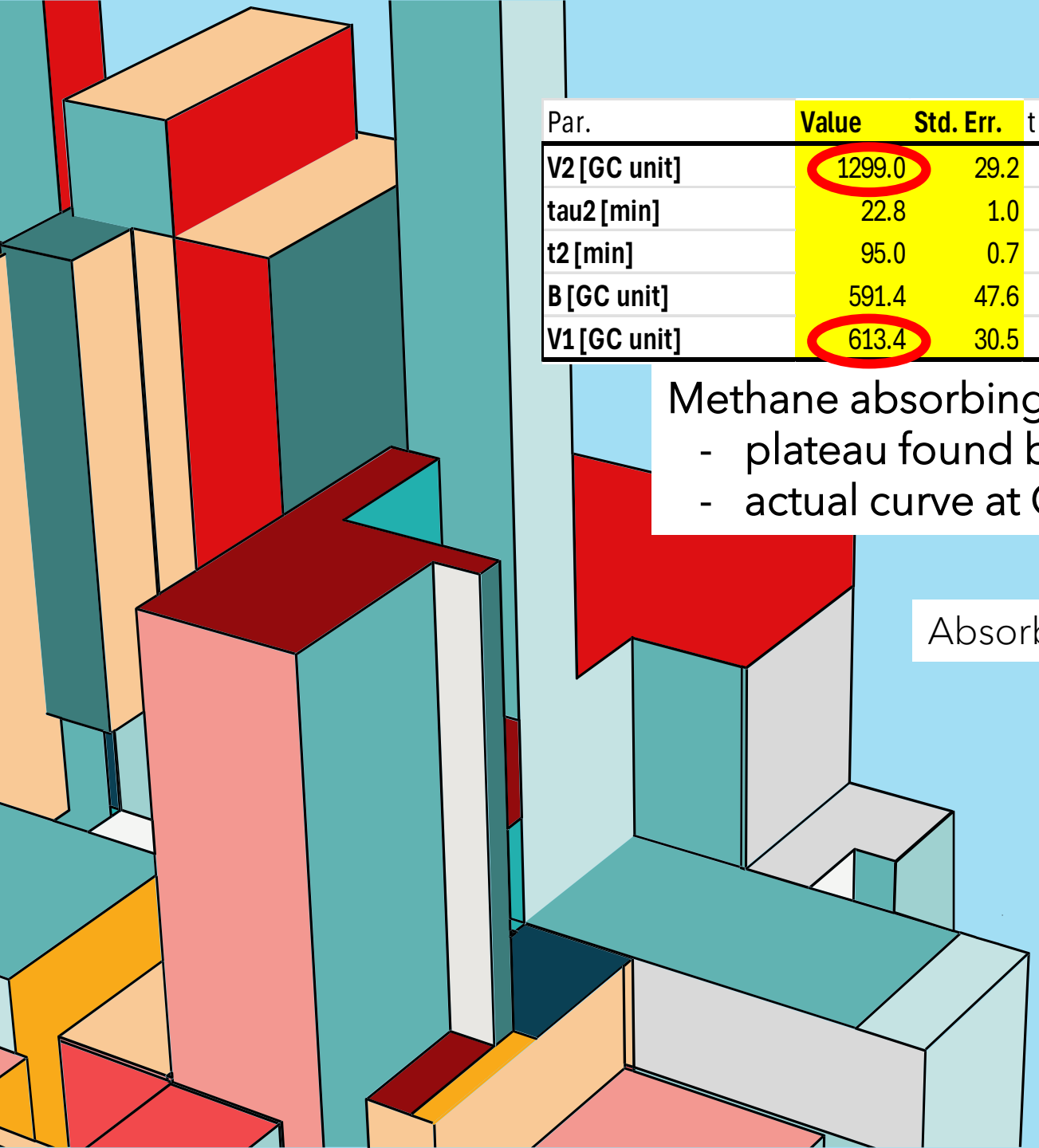
Solverstat output

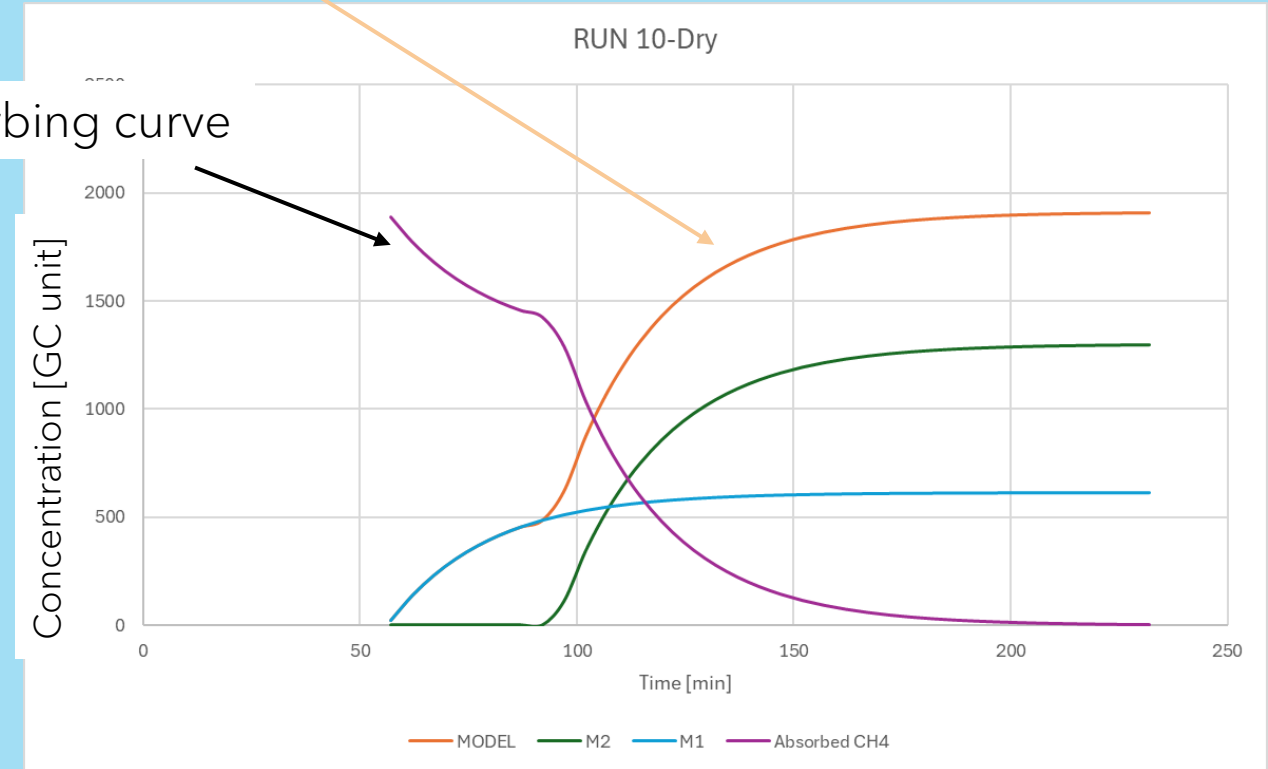
CH4 ABSORBING CURVE

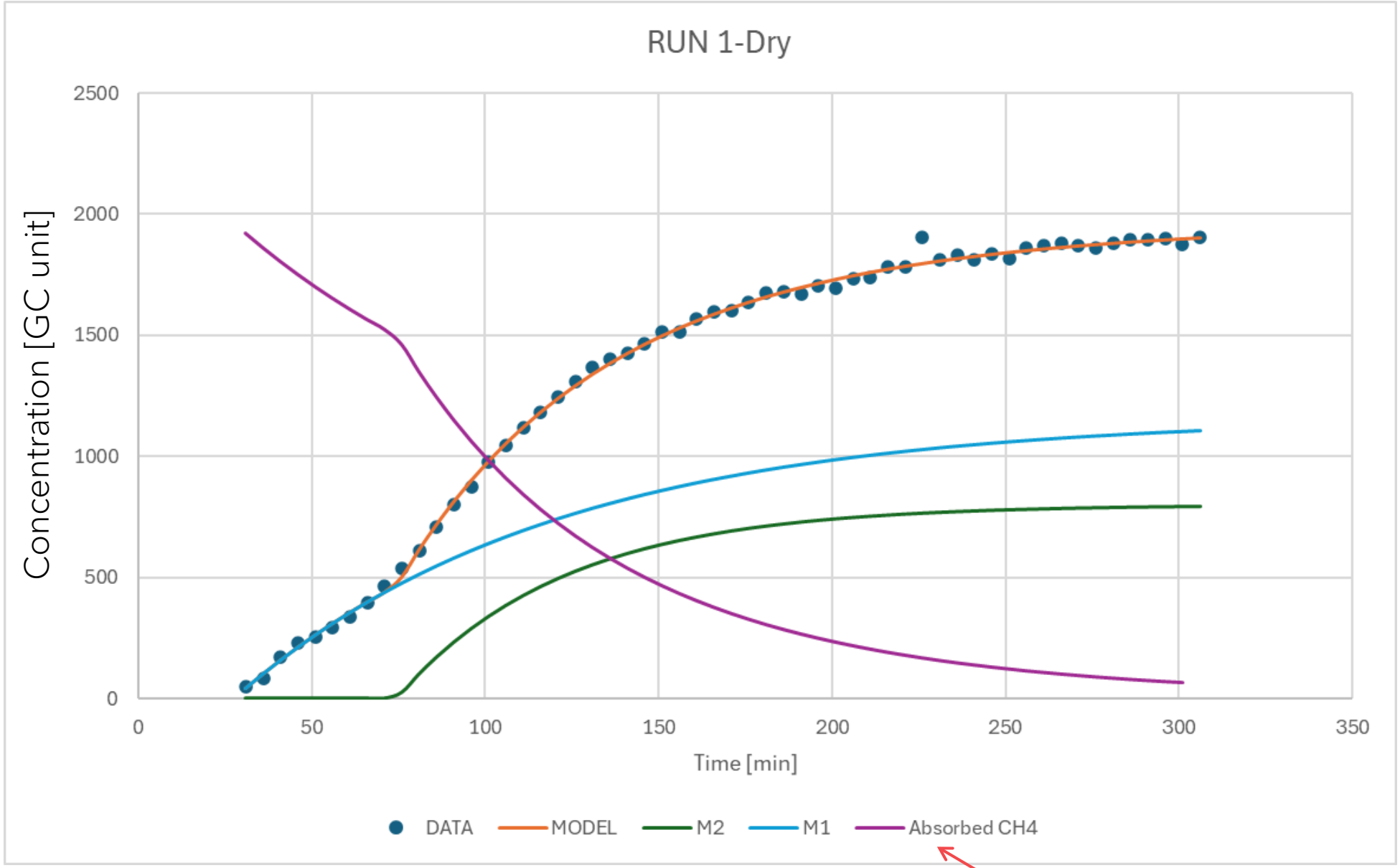
Par.	Value	Std. Err.	t calc.	Crit. t(.05)	Low. CI(.95)	Up. CI(.95)	Passed Prob.	Check	CV%
V2 [GC unit]	1299.0	29.2	44.4	2.0	1239.4	1358.6	1.22E-29	Ok	2.25
tau2 [min]	22.8	1.0	23.4	2.0	20.8	24.8	2.96E-21	Ok	4.28
t2 [min]	95.0	0.7	139.9	2.0	93.6	96.3	5.50E-45	Ok	0.71
B [GC unit]	591.4	47.6	12.4	2.0	494.3	688.4	1.40E-13	Ok	8.04
V1 [GC unit]	613.4	30.5	20.1	2.0	551.2	675.6	2.36E-19	Ok	4.97

Methane absorbing curve→ difference (point by point) between:

- plateau found by the fit (*V1+V2*), ie. CH4 at saturation (= IN –leaks)
- actual curve at GC (= OUT)



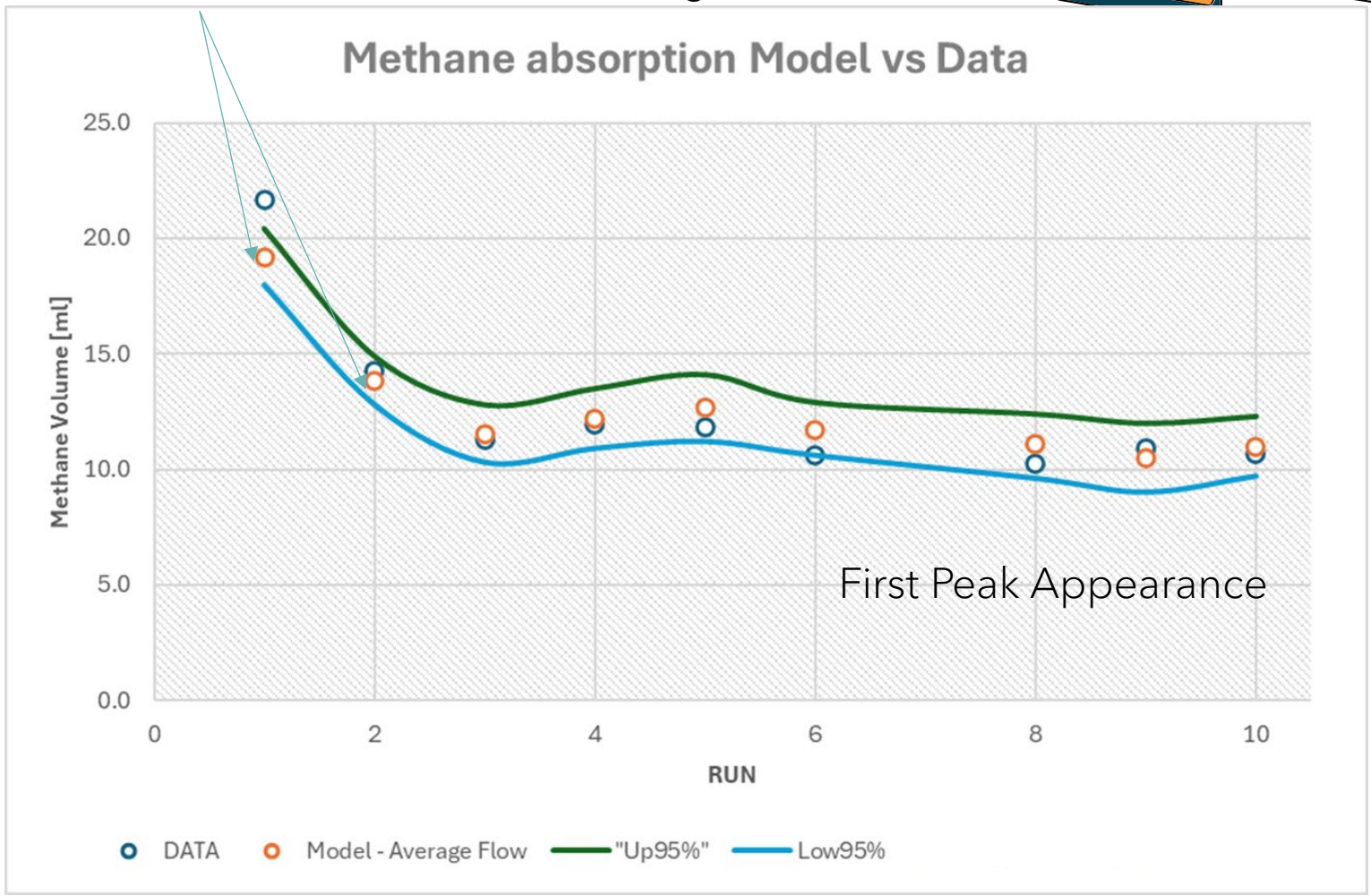




an example

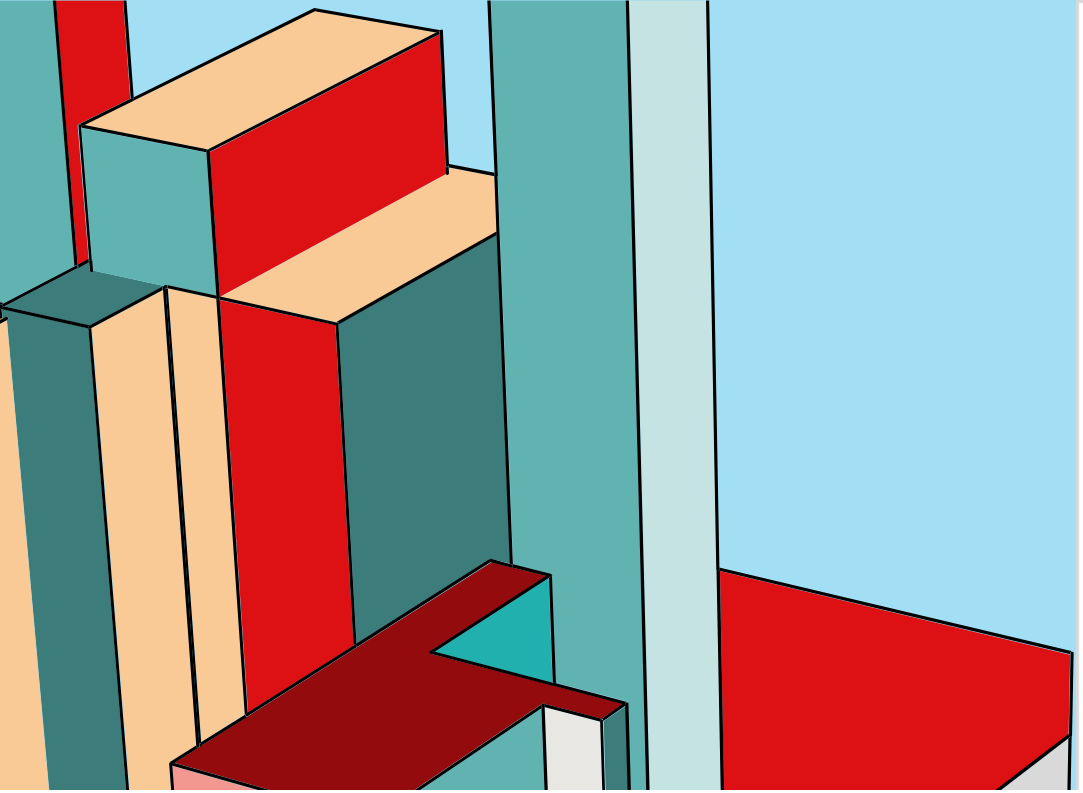
Integral: 20.7 ml

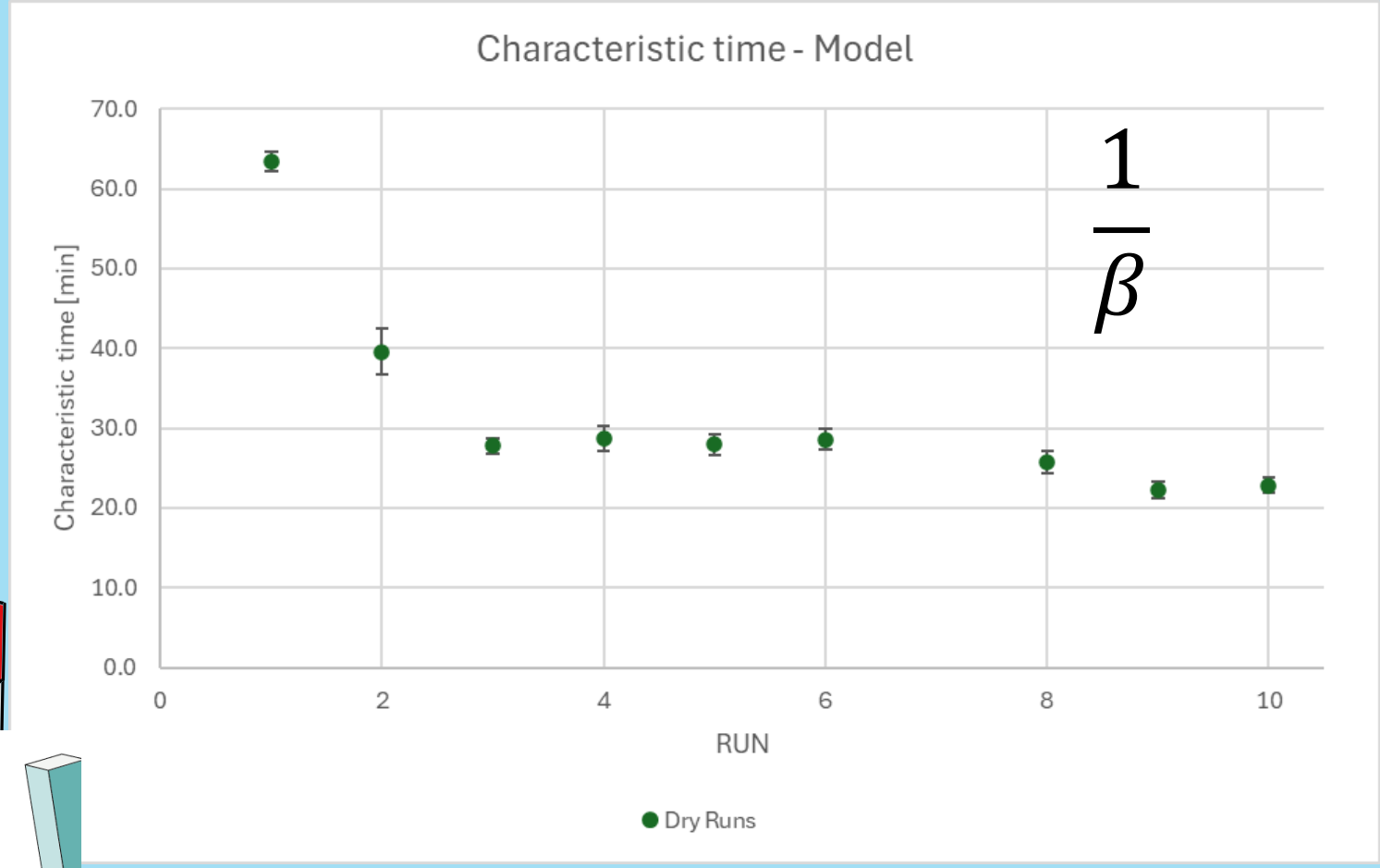
Mode of flow used instead of average flow



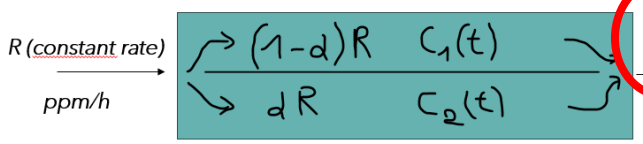
$$ME@95\% = t_{0.05,\nu} \times \sqrt{RSS/\nu}$$

ABSORBED CH4: COMPARISON WITH DATA (→FRANCESCO)





TRAFFIC ISLAND MODEL



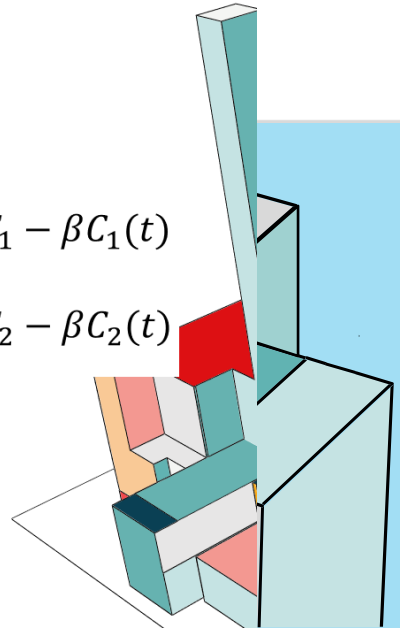
Plus constraint: $F_1 + F_2 = R$
Dry runs had a leakage, so we left F1 and F2 unbound and later we extract the leakage from the fit.

$$\begin{cases} \frac{dC_1(t)}{dt} = F_1 - \beta C_1(t) \\ \frac{dC_2(t)}{dt} = F_2 - \beta C_2(t) \end{cases}$$

$$C_{1GC}(t) = (V_1 - Be^{-\beta(t-t_1)})\,\theta(t-t_1)$$ Early component

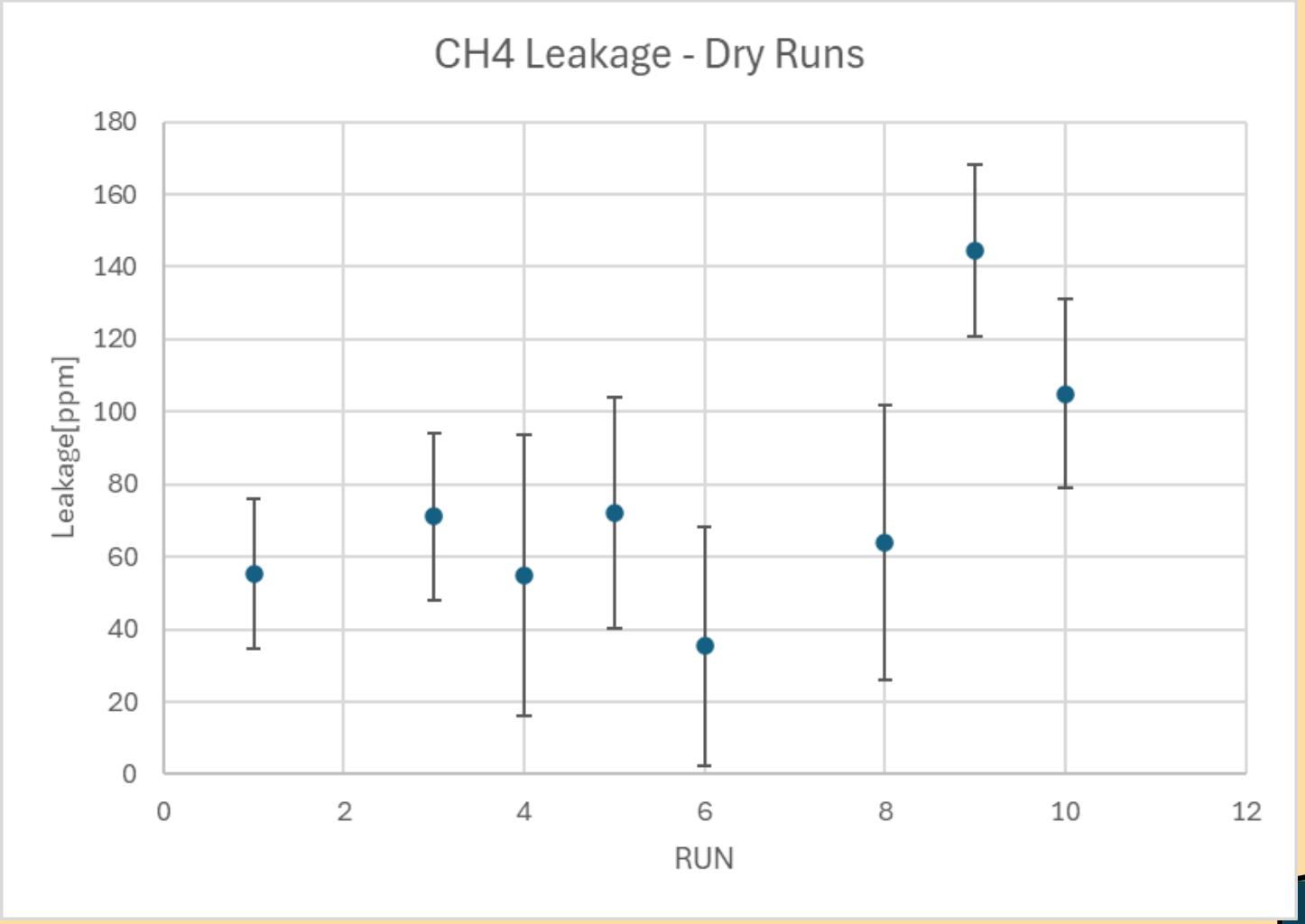
$$C_{2GC}(t) = V_2\left(1 - e^{-\beta(t-t_2)}\right)\theta(t-t_2)$$ Late component

Heaviside



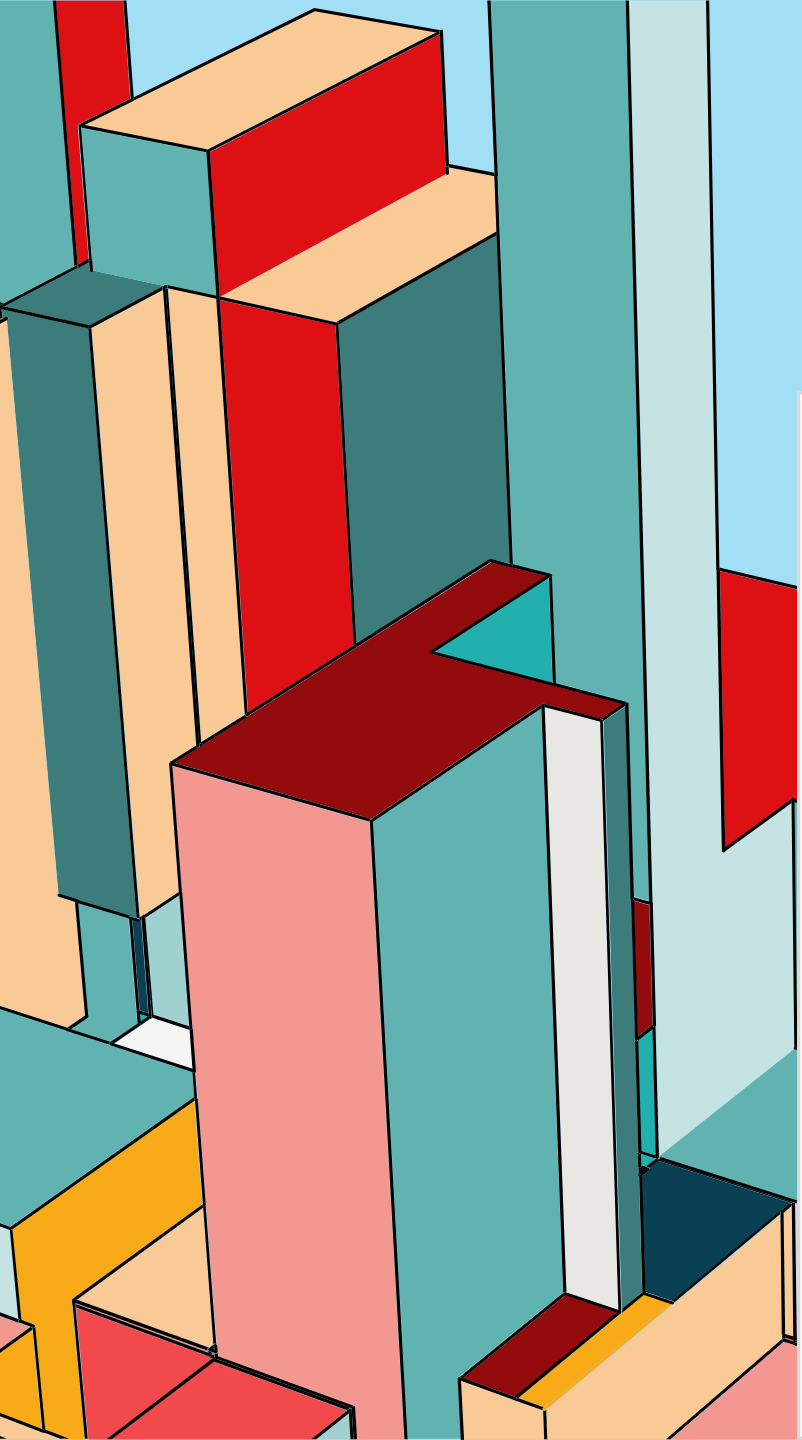
CHARACTERISTIC TIME

LEAKAGE



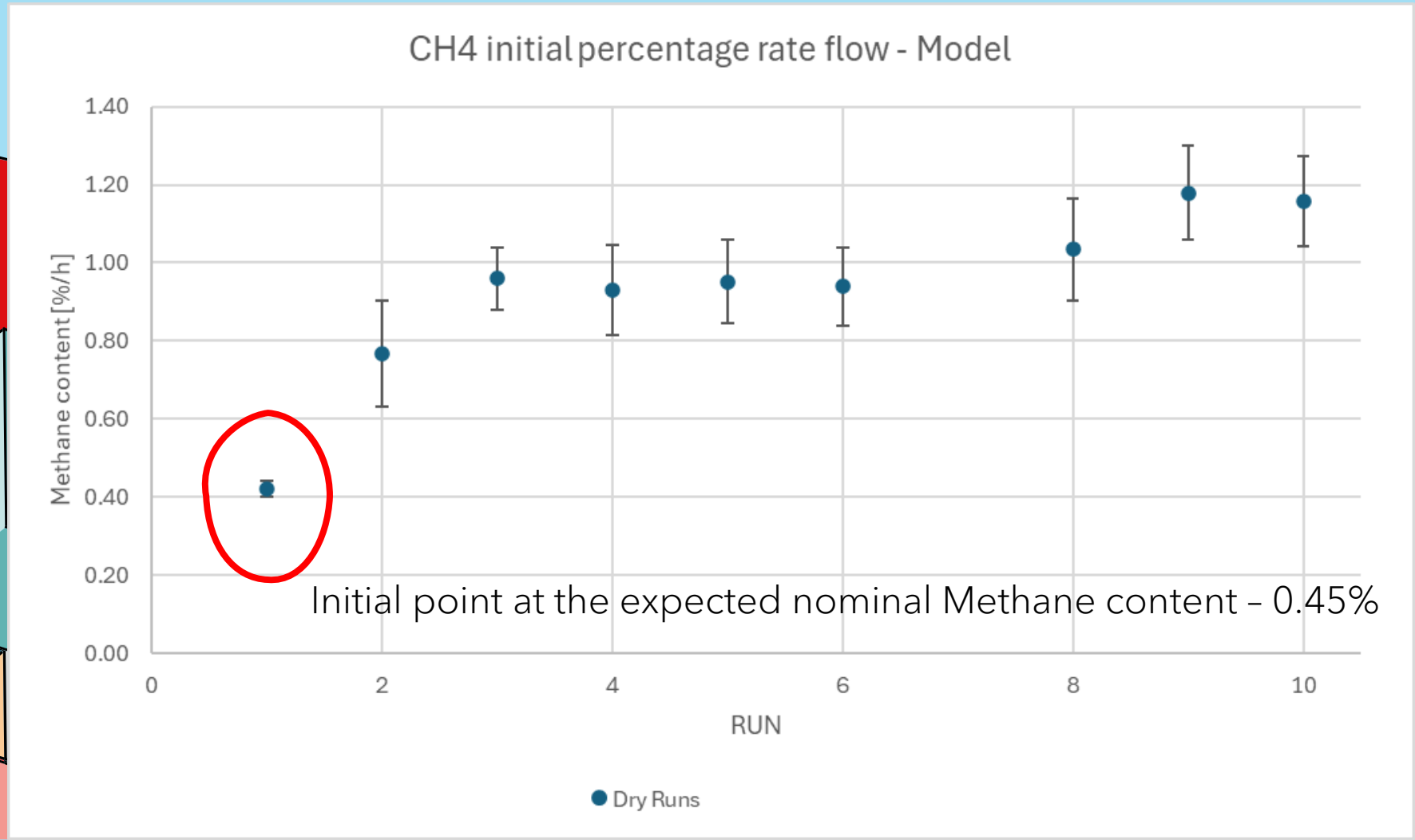
Dry runs had a leakage.

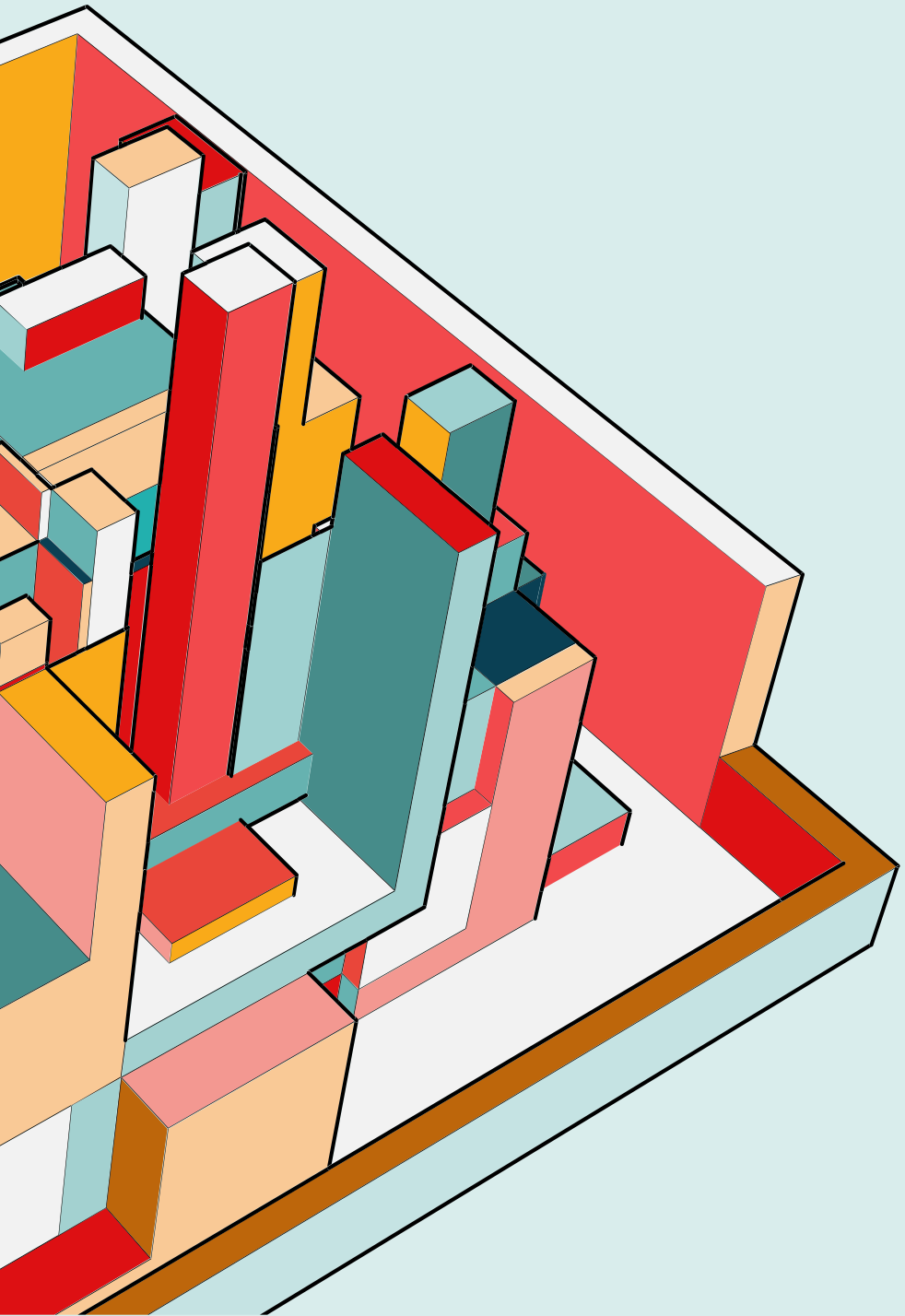
Here calculated by difference from GC calibration ($4509 \pm 12\ ppm$) and fitted plateau



CH4 RATE FLOW

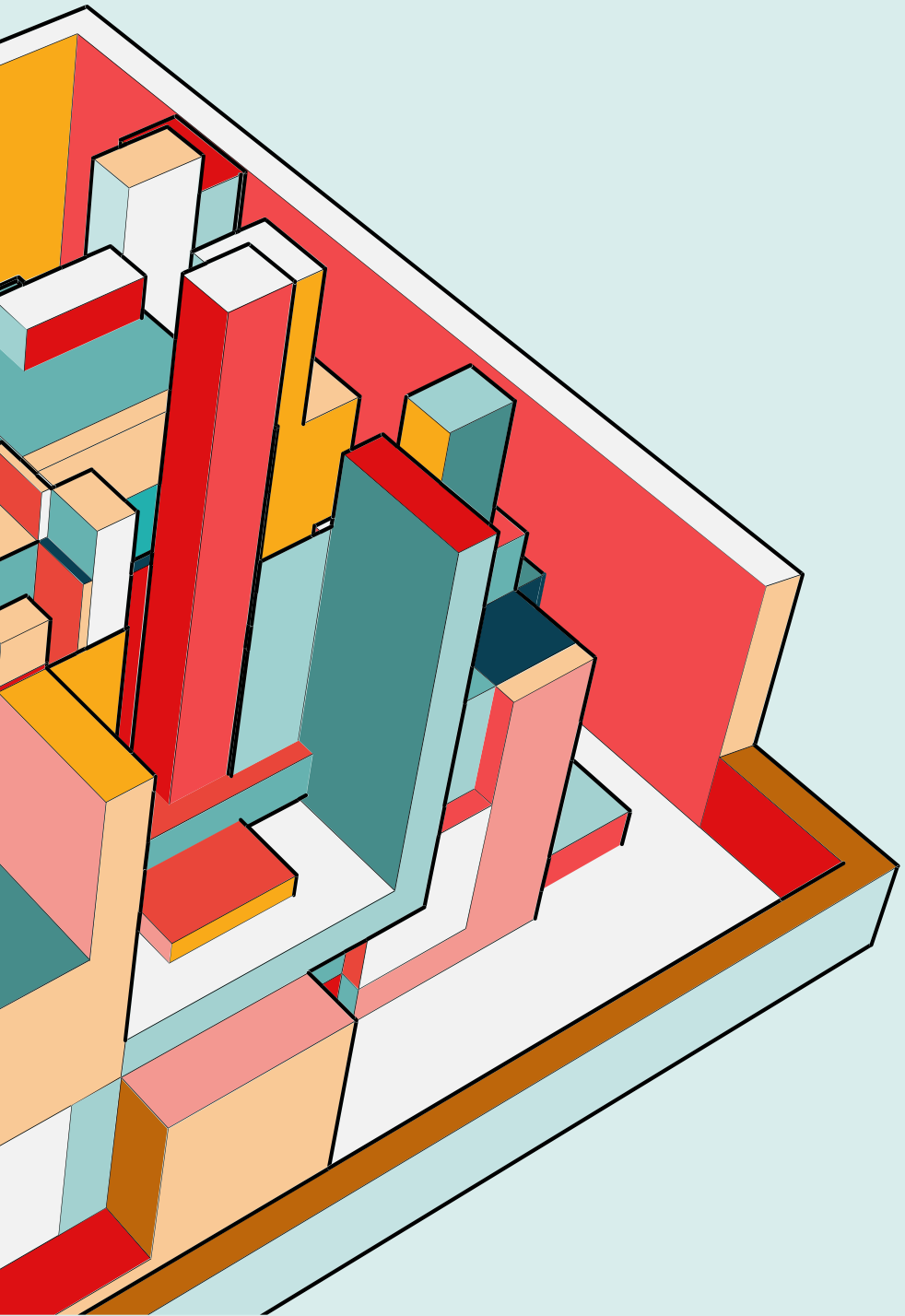
1) Obtained from fit + calibration: plateau x calibration/tau gives [ppm/h]
2) [ppm/h] /10000 → %/h



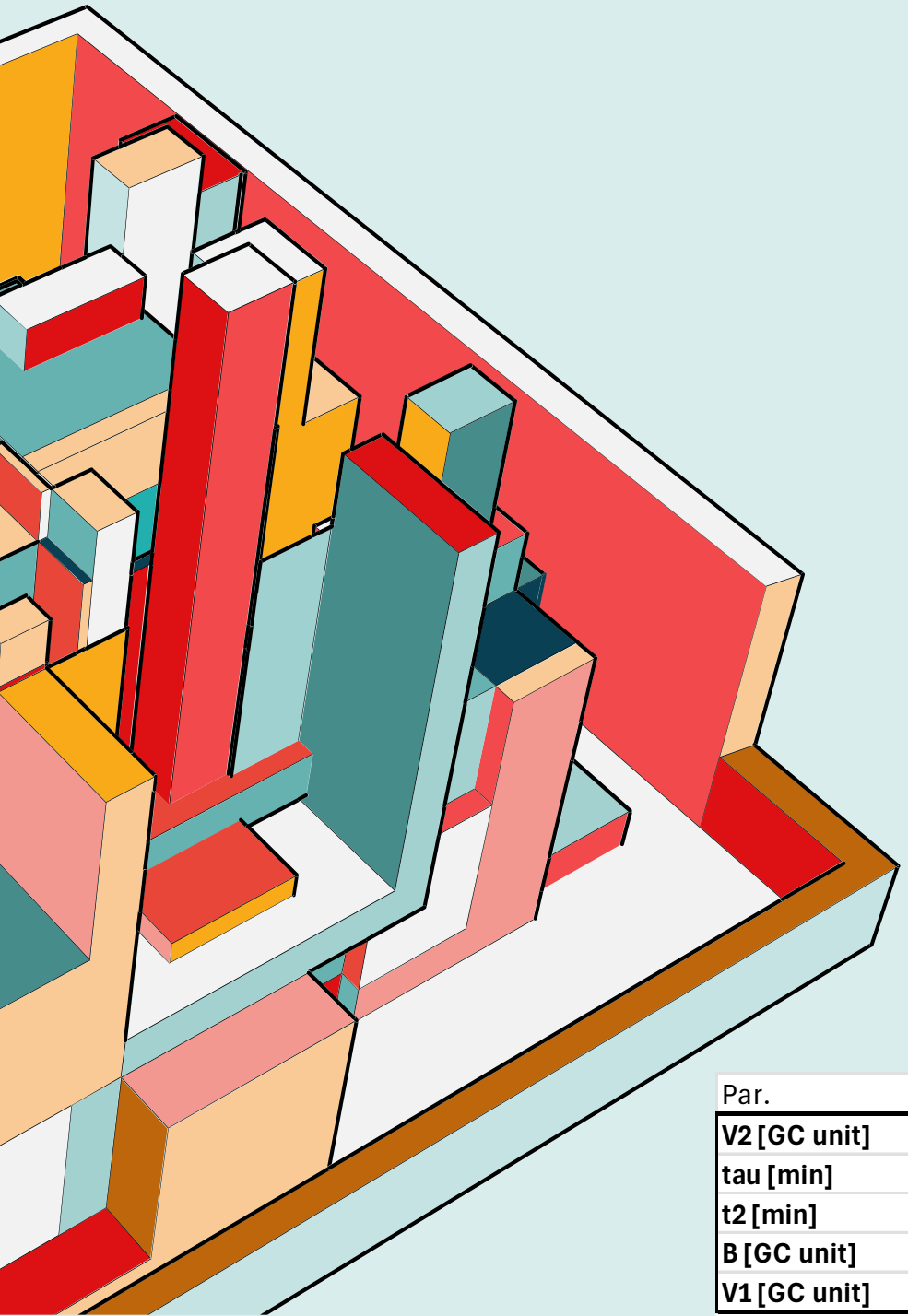


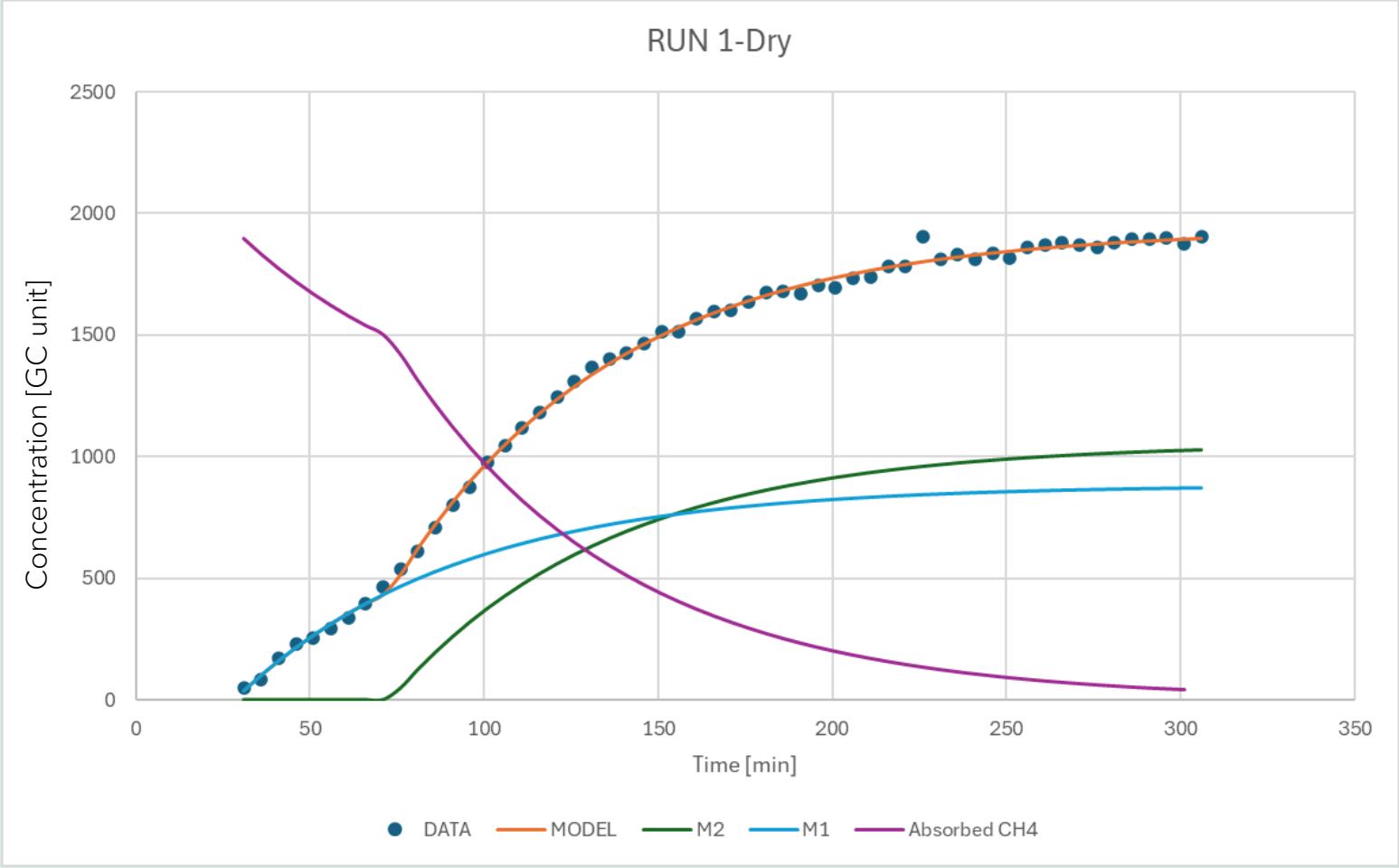
FIRST CONCLUSION -DRY RUNS-

- Model seems to describe the data in a reasonable way
- Dry runs had leakages – from the model we caclulated them to be about 70-100 ppm
- Process has characteristic times from 20 min to 60 min
- Model can calculate the initial methane content in the bottles: only for the first run this is the expected one (0.45%) , then it increases to 1% (→ bad regeneration ?)

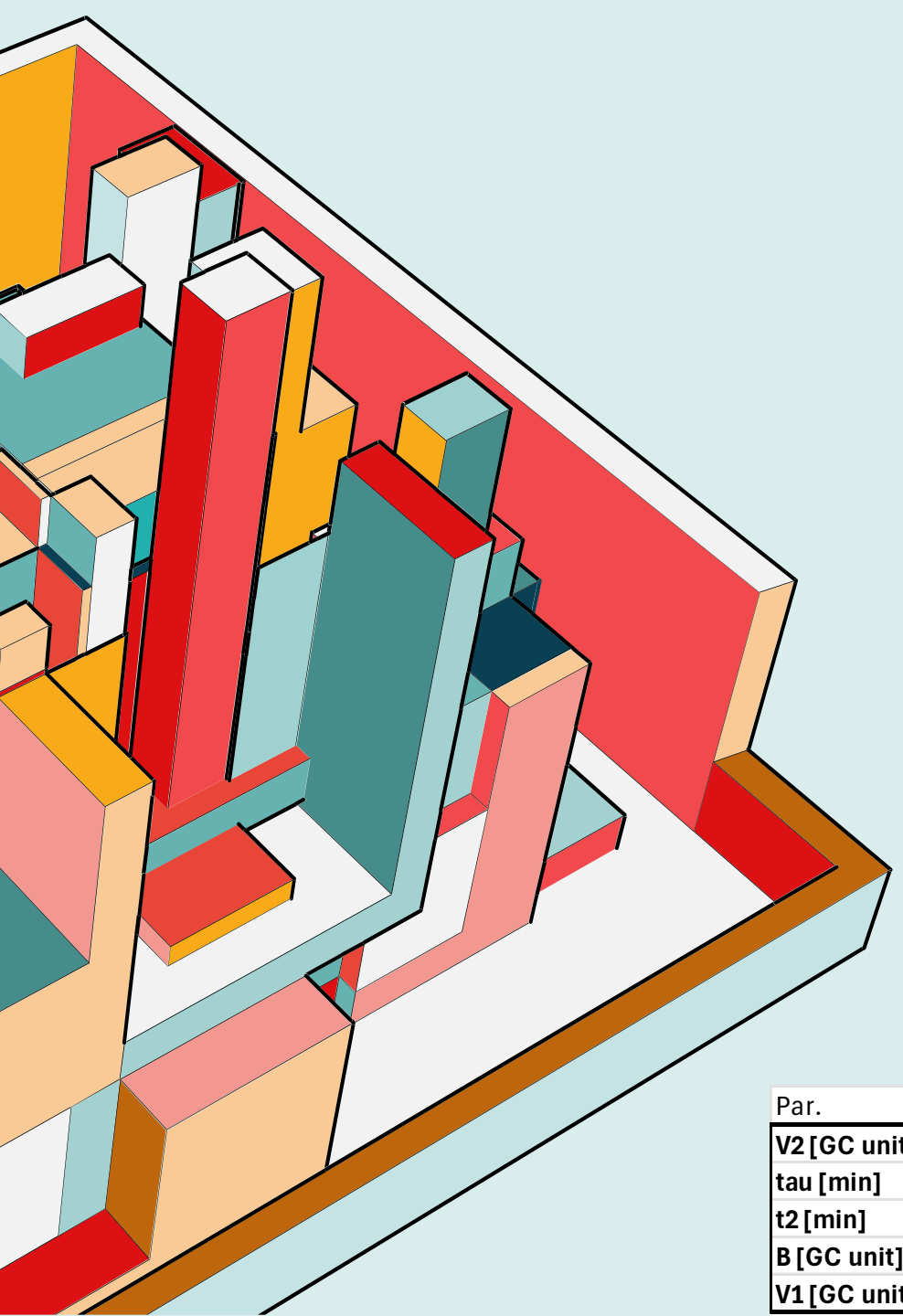


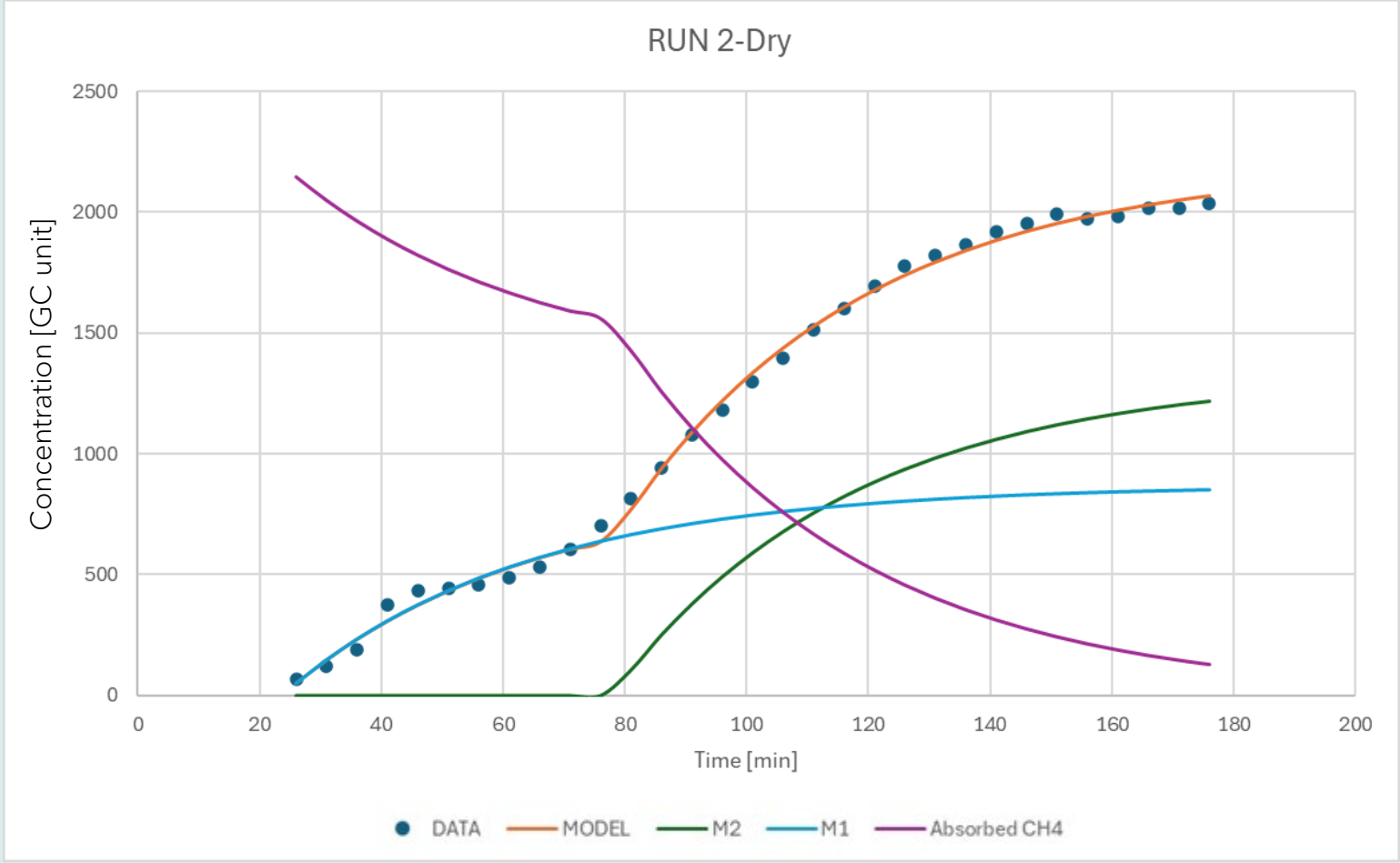
BACKUP



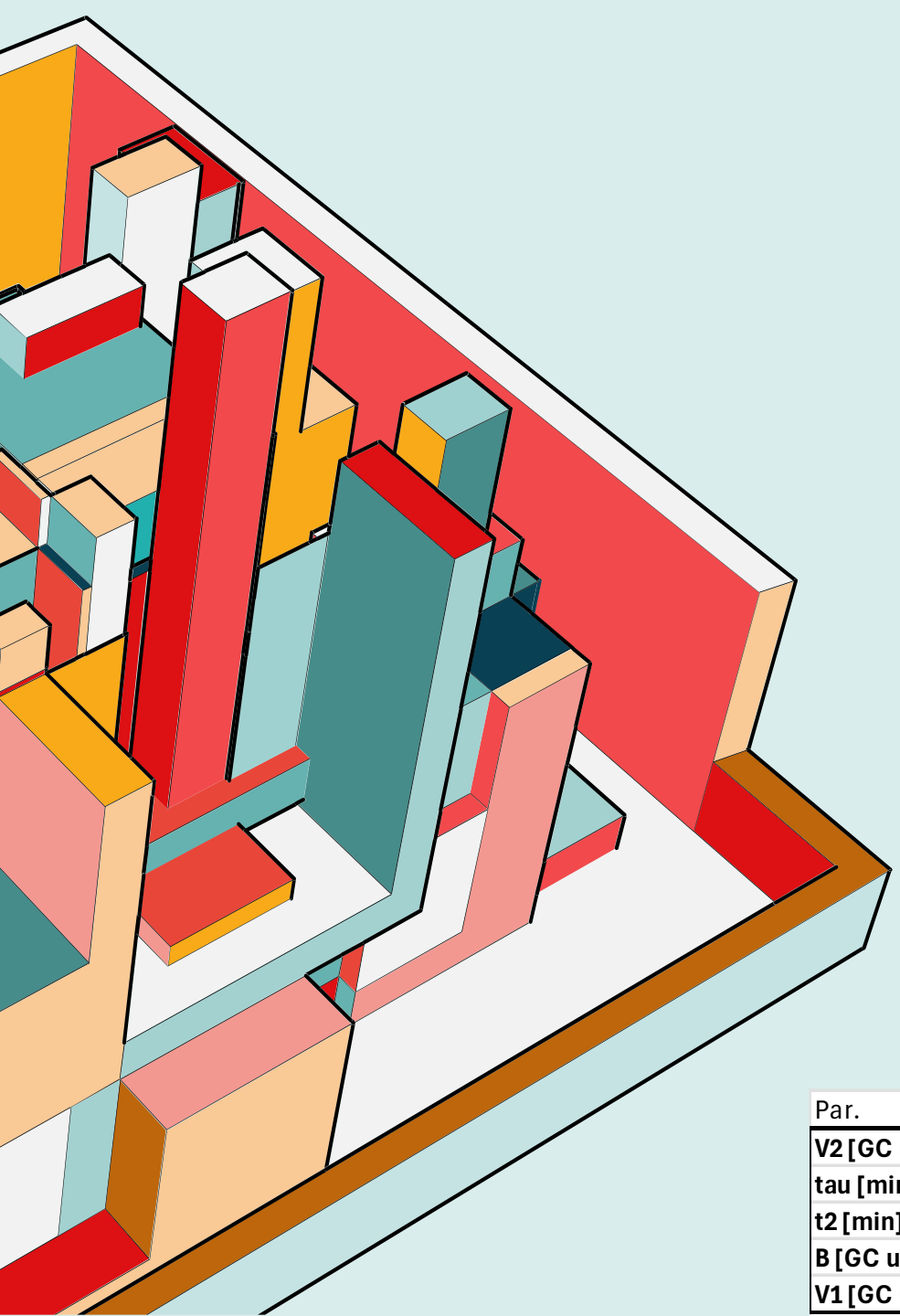


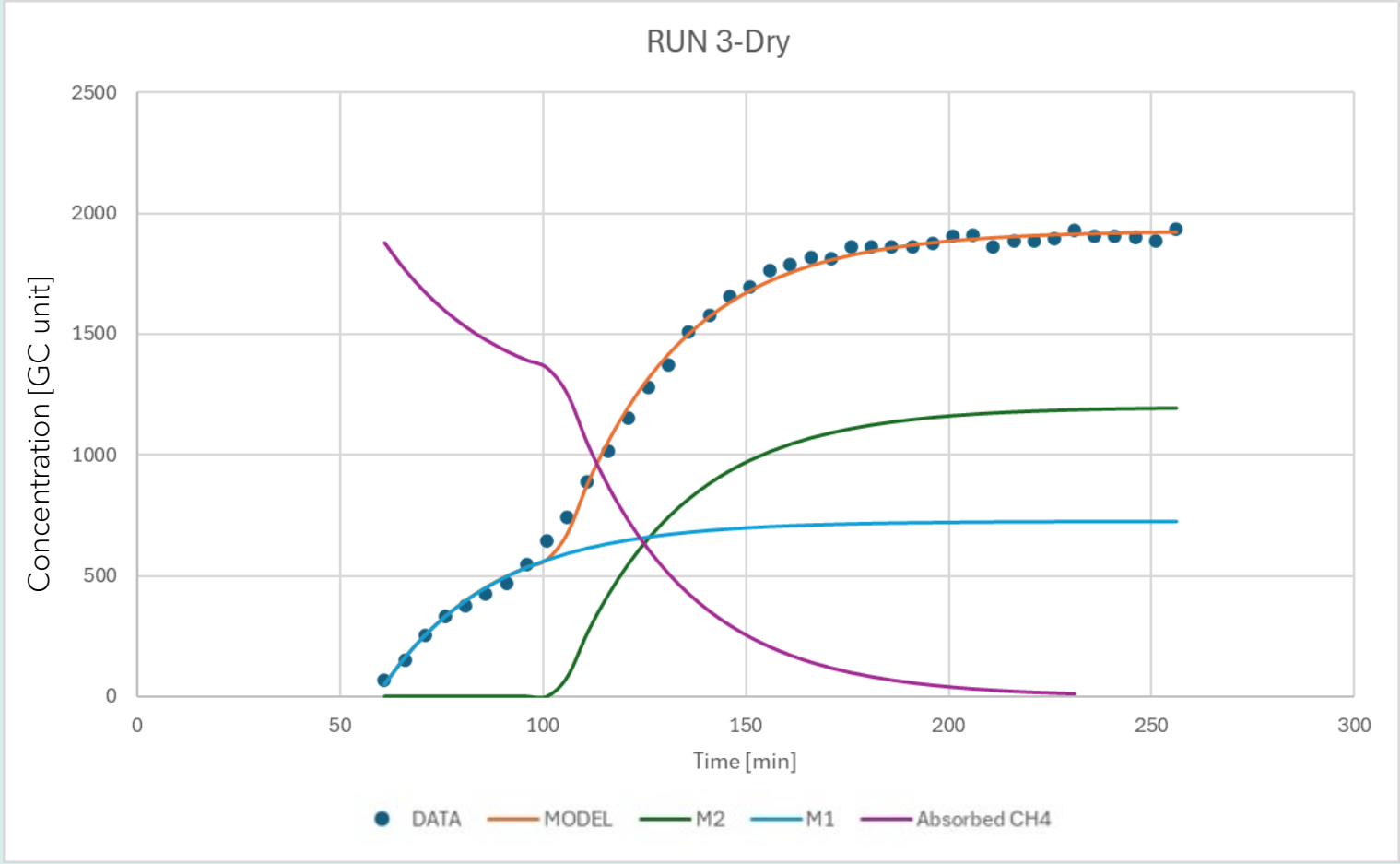
Par.	Value	Std. Err.	t calc.	Crit. t(.05)	Low. CI(.95)	Up. CI(.95)	Passed Prob.	Check	CV%
V2 [GC unit]	1052.5	32.2	32.7	2.0	987.8	1117.3	7.47E-36	Ok	3.06
tau [min]	63.5	1.2	51.6	2.0	61.0	65.9	1.10E-45	Ok	1.94
t2 [min]	73.1	1.0	75.0	2.0	71.1	75.0	7.53E-54	Ok	1.33
B [GC unit]	844.7	42.9	19.7	2.0	758.7	930.8	1.66E-25	Ok	5.07
V1 [GC unit]	881.4	33.7	26.1	2.0	813.7	949.1	3.39E-31	Ok	3.83



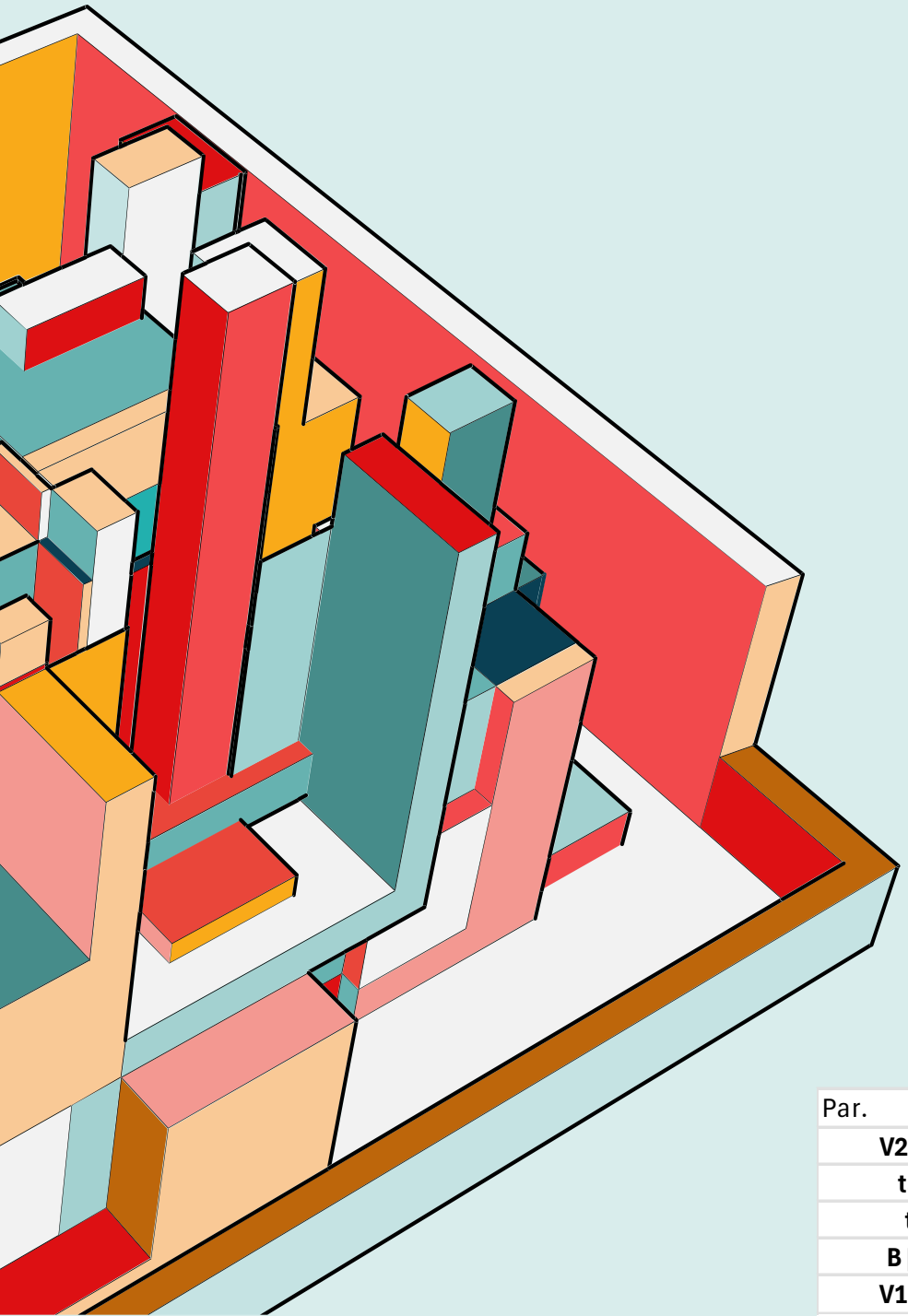


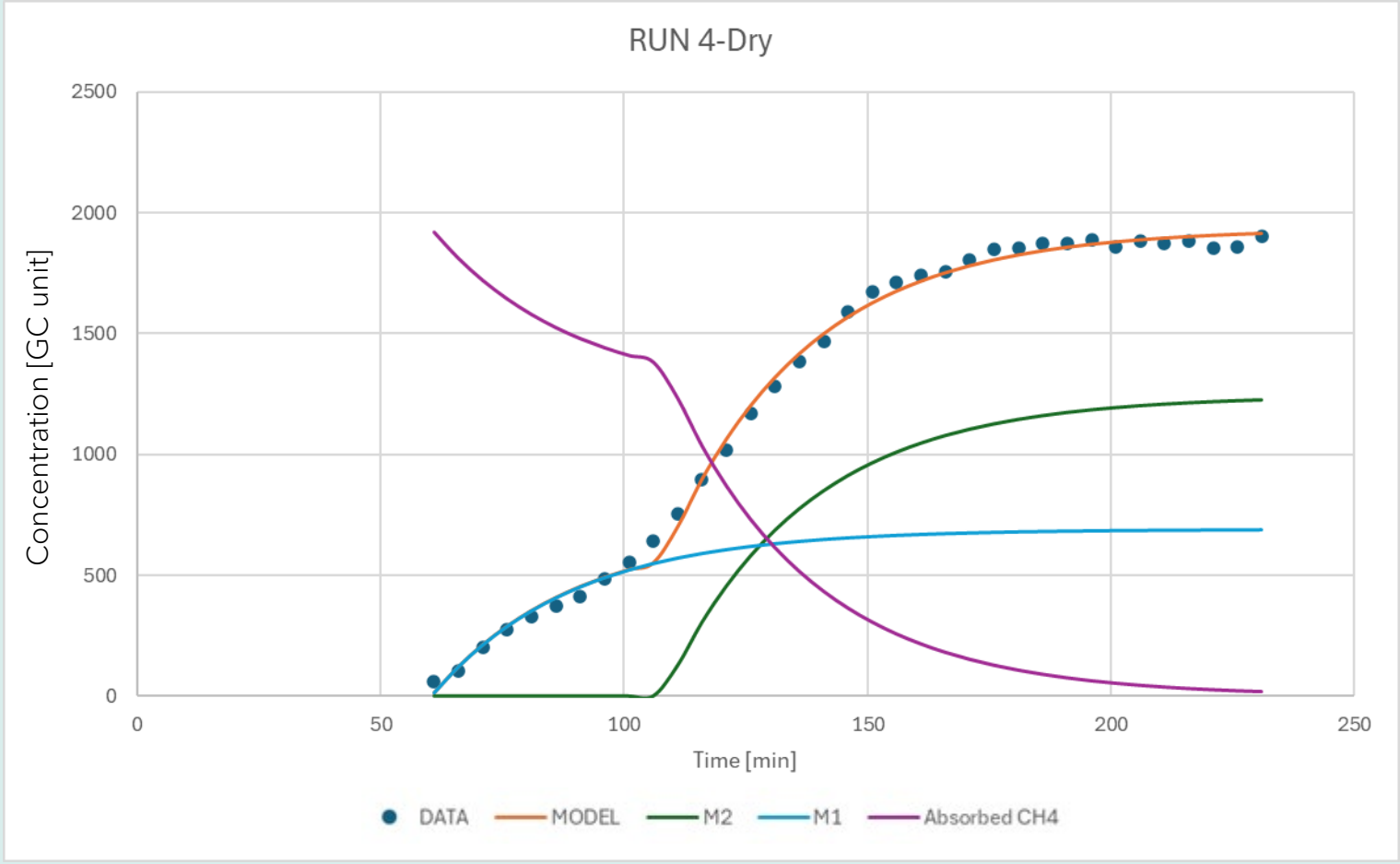
Par.	Value	Std. Err.	t calc.	Crit. t(.05)	Low. CI(.95)	Up. CI(.95)	Passed Prob.	Check	CV%
V2 [GC unit]	1328.4	33.9	39.2	2.1	1258.7	1398.1	1.19E-24	Ok	2.55
tau [min]	39.6	2.9	13.6	2.1	33.6	45.6	2.63E-13	Ok	7.37
t2 [min]	77.7	1.1	72.8	2.1	75.5	79.9	1.38E-31	Ok	1.37
B [GC unit]	815.9	57.6	14.2	2.1	697.4	934.4	9.96E-14	Ok	7.07
V1 [GC unit]	867.6	45.5	19.1	2.1	774.0	961.1	8.38E-17	Ok	5.25



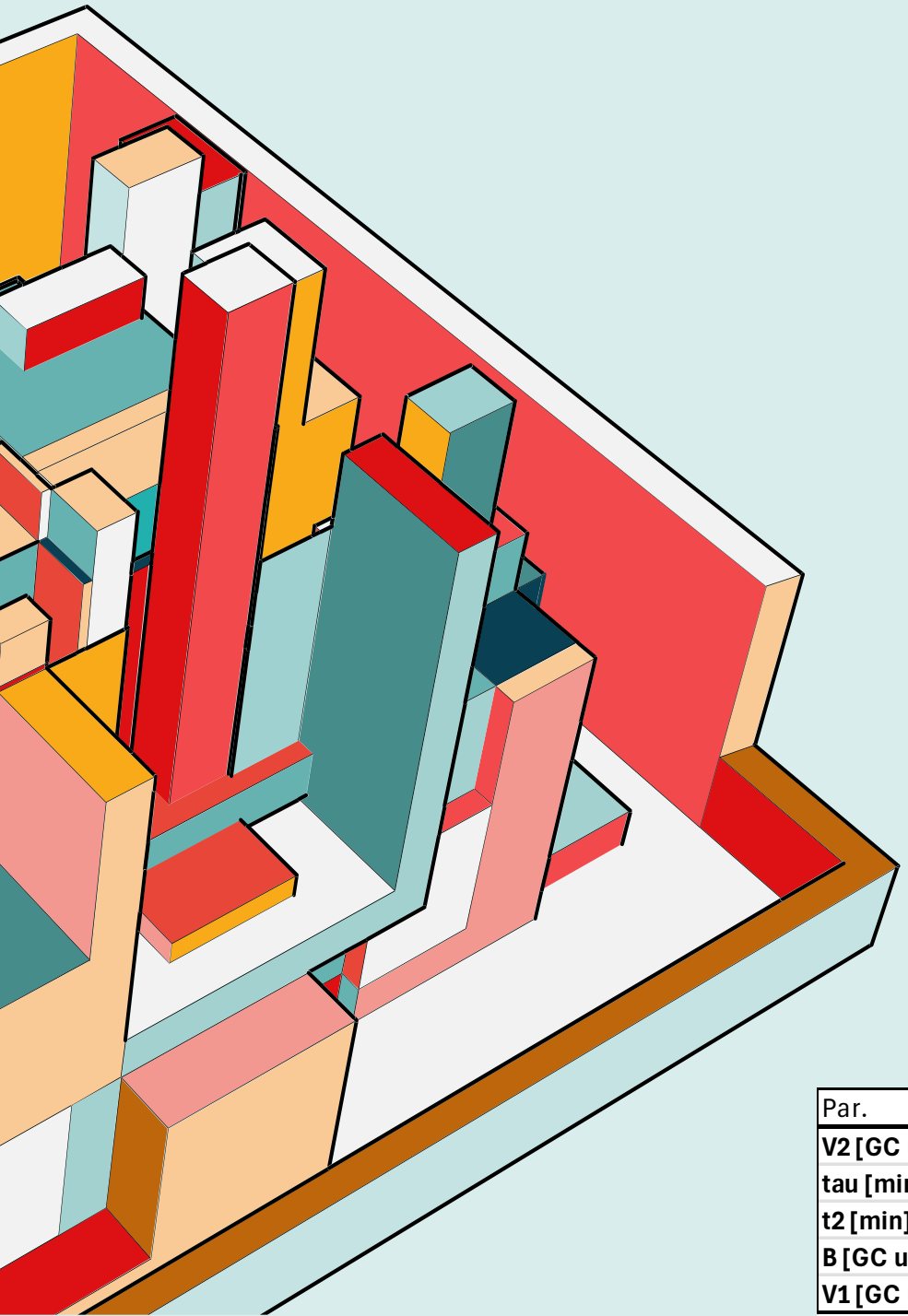


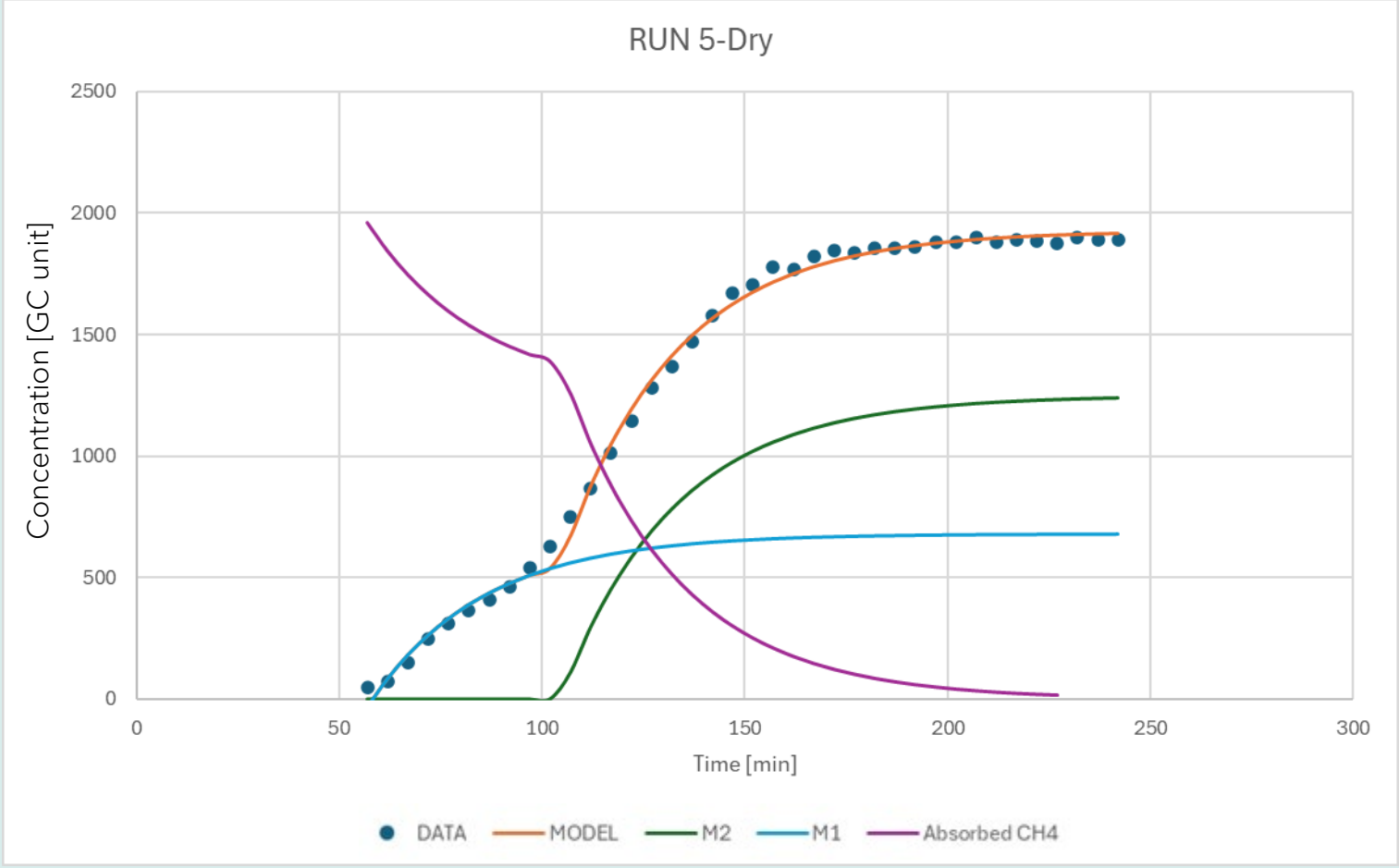
Par.	Value	Std. Err.	t calc.	Crit. t(.05)	Low. CI(.95)	Up. CI(.95)	Passed Prob.	Check	CV%
V2 [GC unit]	1200.9	25.5	47.1	2.0	1149.2	1252.7	6.07E-34	Ok	2.12
tau [min]	27.8	1.0	27.7	2.0	25.7	29.8	7.22E-26	Ok	3.61
t2 [min]	104.1	0.7	149.9	2.0	102.6	105.5	6.18E-52	Ok	0.67
B [GC unit]	677.9	40.8	16.6	2.0	595.1	760.7	1.86E-18	Ok	6.02
V1 [GC unit]	726.2	27.1	26.8	2.0	671.3	781.1	2.15E-25	Ok	3.73



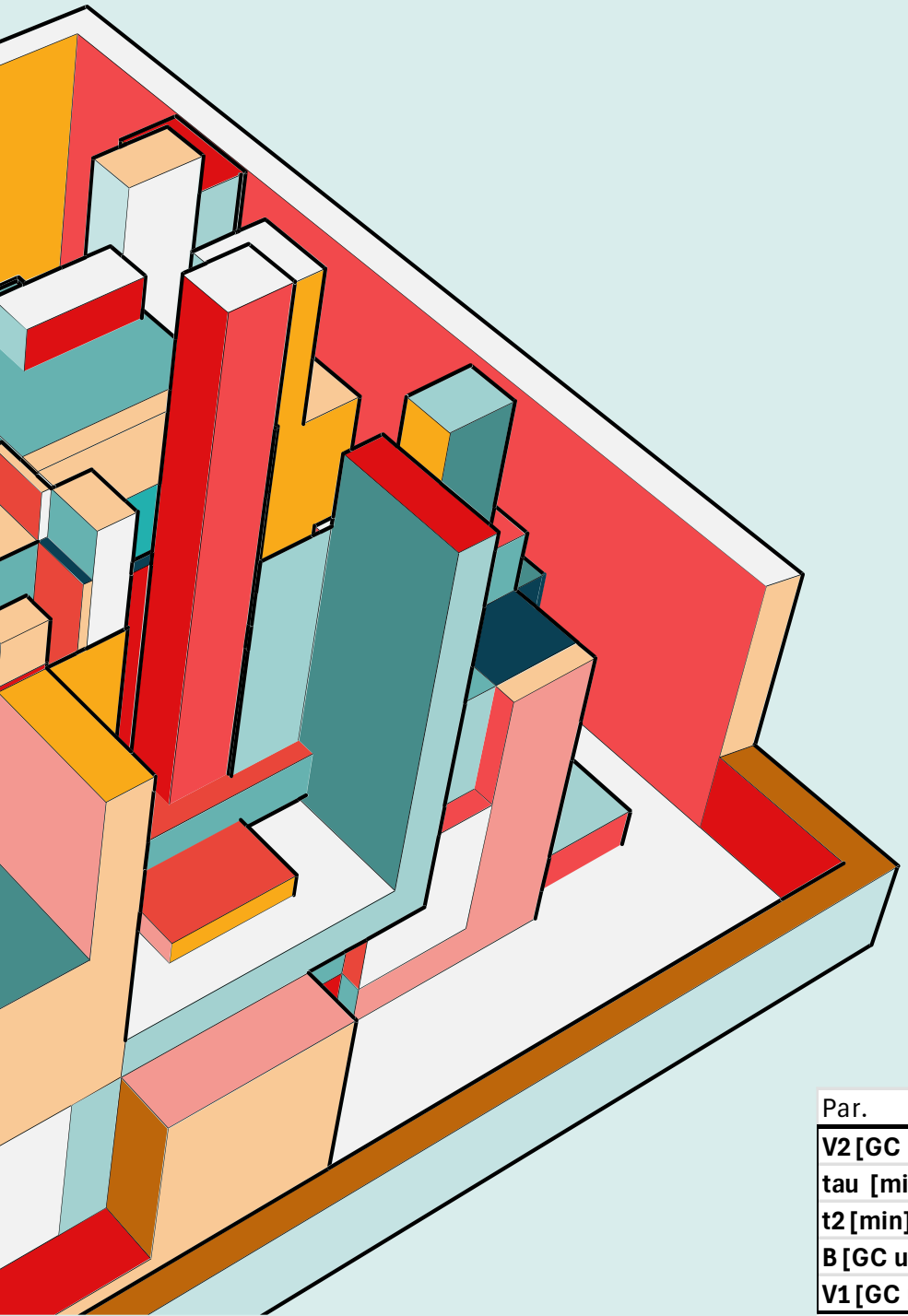


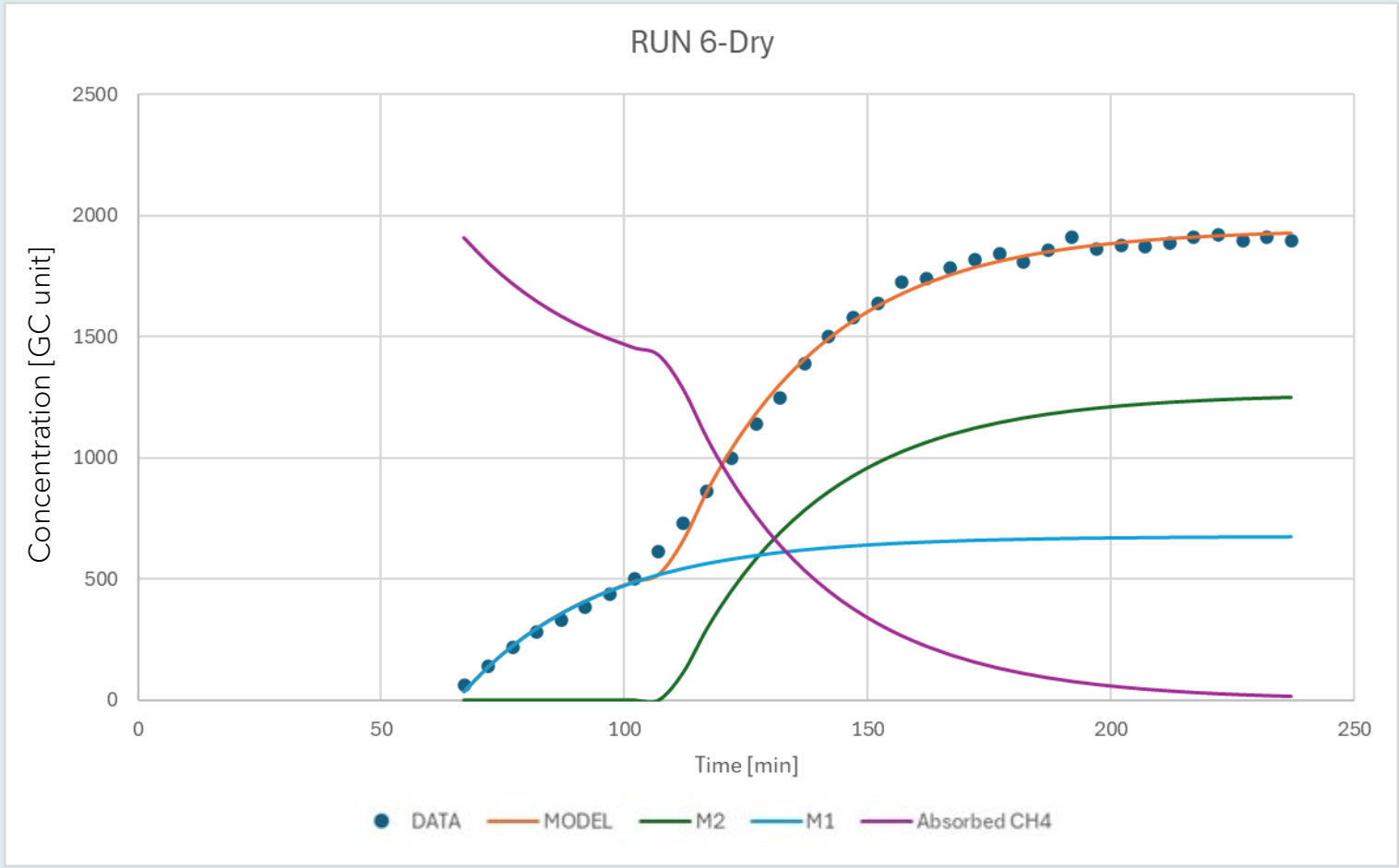
Par.	Value	Std. Err.	t calc.	Crit. t(.05)	Low. CI(.95)	Up. CI(.95)	Passed Prob.	Check	CV%
V2 [GC unit]	1242.5	28.7	43.3	2.0	1183.8	1301.2	1.36E-28	Ok	2.31
tau [min]	28.7	1.5	18.9	2.0	25.6	31.8	3.41E-18	Ok	5.30
t2 [min]	107.9	0.9	124.2	2.0	106.2	109.7	3.01E-42	Ok	0.81
B [GC unit]	679.5	48.1	14.1	2.0	581.2	777.7	8.54E-15	Ok	7.08
V1 [GC unit]	691.7	32.1	21.5	2.0	626.0	757.3	8.69E-20	Ok	4.65



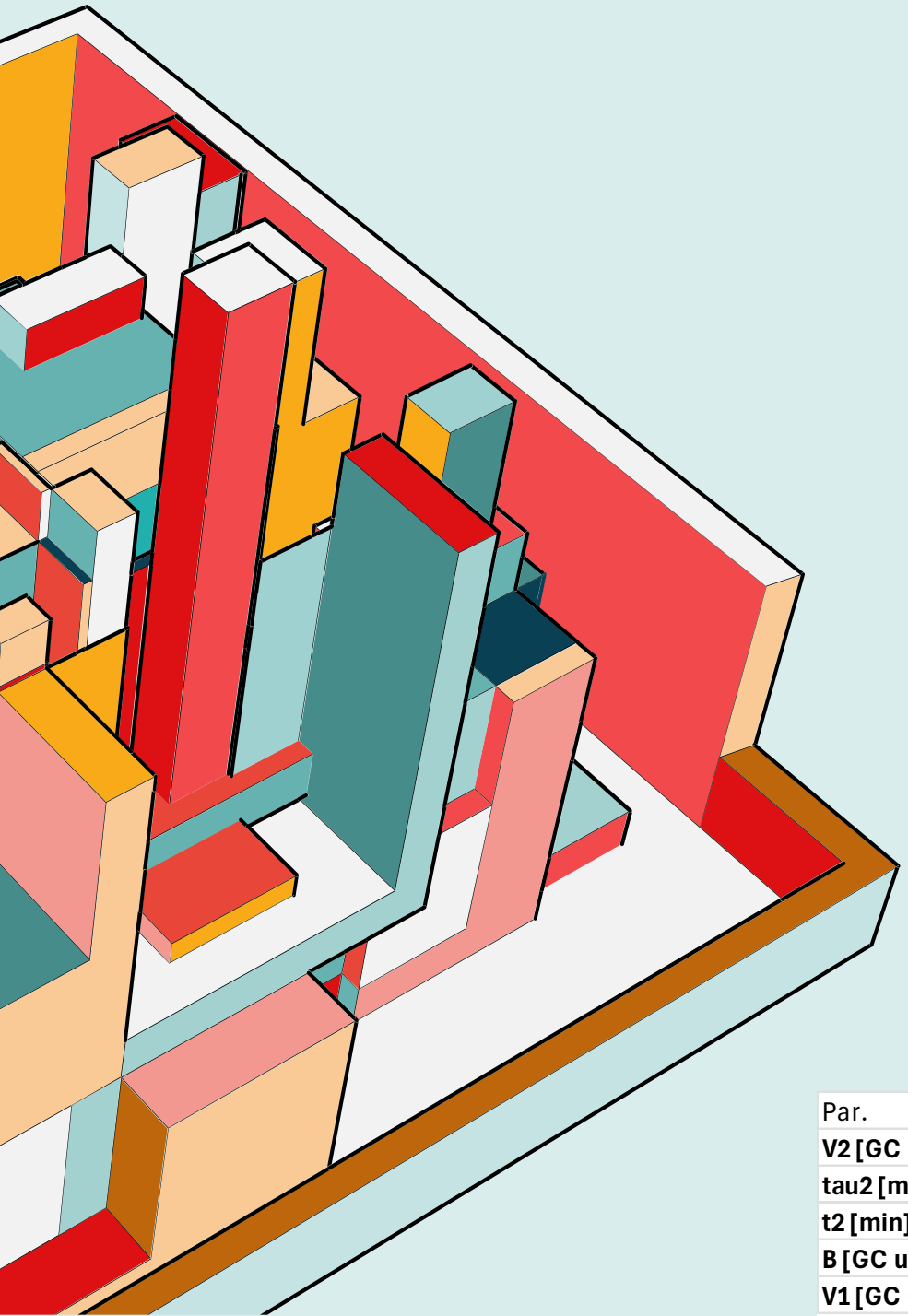


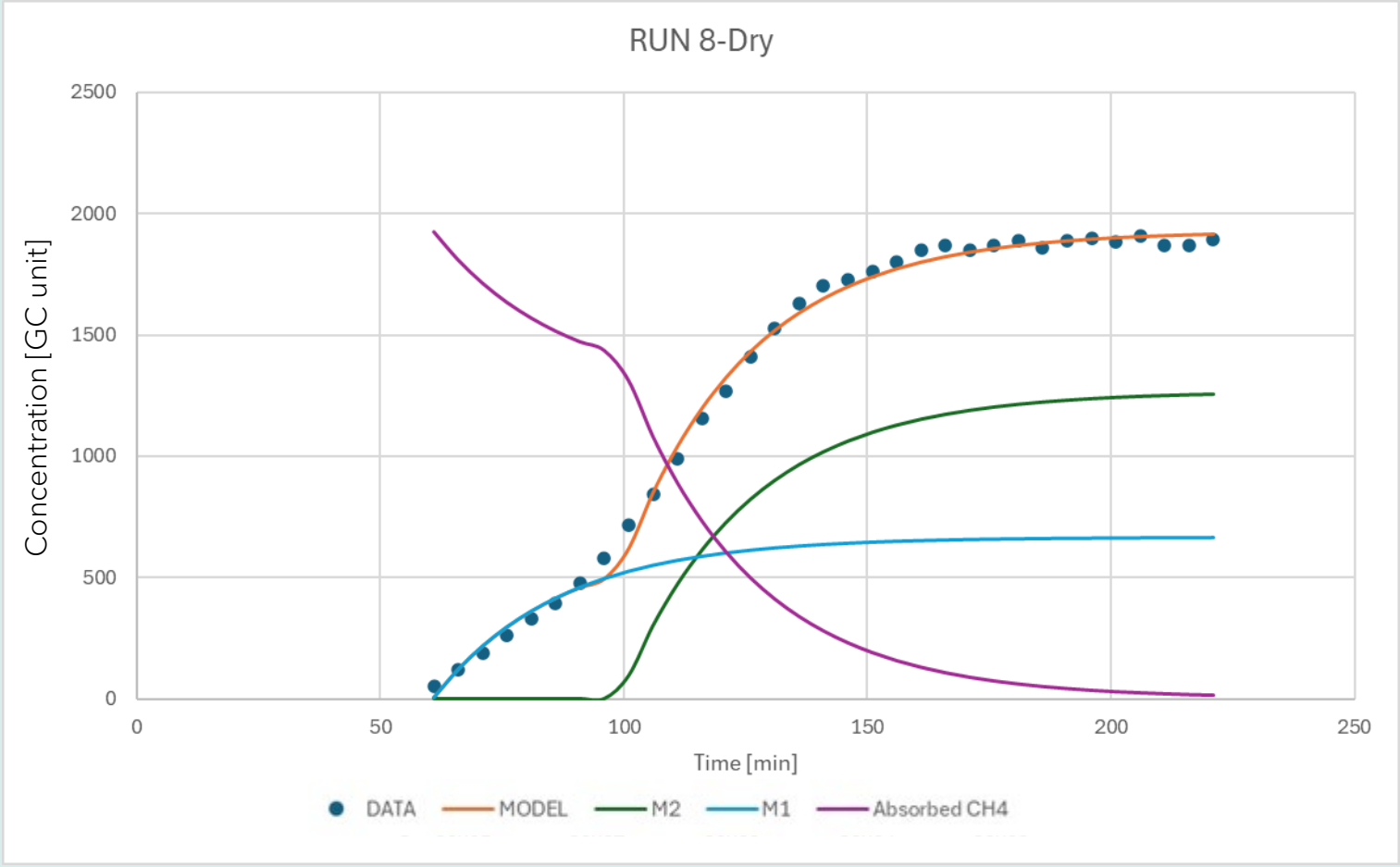
Par.	Value	Std. Err.	t calc.	Crit. t(.05)	Low. CI(.95)	Up. CI(.95)	Passed Prob.	Check	CV%
V2 [GC unit]	1246.2	28.5	43.7	2.0	1188.3	1304.2	8.40E-31	Ok	2.29
tau [min]	28.0	1.3	20.9	2.0	25.3	30.7	1.32E-20	Ok	4.78
t2 [min]	104.5	0.8	124.5	2.0	102.8	106.2	1.10E-45	Ok	0.80
B [GC unit]	712.1	48.9	14.6	2.0	612.7	811.5	6.15E-16	Ok	6.86
V1 [GC unit]	680.4	31.1	21.9	2.0	617.2	743.6	3.16E-21	Ok	4.57



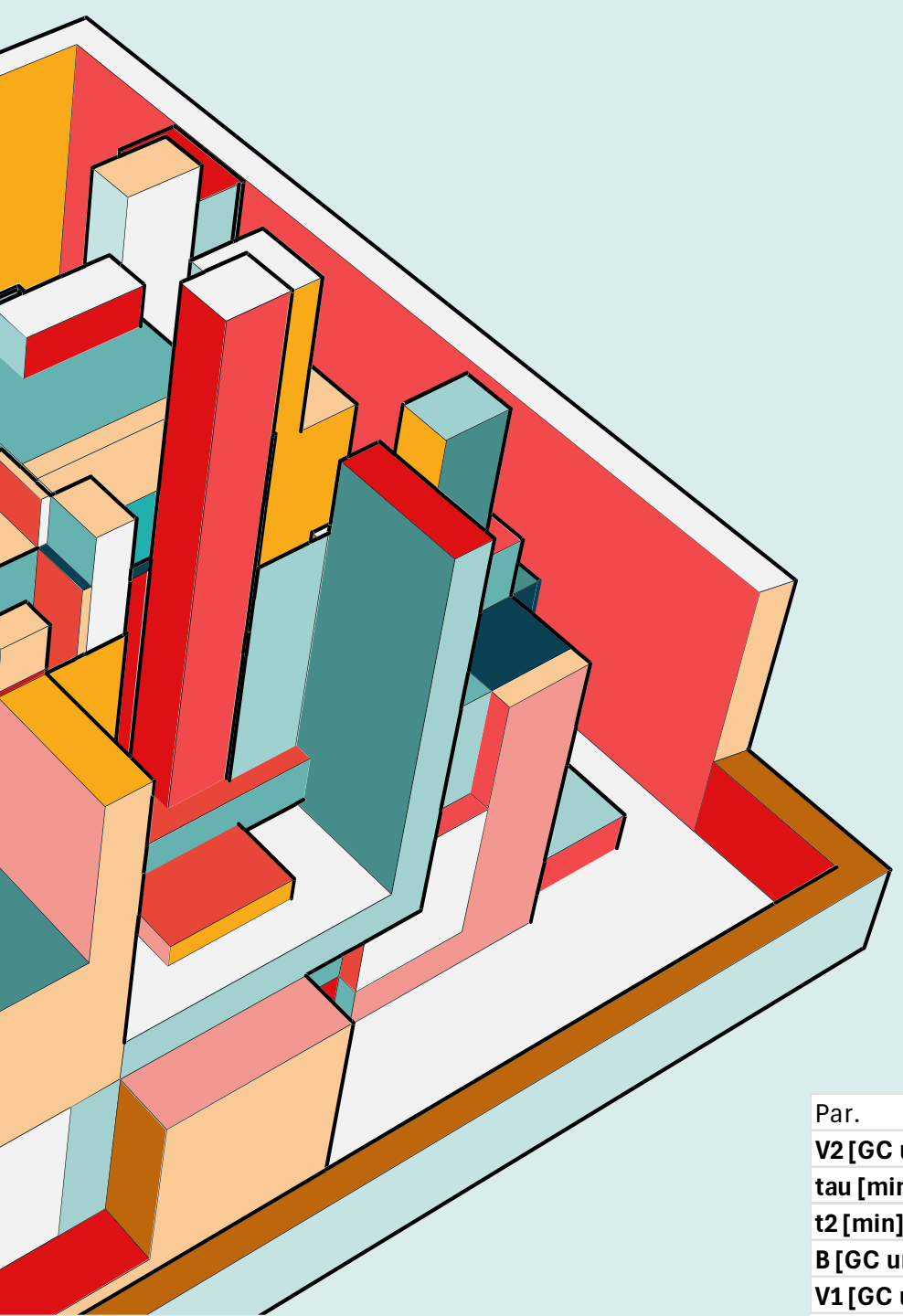


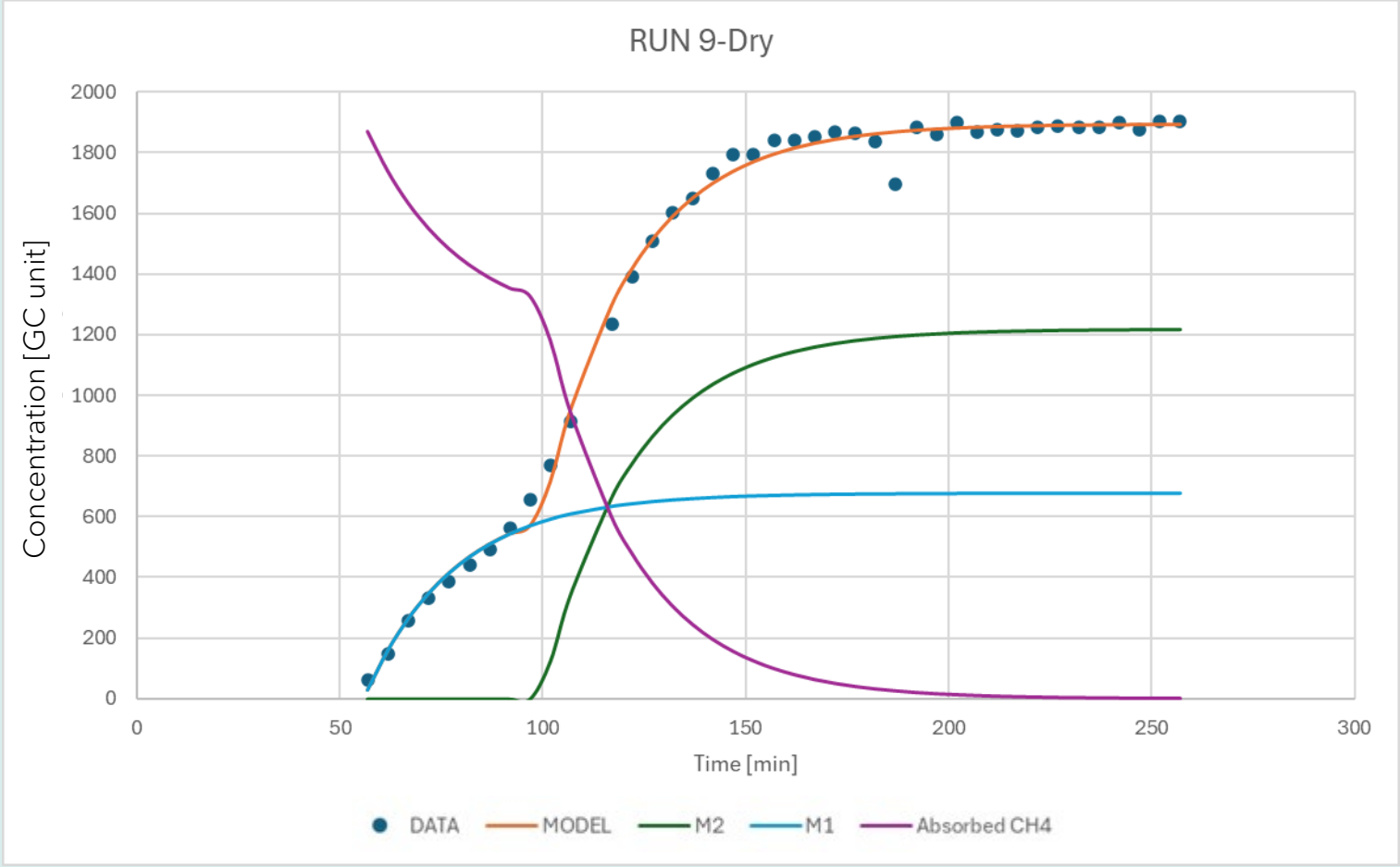
Par.	Value	Std. Err.	t calc.	Crit. t(.05)	Low. CI(.95)	Up. CI(.95)	Passed Prob.	Check	CV%
V2 [GC unit]	1264.2	29.0	43.5	2.0	1204.9	1323.4	1.12E-28	Ok	2.30
tau [min]	28.6	1.3	22.0	2.0	25.9	31.2	4.45E-20	Ok	4.54
t2 [min]	109.3	0.8	137.6	2.0	107.7	111.0	1.42E-43	Ok	0.73
B [GC unit]	642.1	46.8	13.7	2.0	546.5	737.7	1.83E-14	Ok	7.29
V1 [GC unit]	678.5	31.6	21.5	2.0	614.0	743.0	8.89E-20	Ok	4.65



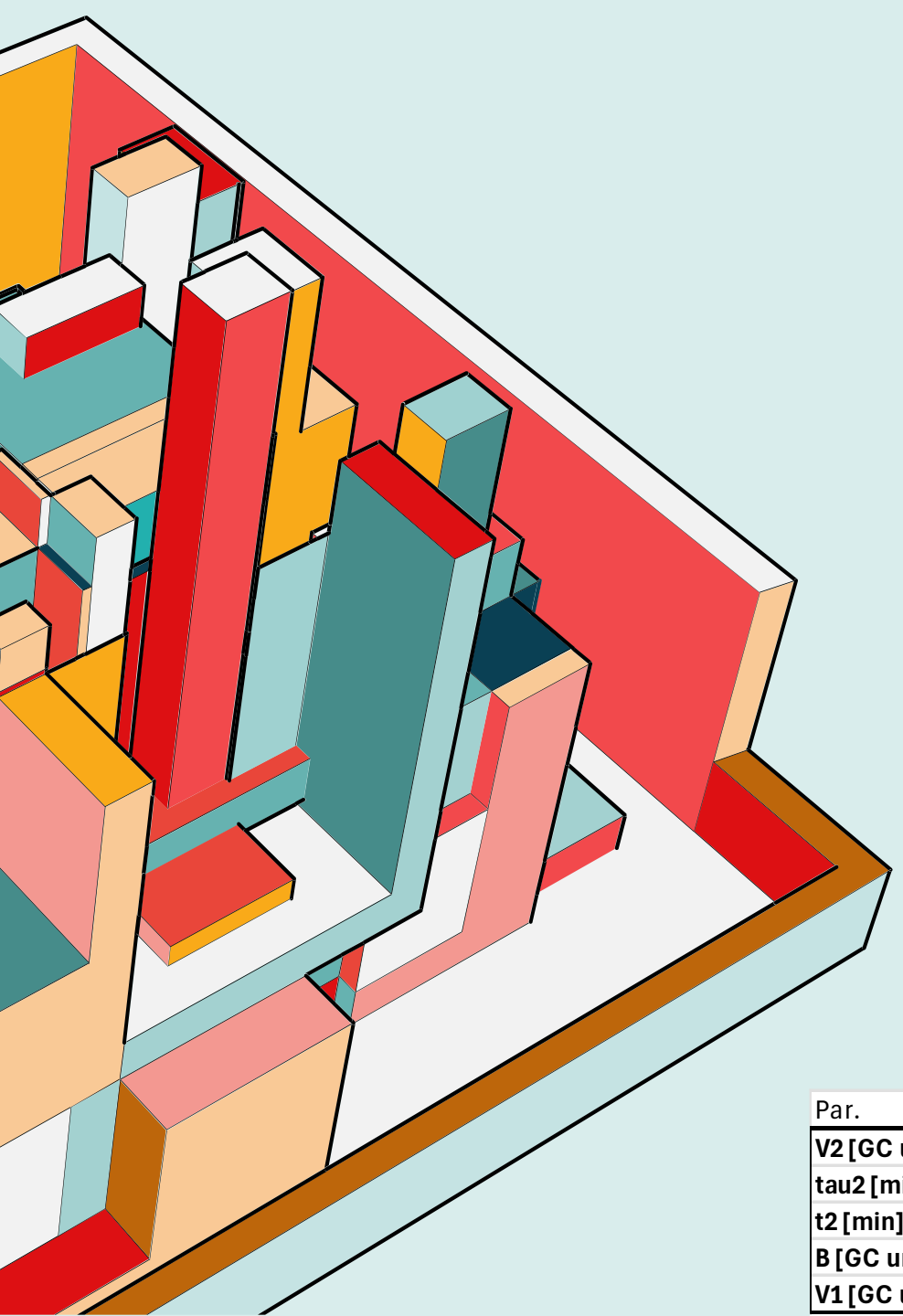


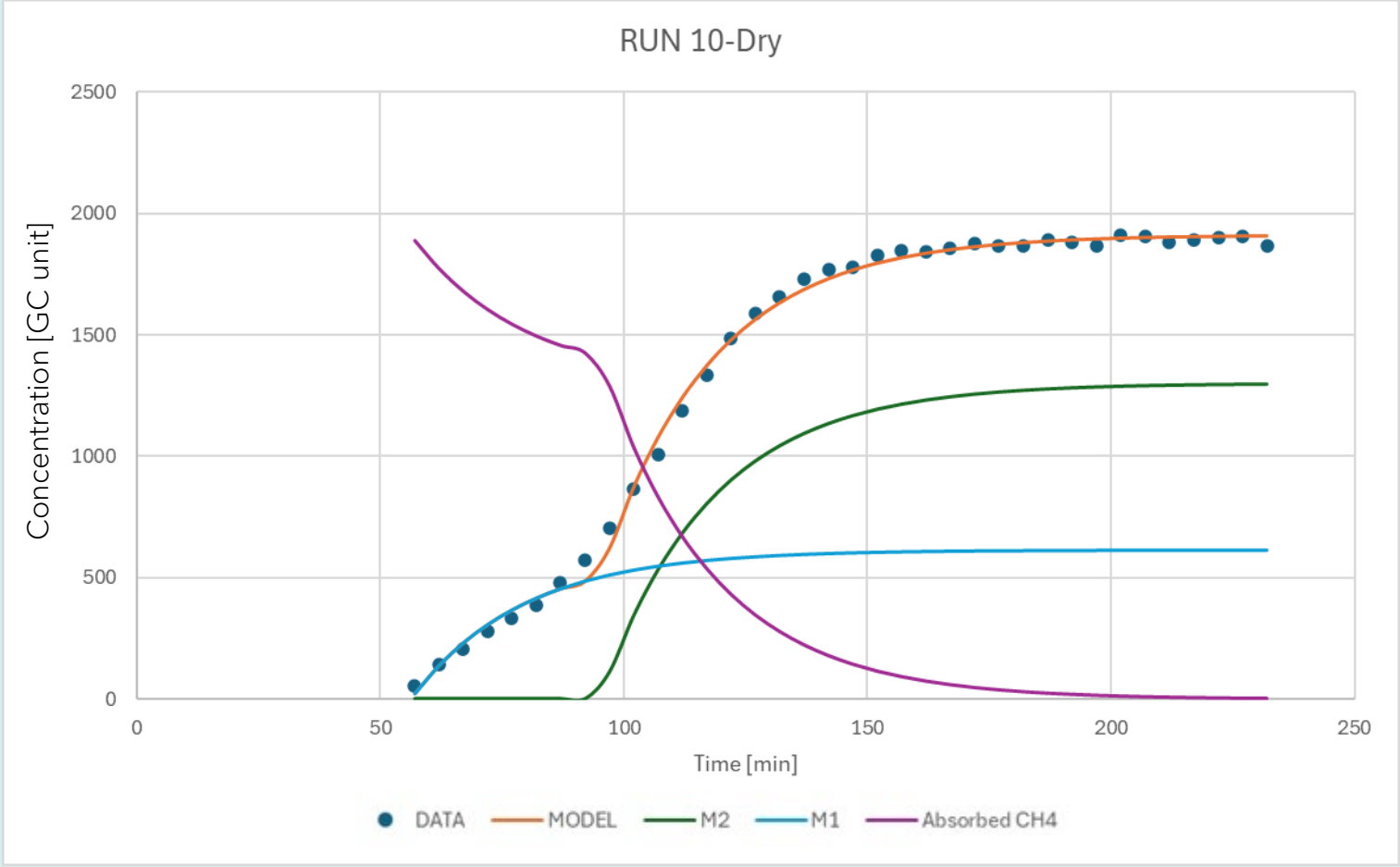
Par.	Value	Std. Err.	t calc.	Crit. t(.05)	Low. CI(.95)	Up. CI(.95)	Passed Prob.	Check	CV%
V2 [GC unit]	1264.8	37.5	33.7	2.0	1187.9	1341.6	3.28E-24	Ok	2.97
tau2 [min]	25.8	1.4	18.4	2.0	22.9	28.7	3.67E-17	Ok	5.44
t2 [min]	99.0	0.9	110.7	2.0	97.2	100.8	1.51E-38	Ok	0.90
B [GC unit]	659.8	59.8	11.0	2.0	537.4	782.3	1.03E-11	Ok	9.06
V1 [GC unit]	665.5	40.4	16.5	2.0	582.7	748.3	6.24E-16	Ok	6.07





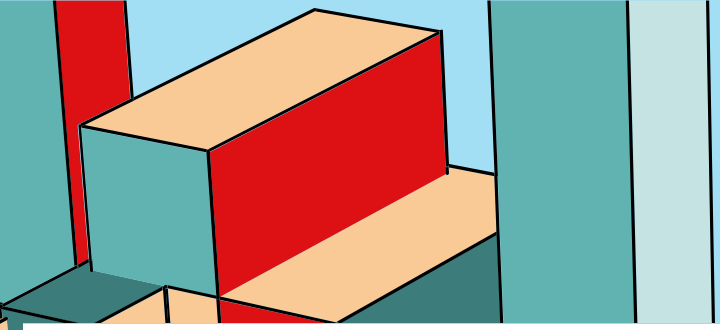
Par.	Value	Std. Err.	t calc.	Crit. t(.05)	Low. CI(.95)	Up. CI(.95)	Passed Prob.	Check	CV%
V2 [GC unit]	1217.6	26.2	46.5	2.0	1164.5	1270.7	4.51E-33	Ok	2.15
tau [min]	22.2	1.0	22.6	2.0	20.2	24.2	1.82E-22	Ok	4.42
t2 [min]	99.6	0.7	144.4	2.0	98.2	101.0	3.53E-50	Ok	0.69
B [GC unit]	650.8	44.2	14.7	2.0	561.2	740.4	1.40E-16	Ok	6.78
V1 [GC unit]	677.8	27.4	24.8	2.0	622.2	733.3	8.89E-24	Ok	4.04



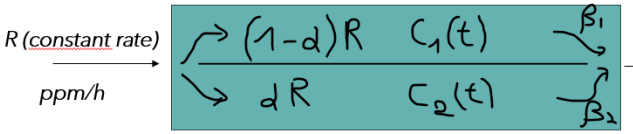


Par.	Value	Std. Err.	t calc.	Crit. t(.05)	Low. CI(.95)	Up. CI(.95)	Passed Prob.	Check	CV%
V2 [GC unit]	1299.0	29.2	44.4	2.0	1239.4	1358.6	1.22E-29	Ok	2.25
tau2 [min]	22.8	1.0	23.4	2.0	20.8	24.8	2.96E-21	Ok	4.28
t2 [min]	95.0	0.7	139.9	2.0	93.6	96.3	5.50E-45	Ok	0.71
B [GC unit]	591.4	47.6	12.4	2.0	494.3	688.4	1.40E-13	Ok	8.04
V1 [GC unit]	613.4	30.5	20.1	2.0	551.2	675.6	2.36E-19	Ok	4.97

TRAFFIC ISLAND MODEL WITH 2 OUTPUT RATES



TRAFFIC ISLAND MODEL: TWO OUTPUT RATES



$$\begin{cases} \frac{dC_1(t)}{dt} = F_1 - \beta_1 C_1(t) \\ \frac{dC_2(t)}{dt} = F_2 - \beta_2 C_2(t) \end{cases}$$

$$C_{1GC}(t) = (V_1 - Be^{-\beta_1(t-t_1)})\,\theta(t-t_1)$$ Early component

$$C_{2GC}(t) = V_2\left(1 - e^{-\beta_2(t-t_2)}\right)\theta(t-t_2)$$ Late component

Heaviside

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