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Estimation of secondary organic aerosol formation parameters for the volatility basis set combining thermodenuder, isothermal dilution, and yield measurements

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S1. Constructing Data for Evaluation

Table S1: Values of the true properties (volatility distribution of the products, vaporization enthalpy, accommodation coefficient) for three SOA systems used to generate data for pseudo-experiments A, B and C.

Exp.	**"True" Properties**
A	4 bins $C_i^* = [10^0\ 10^1\ 10^2\ 10^3]$ μg m^{-3} $\alpha_i = [0.07\ 0.038\ 0.179\ 0.300]$ $\Delta H_{vap} = 30$ kJ mol^{-1} $\alpha_m = 0.5$
B	7 bins $C_i^* = [10^{-2}\ 10^{-1}\ 10^0\ 10^1\ 10^2\ 10^3\ 10^4]$ μg m^{-3} $\alpha_i = [0.001\ 0.012\ 0.037\ 0.088\ 0.099\ 0.250\ 0.800]$ $\Delta H_{vap} = 30$ kJ mol^{-1} $\alpha_m = 0.5$
C	4 bins $C_i^* = [10^{-2}\ 10^{-1}\ 10^0\ 10^1]$ μg m^{-3} $\alpha_i = [0.118\ 0.094\ 0.116\ 0.247]$ $\Delta H_{vap} = 115$ kJ mol^{-1} $\alpha_m = 0.01$

Table S2: "Experimental" conditions and properties used to obtain the "measurements" of TD and isothermal dilution for pseudo-experiments A, B and C.

Exp.	Initial Concentration ($\mu g\ m^{-3}$)	Mean Volume Diameter (nm)	Dilution Ratio	TD Residence Time (s)	SOA Density ($g\ cm^{-3}$)
A	20	200	10	17	1.5
B	20	200	10	17	1.5
C	190	145	17	50	1.3

S2. Metrics

Table S3: Number of solutions under the <5% threshold for the 8 different tests and two values of the sum of the yields $\Sigma(\alpha_i)$.

Test	**$\Sigma(\alpha_i)$ < 1.0**		**$\Sigma(\alpha_i)$ < 2.0**	
	Simulations	**"Good" Solutions**	**Simulations**	**"Good" Solutions**
A1	126,120	148	367,640	186
A2	22,320	16	39,480	16
A3	126,120	16	367,640	16
A4	126,120	115	367,640	126
B1	126,120	82	367,640	107
B2	126,120	50	367,640	53
C1	126,120	3,479	367,640	3,479
C2	126,120	1,067	367,640	1,976

Table S4: Relative errors (%) between the “true” and estimated parametrization.

Test	ΔH_{vap}	α_m	Stoichiometric Coefficients for each volatility bin					
			10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}
A1	9.7	65.8			15	87	41	15
A2	6.8	61.5			12	76	60	-
A3	6.8	61.5		-	12	76	60	-
A4	13.3	60.0			12	115	6	13
B1	12.8	77.7	-	-	42	58	277	10
B2	21.7	76.5	-	-	35	42	195	6
C1	9.1	89.7	7	23	33	13		
C2	20.7	54.1	-	-	258	42	-	-

S3. Effect on the Estimated Parameters in the Abscence of Yield Measurements (TD and isothermal dilution)

Table S5: The *mean normilized error* between the “true” and estimated values (MNE_T) for the different tests when only TD and isothermal dilution measurements are provided as inputs.

Test	Yield				TD	Dilution
	5 °C	15 °C	25 °C	35 °C		
A1	102.3	104.9	105.4	103.9	10.6	9.9
A2	135.2	139.1	140.0	138.2	10.8	9.7
A3	169.6	177.7	182.0	182.9	11.6	15.7
A4	102.3	104.9	105.4	103.9	10.6	9.9
B1	69.6	63.3	57.2	51.9	1.9	11.8
B2	69.6	63.3	57.2	51.9	1.9	11.8
C1	21.4	23.2	28.0	38.9	8.3 (110 °C)* 13.7 (140 °C)*	3.1
C2	6.0	14.4	21.3	25.4	7.9 (110 °C)* 23.3 (140 °C)*	3.4

* The errors for TD were calculated up to the denoted temperature in the parenthesis.

Table S6: The average relative standard deviation (*ARSD*) for the different tests when only TD and isothermal dilution measurements are provided as inputs.

Test	Yield				TD	Dilution
	5 ºC	15 ºC	25 ºC	35 ºC		
A1	132.1	136.2	138.4	139.2	25.1	36.3
A2	165.3	171.0	173.9	174.8	25.7	37.4
A3	194.0	204.5	211.9	216.9	23.2	34.2
A4	132.1	136.2	138.4	139.2	25.1	36.3
B1	90.6	84.3	79.5	77.0	23.1	30.6
B2	90.6	84.3	79.5	77.0	23.1	30.6
C1	40.6	42.3	48.1	60.1	23.6*	16.5
C2	32.9	34.7	38.6	44.2	28.5*	11.9

* The *ARSD* for the TD MFR values were calculated in the 20–120 ºC temperature range.

Table S7: Relative errors (%) between the "true" and estimated parametrization when only TD and isothermal dilution measurements are provided as inputs.

Test	**ΔH_{vap}**	**α_m**	**Stoichiometric Coefficients for each volatility bin**					
			10^{-2}	**10^{-1}**	**10^{0}**	**10^{1}**	**10^{2}**	**10^{3}**
A1	6.0	56.3			44	401	45	41
A2	6.9	57.2			66	500	77	-
A3	3.8	49.5		-	35	726	56	-
A4	6.0	56.3			44	401	45	41
B1	4.3	59.4	-	-	123	11	314	30
B2	4.3	59.4	-	-	123	11	314	30
C1	7.5	127.4	37	57	65	21		
C2	18.2	75.7	-	-	125	300	-	-

S4. Sensitivity tests to the upper limit of the sum of the yields

Table S8: True and estimated volatility distribution of the products for 8 different tests for $\Sigma(\alpha_i) < 2.0$. The uncertainty of the estimates (±σ) is also included.

TEST	ΔH_{vap} (kJ mol^{-1})	*log*(α_m)	Stoichiometric Coefficients (α_i) at C_i^* (μg m^{-3})						
			10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
True A	**30**	**-0.30**	-	-	**0.070**	**0.038**	**0.179**	**0.300**	-
A1	32.9±9.6	-0.82±0.50	-	-	0.057 ±0.024	0.069 ±0.051	0.258 ±0.134	0.349 ±0.258	-
A2	32.1±9.9	-0.72±0.45	-	-	0.062 ±0.021	0.067 ±0.053	0.286 ±0.132	-	-
A3	32.1±9.8	-0.72±0.45	-	0.000 ±0.000	0.062 ±0.021	0.067 ±0.053	0.286 ±0.132	-	-
A4	34.2±9.1	-0.71±0.45	-	-	0.061 ±0.021	0.082 ±0.049	0.185 ±0.086	0.301 ±0.238	-
True B	**30**	**-0.30**	**0.001**	**0.012**	**0.037**	**0.088**	**0.099**	**0.250**	**0.800**
B1	33.0±9.5	-0.96±0.21	-	-	0.052 ±0.010	0.035 ±0.039	0.376 ±0.127	0.333 ±0.254	-
B2	36.7±7.4	-0.93±0.25	-	-	0.050 ±0.000	0.051 ±0.038	0.288 ±0.103	0.261 ±0.222	-
True C	**115**	**-2.02**	**0.118**	**0.094**	**0.116**	**0.247**	-	-	-
C1	104.6±24.0	-1.74±0.97	0.126 ±0.086	0.116 ±0.090	0.154 ±0.116	0.216 ±0.126	-	-	-
C2	95.2±16.7	-2.59±0.71	-	-	0.409 ±0.097	0.147 ±0.120	0.173 ±0.148	0.148 ±0.215	-

Table S9: The *mean normilized error* between the "true" and estimated values (MNE_T) for the different tests when $\Sigma(\alpha_i) < 2.0$.

Test	**Yield**				**TD**	**Dilution**
	5 °C	**15 °C**	**25 °C**	**35 °C**		
A1	26.2	21.8	17.5	13.5	5.7	18.4
A2	21.4	19.5	16.9	14.1	6.3	18.5
A3	21.4	19.5	16.9	14.1	6.3	18.5
A4	20.9	18.5	15.7	12.8	6.2	23.0
B1	32.5	22.7	14.8	9.4	1.9	12.5
B2	24.6	15.6	8.9	6.4	2.2	18.7
C1	6.2	6.8	9.6	15.5	4.4 (110 °C)*	2.7
C2	29.2	14.6	8.8	11.0	8.4 (110 °C)*	4.2

S4. References

Tikkanen, O.-P., Hämäläinen, V., Rovelli, G., Lipponen, A., Shiraiwa, M., Reid, J. P., Lehtinen, K. E. J., and Yli-Juuti, T.: Optimization of process models for determining volatility distribution and viscosity of organic aerosols from isothermal particle evaporation data, Atmos. Chem. Phys., 19, 9333–9350, https://doi.org/10.5194/acp-19-9333-2019, 2019.

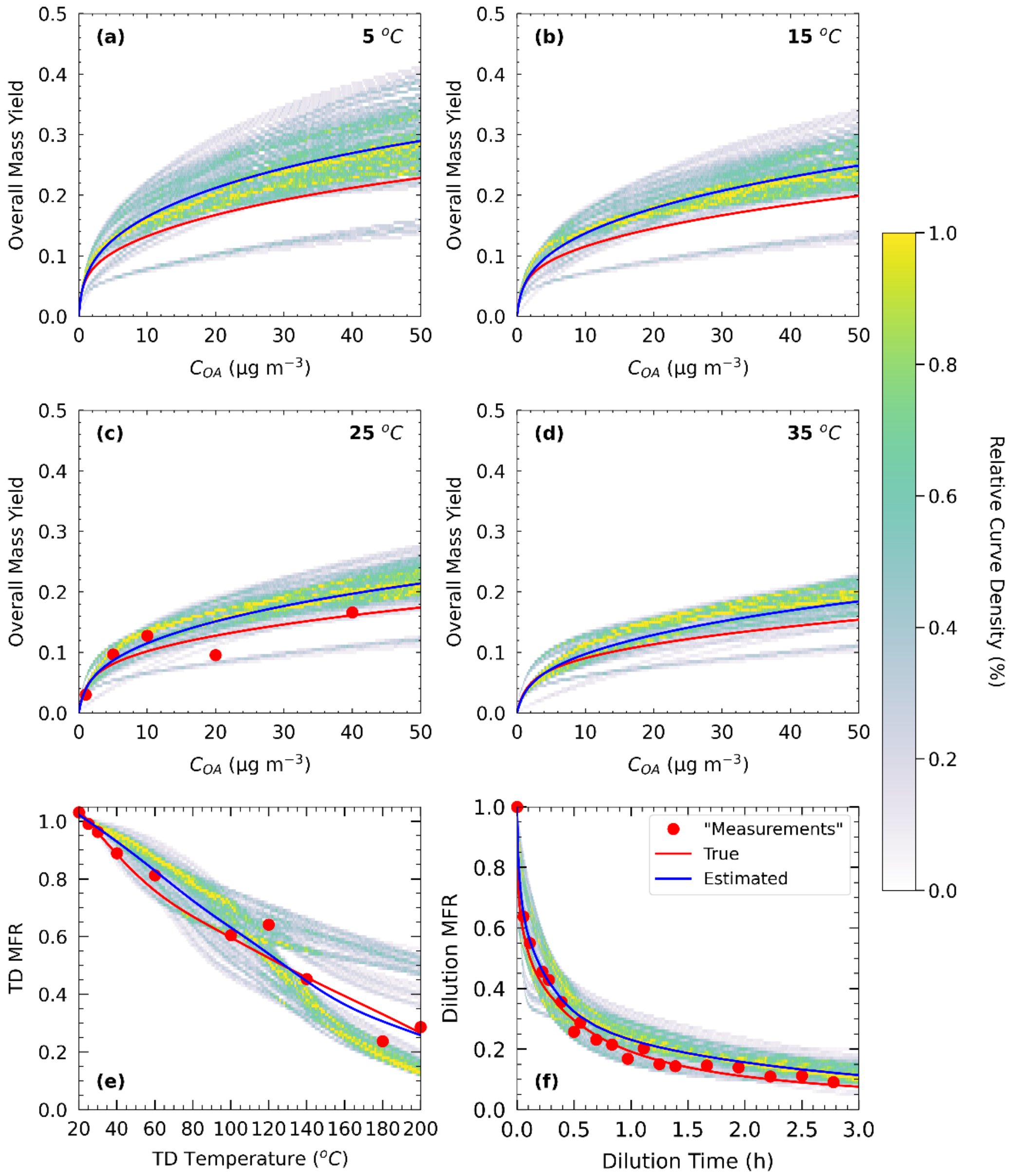

Figure S1: "Measurements" of Test A1 in Experiment A (red dots), true (red line) and estimated (blue line) yields at (**a**) 5 °C, (**b**) 15 °C, (**c**) 25 °C, and (**d**) 35 °C), (**e**) TD (thermogram), and (**f**) dilution (areogram) values. The relative curve density is calculated by discretizing the dependent variable Y and independent X variable into grids, counting how many curves go through a grid box and finally normalized by the highest count in every X column (Tikkanen et al., 2019).

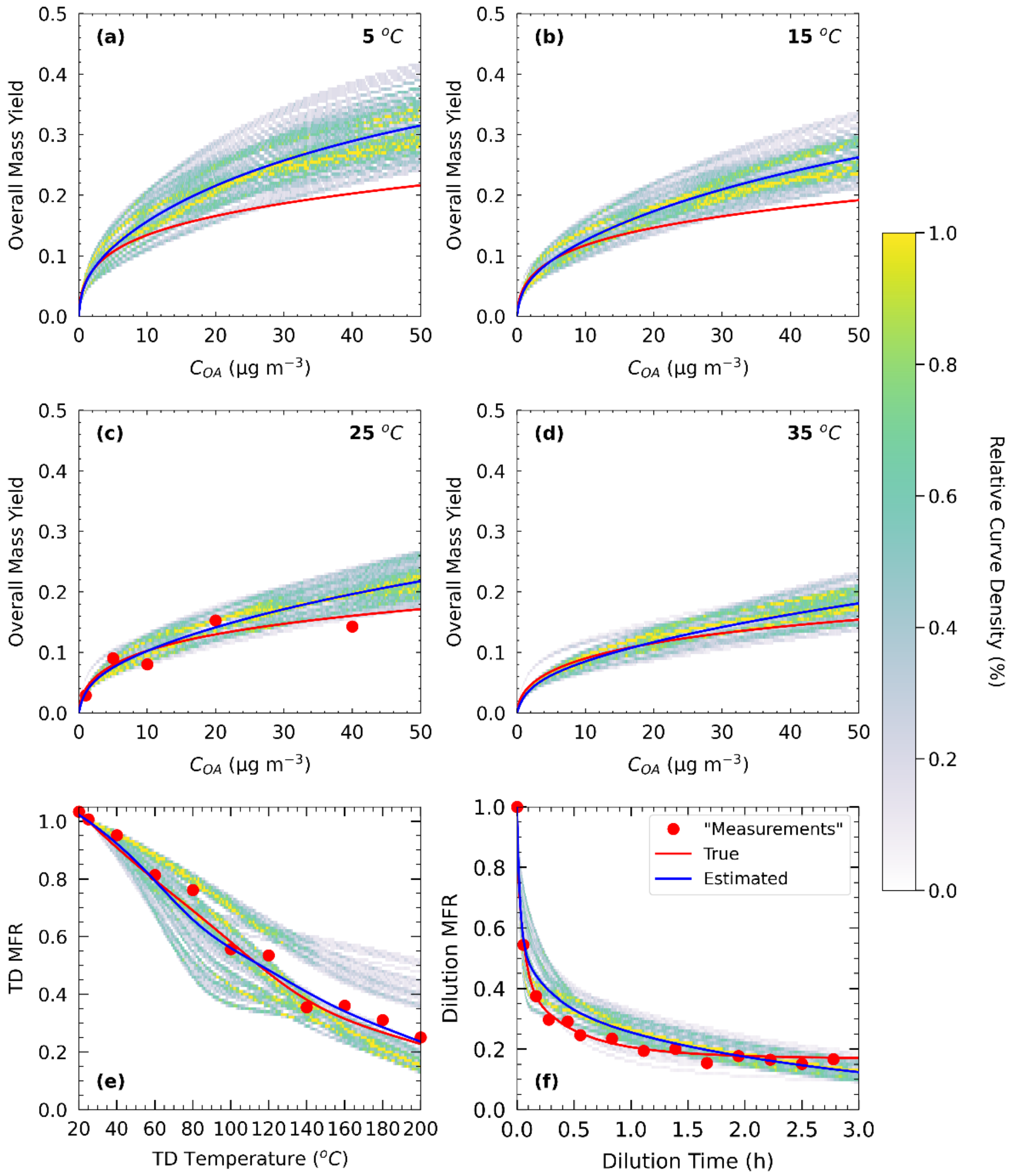

Figure S2: "Measurements" of Test B1 in Experiment B (red dots), true (red line) and estimated (blue line) yields at (**a**) 5 °C, (**b**) 15 °C, (**c**) 25 °C, and (**d**) 35 °C), (**e**) TD (thermogram), and (**f**) dilution (areogram) values. The relative curve density is calculated by discretizing the dependent variable Y and independent X variable into grids, counting how many curves go through a grid box and finally normalized by the highest count in every X column (Tikkanen et al., 2019).

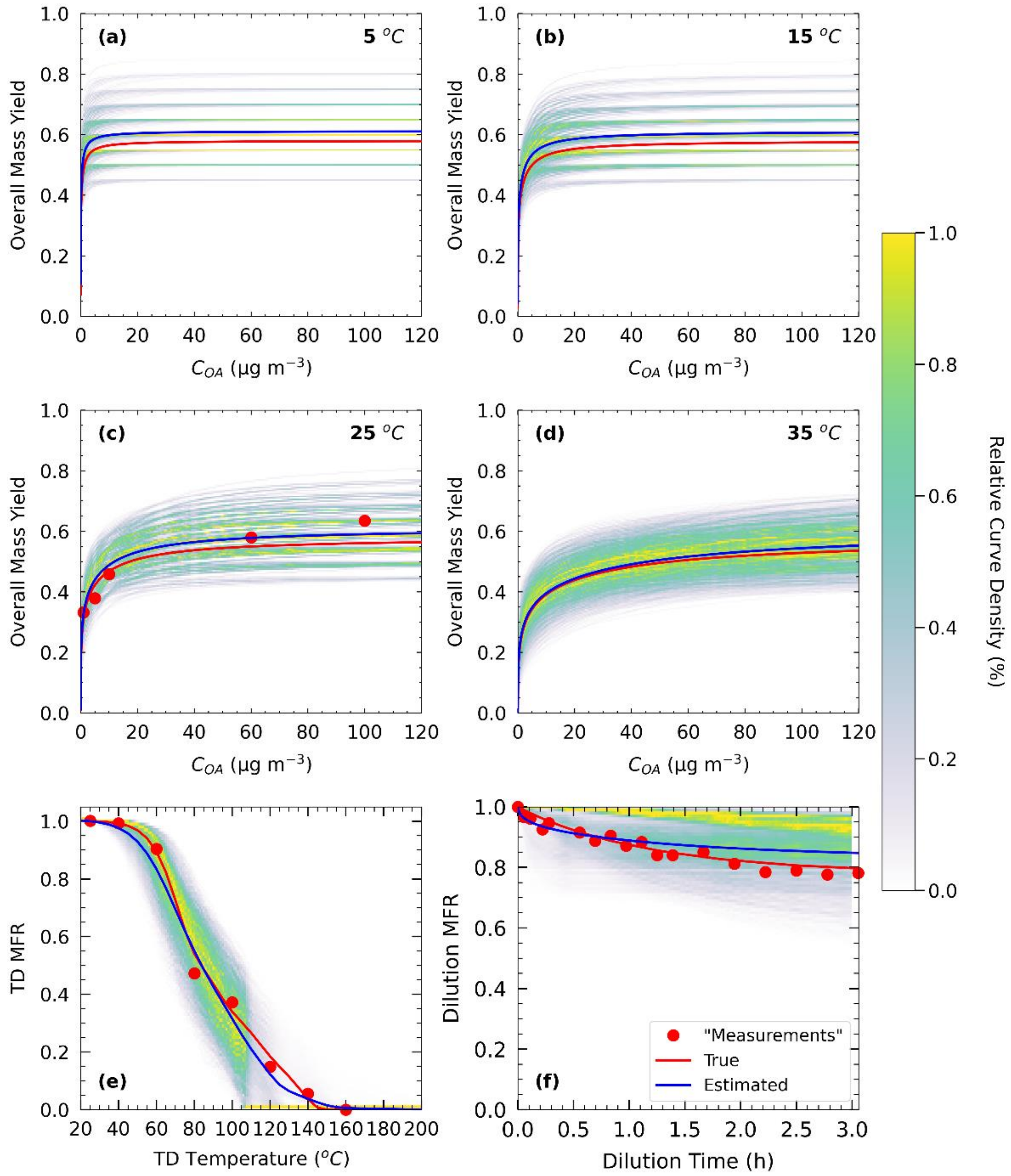

Figure S3: "Measurements" of Test C1 in Experiment C (red dots), true (red line) and estimated (blue line) yields at (**a**) 5 ºC, (**b**) 15 ºC, (**c**) 25 ºC, and (**d**) 35 ºC), (**e**) TD (thermogram), and (**f**) dilution (areogram) values. The relative curve density is calculated by discretizing the dependent variable Y and independent X variable into grids, counting how many curves go through a grid box and finally normalized by the highest count in every X column (Tikkanen et al., 2019).

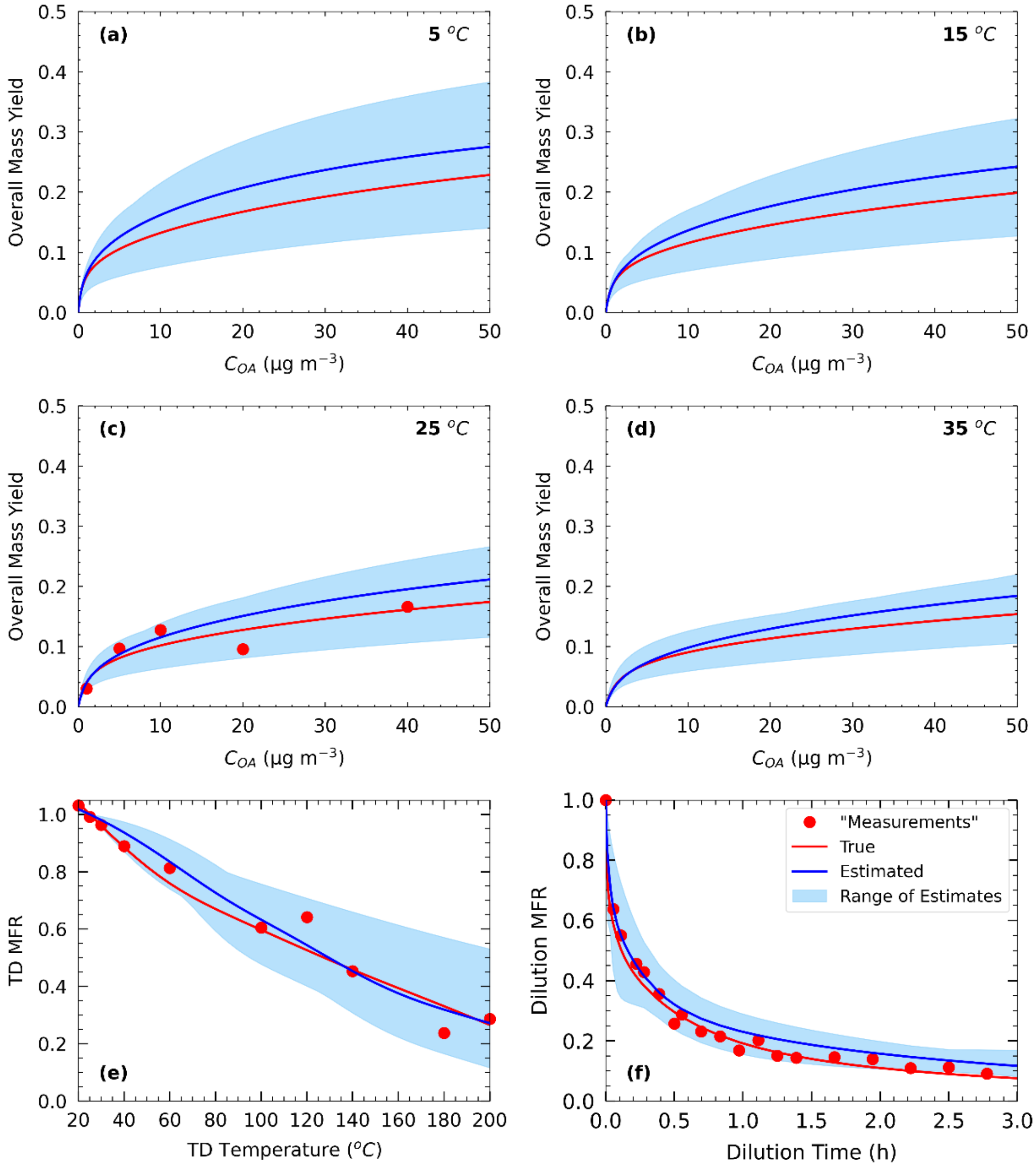

Figure S4: "Measurements" of Test A2 in Experiment A (red dots), true (red line) and estimated (blue line) yields at (**a**) 5 °C, (**b**) 15 °C, (**c**) 25 °C, and (**d**) 35 °C), (**e**) TD (thermogram), and (**f**) dilution (areogram) values. The blue area shows the range of good solutions.

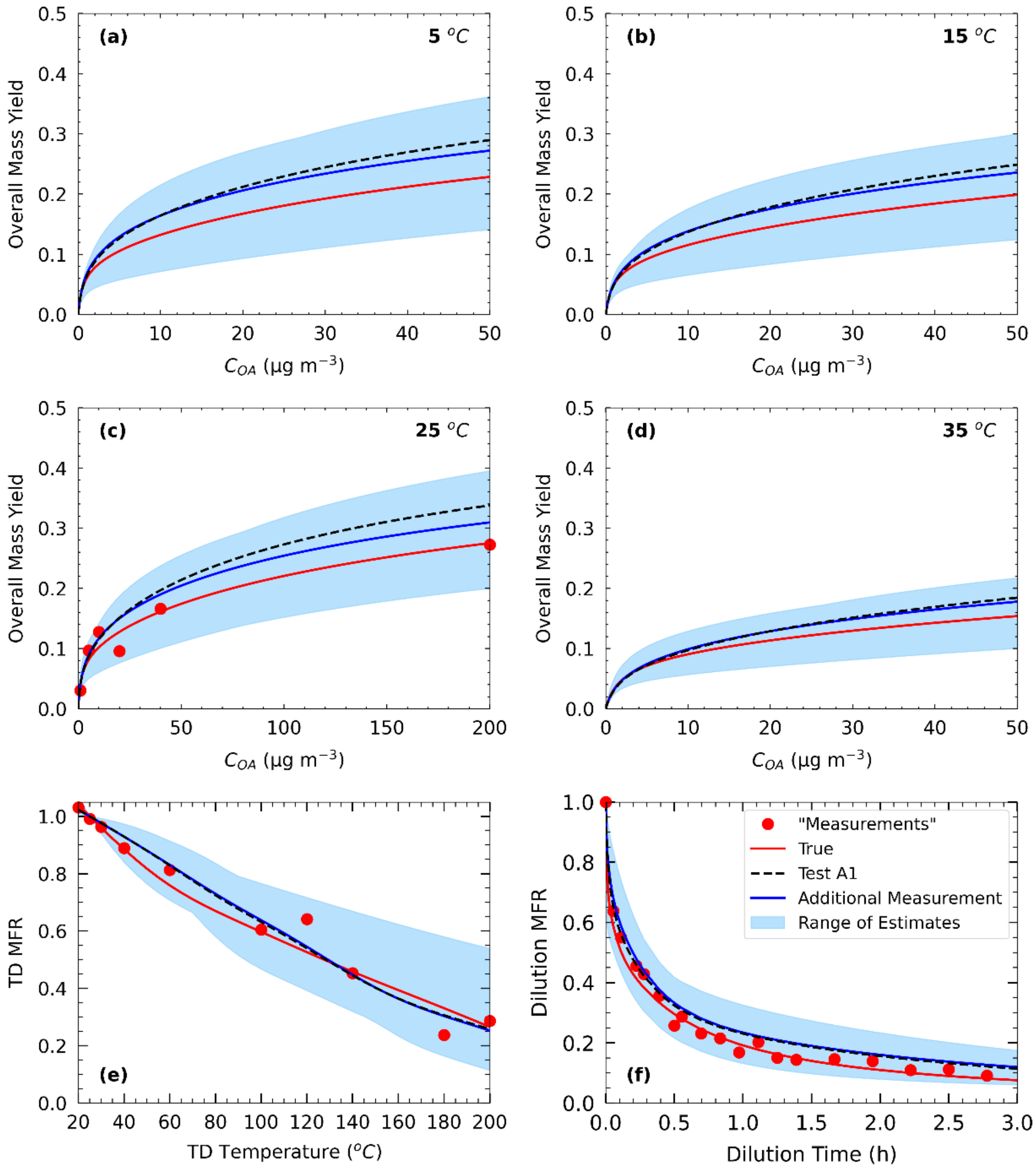

Figure S5: "Measurements" of Test A4 in Experiment A (red dots), true (red line) and estimated (blue line) yields at (**a**) 5 °C, (**b**) 15 °C, (**c**) 25 °C, and (**d**) 35 °C), (**e**) TD (thermogram), and (**f**) dilution (areogram) values. The blue area shows the range of good solutions of Test A4. The black dashed line corresponds to the estimated yields, thermogram and areogram in Test A1.

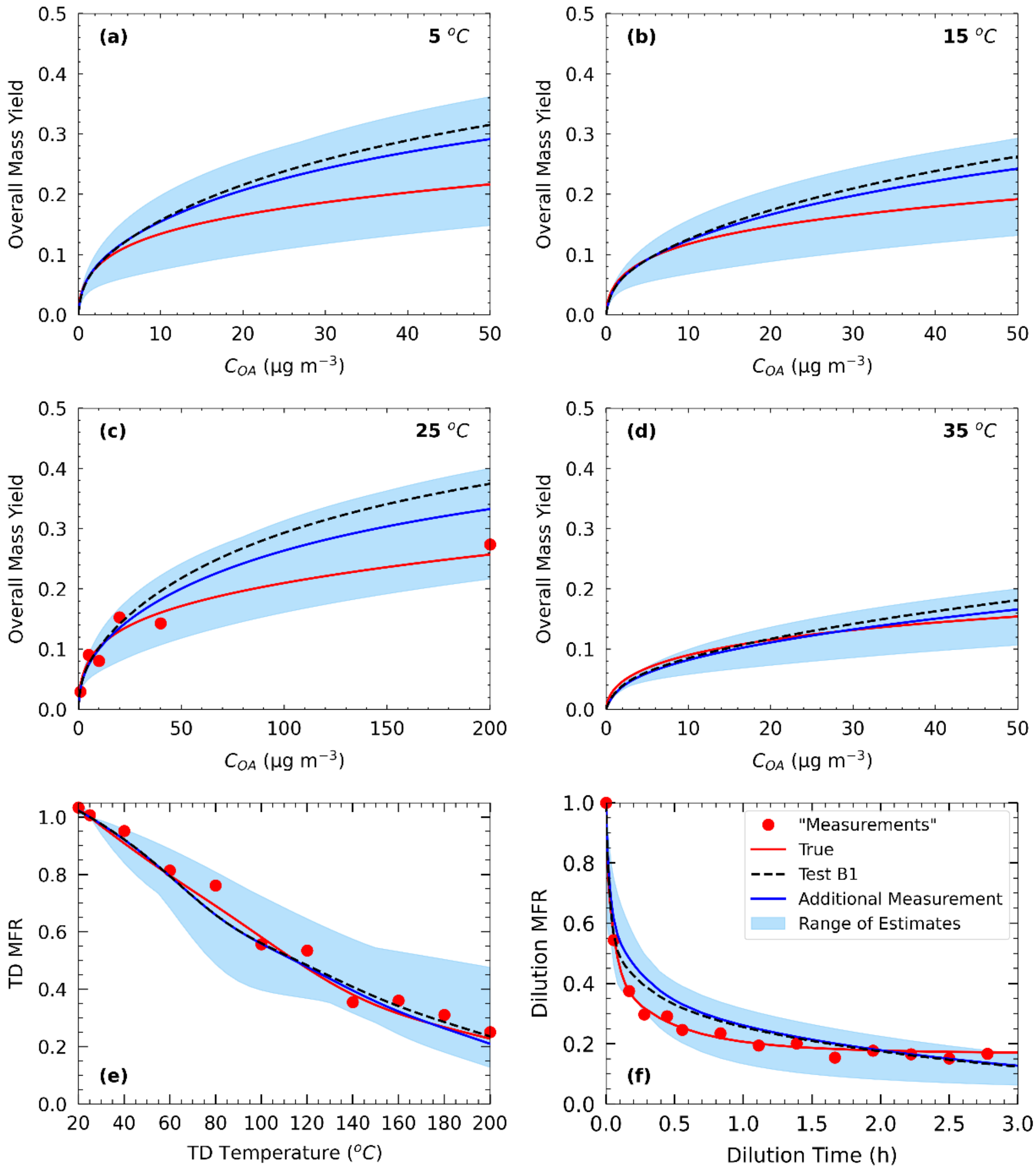

Figure S6: "Measurements" of Test B2 in Experiment B (red dots), true (red line) and estimated (blue line) yields at (**a**) 5 °C, (**b**) 15 °C, (**c**) 25 °C, and (**d**) 35 °C), (**e**) TD (thermogram), and (**f**) dilution (areogram) values. The blue area shows the range of good solutions of Test B2. The black dashed line corresponds to the estimated yields, thermogram and areogram in Test B1.

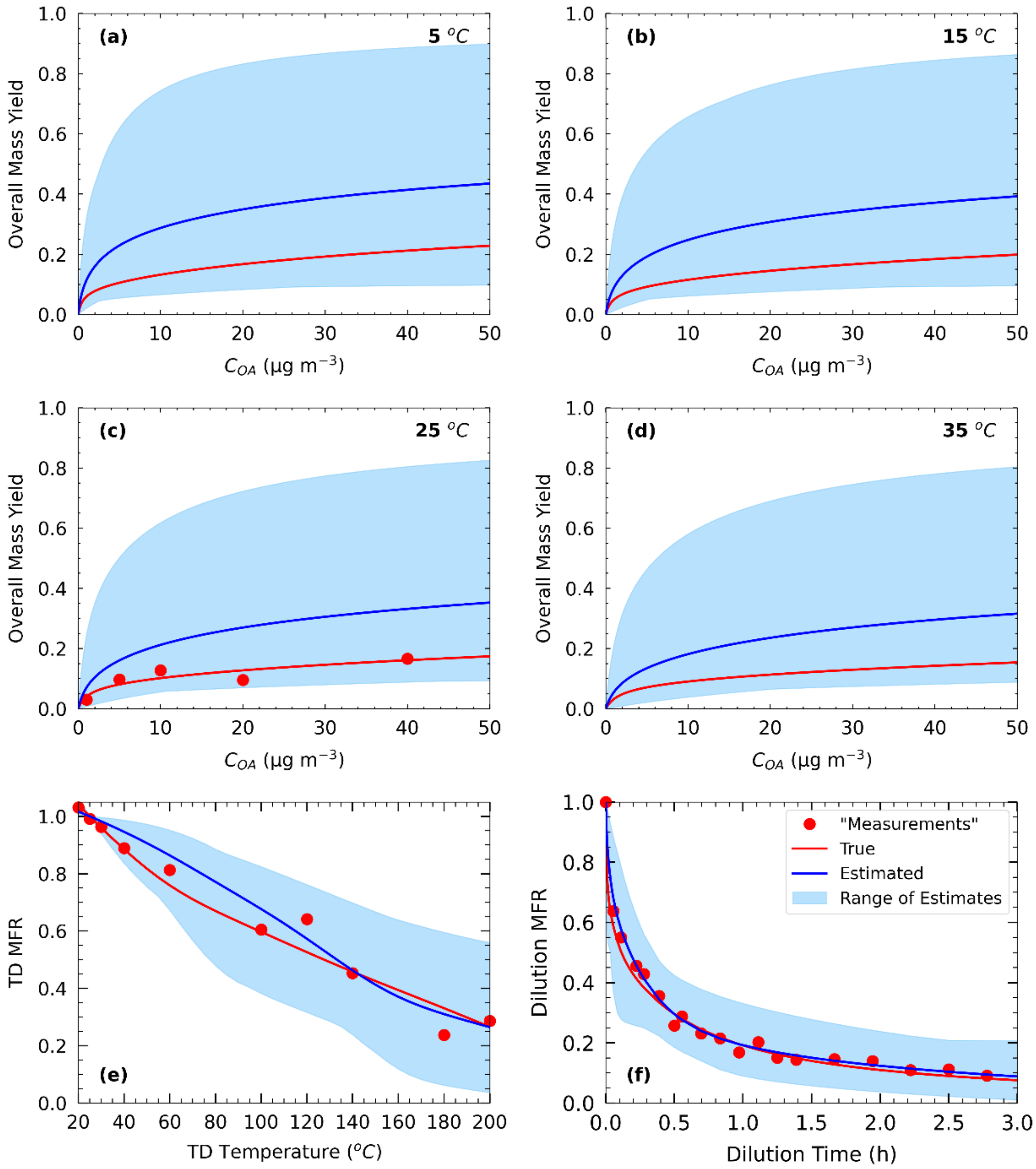

Figure S7: "Measurements" of Test A1 in Experiment A (red dots), true (red line) and estimated (blue line) yields at (**a**) 5 °C, (**b**) 15 °C, (**c**) 25 °C, and (**d**) 35 °C), (**e**) TD (thermogram), and (**f**) dilution (areogram) values when only TD and isothermal dilution measurements are provided as inputs. The blue area shows the range of good solutions of Test A1.

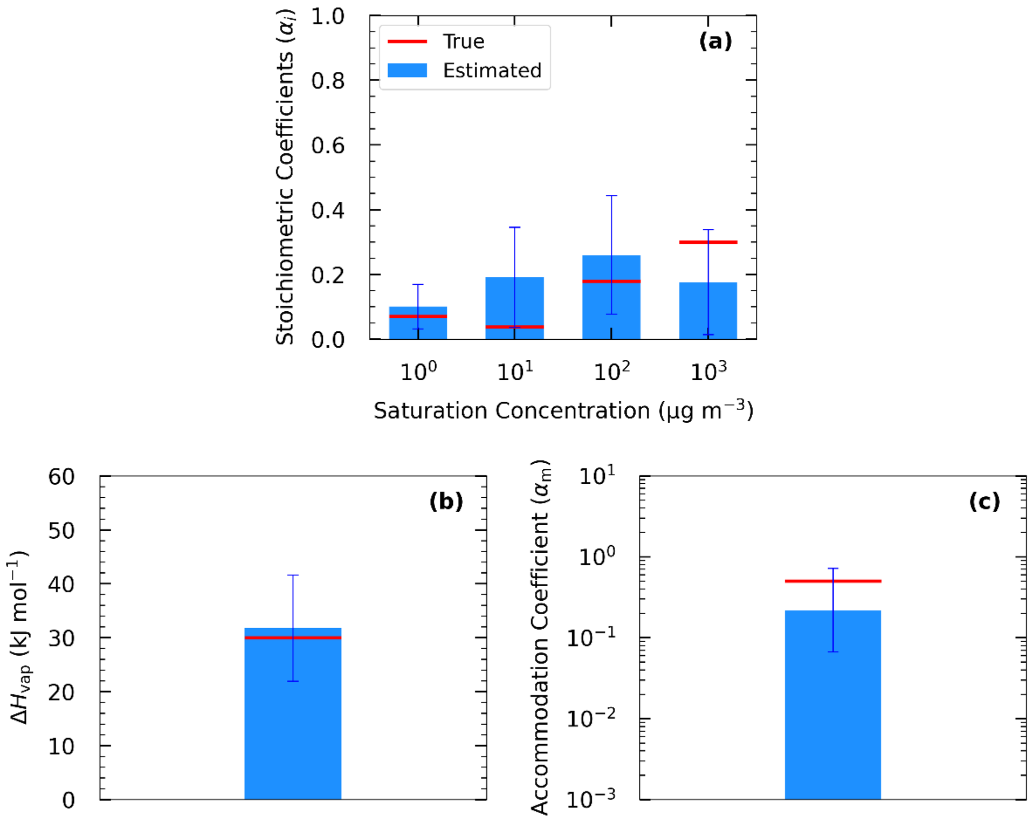

Figure S8. Estimated (bars) and true (red lines) parameter values of Experiment A in Test A1 combining only TD and isothermal dilution measurements for: **(a)** the volatility distribution of the products, **(b)** ΔH_{vap}, and **(c)** α_m. The error bars represent the uncertainty of the estimated values.

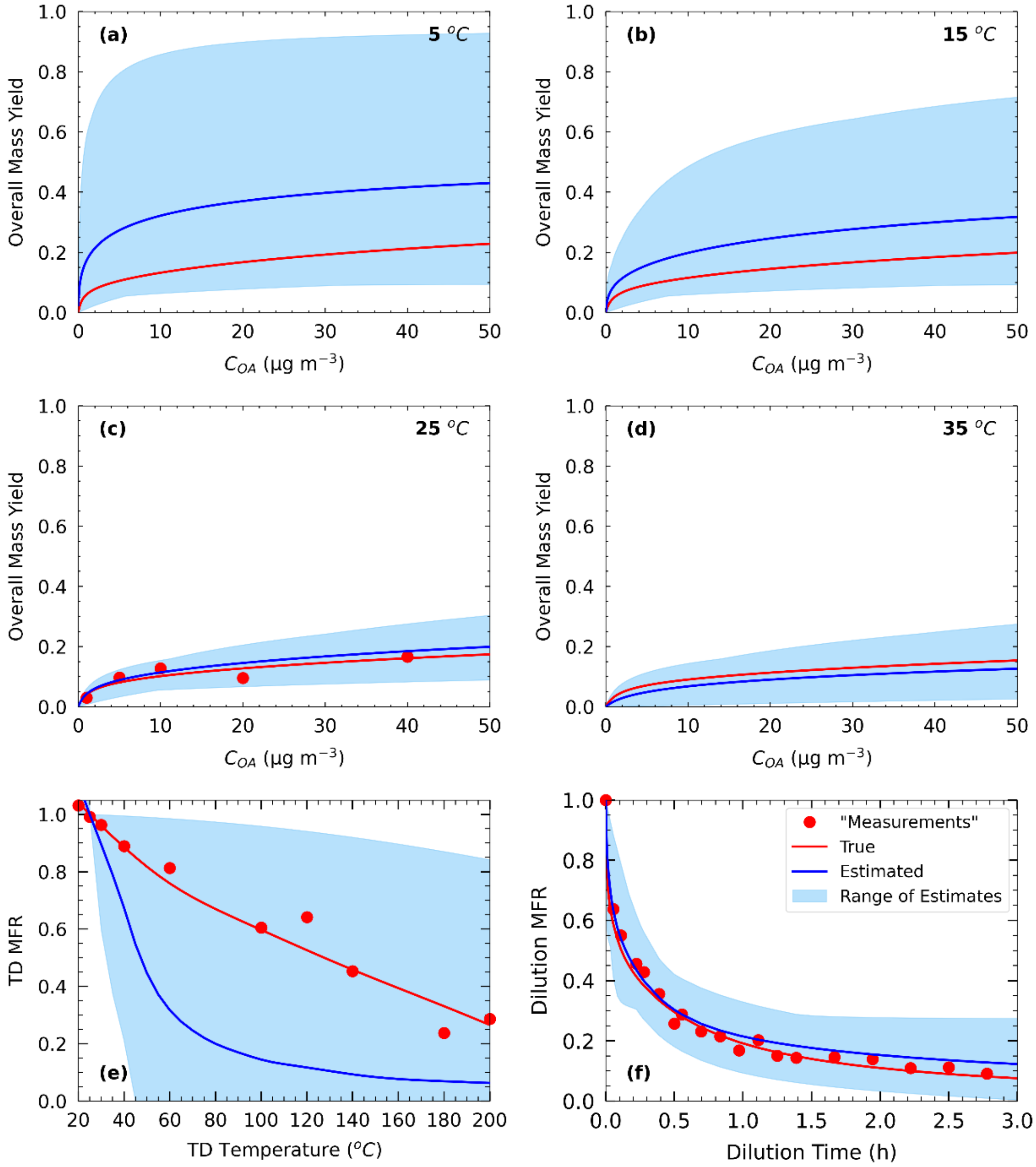

Figure S9: "Measurements" of Test A1 in Experiment A (red dots), true (red line) and estimated (blue line) yields at (**a**) 5 °C, (**b**) 15 °C, (**c**) 25 °C, and (**d**) 35 °C), (**e**) TD (thermogram), and (**f**) dilution (areogram) values when only yield and isothermal dilution measurements are provided as inputs. The blue area shows the range of good solutions of Test A1.

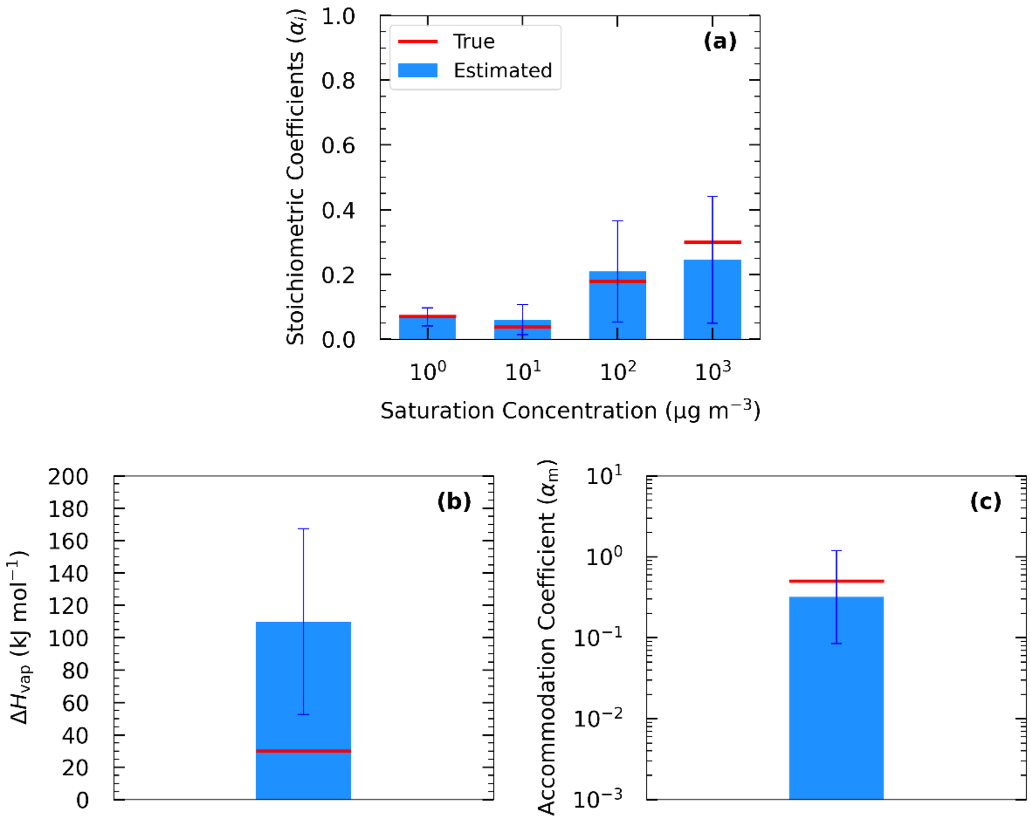

Figure S10. Estimated (bars) and true (red lines) parameter values of Experiment A in Test A1 combining only yield and isothermal dilution measurements for: **(a)** the volatility distribution of the products, **(b)** ΔH_{vap}, and **(c)** α_m. The error bars represent the uncertainty of the estimated values.

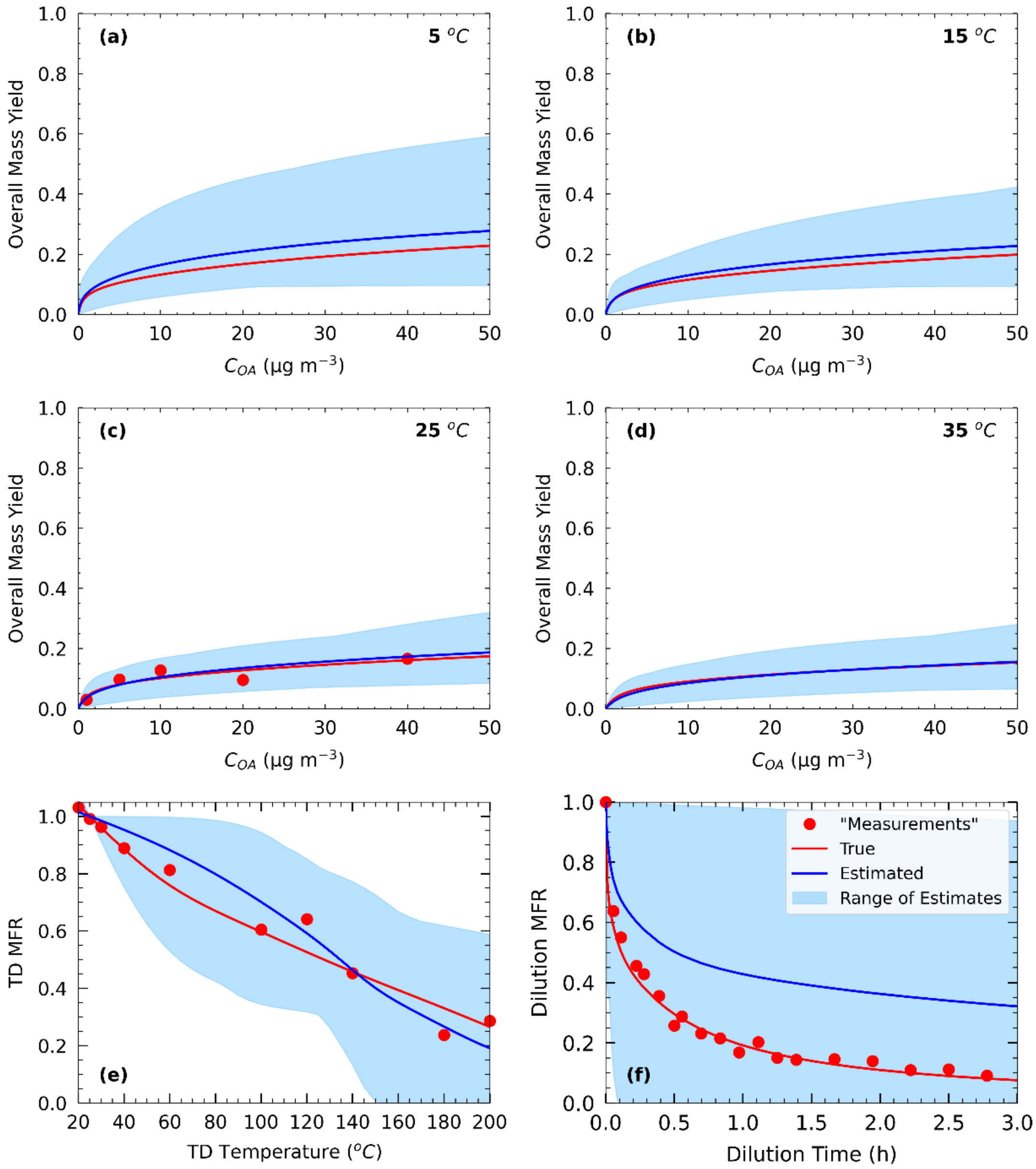

Figure S11: "Measurements" of Test A1 in Experiment A (red dots), true (red line) and estimated (blue line) yields at (**a**) 5 °C, (**b**) 15 °C, (**c**) 25 °C, and (**d**) 35 °C), (**e**) TD (thermogram), and (**f**) dilution (areogram) values when only yield and TD measurements are provided as inputs. The blue area shows the range of good solutions of Test A1.

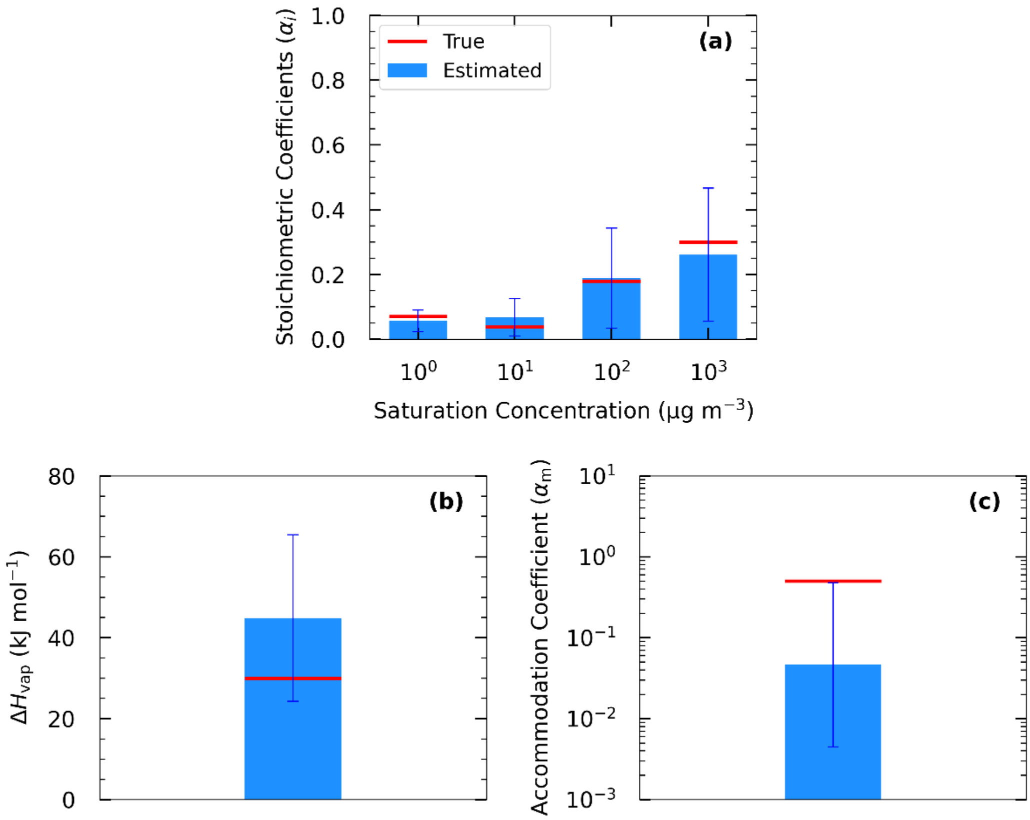

Figure S12. Estimated (bars) and true (red lines) parameter values of Experiment A in Test A1 combining only yield and TD measurements for: **(a)** the volatility distribution of the products, **(b)** ΔH_{vap}, and **(c)** α_m. The error bars represent the uncertainty of the estimated values.