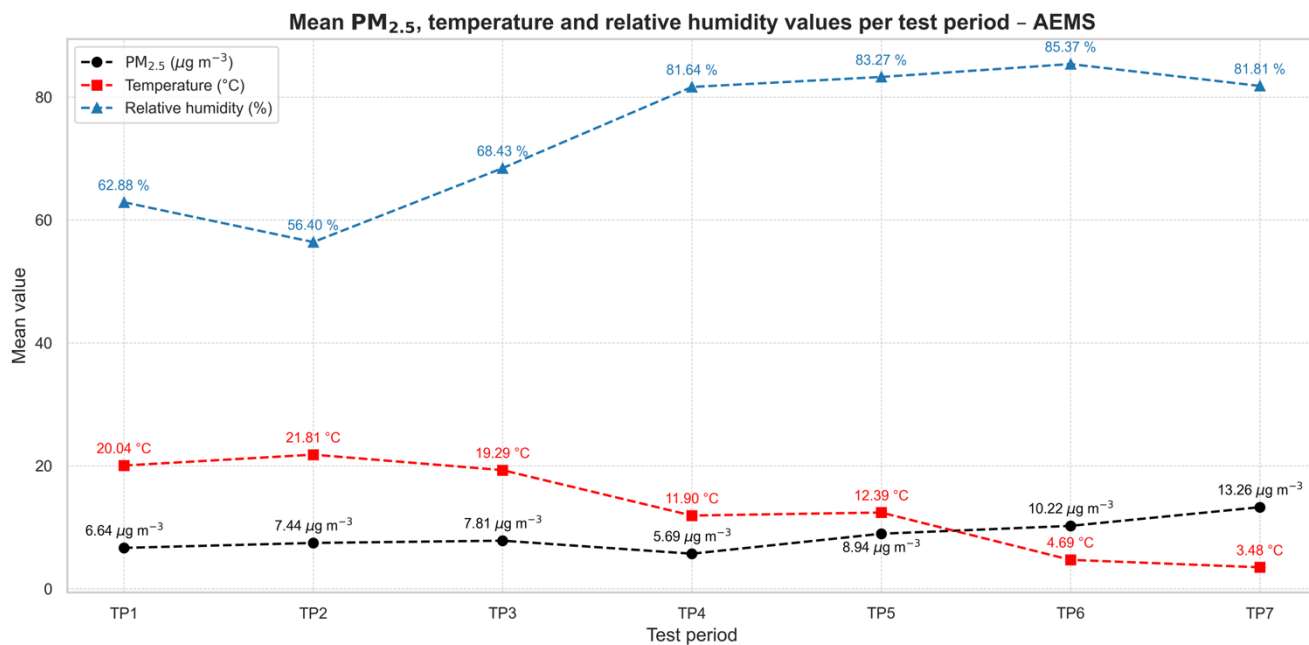
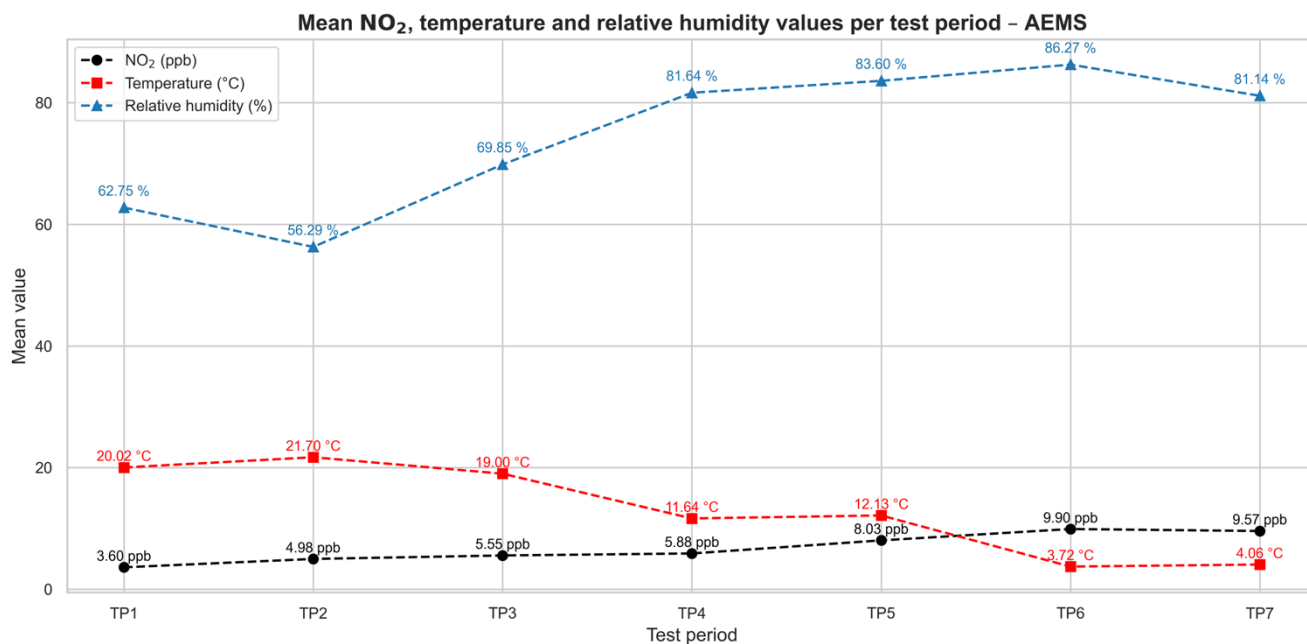


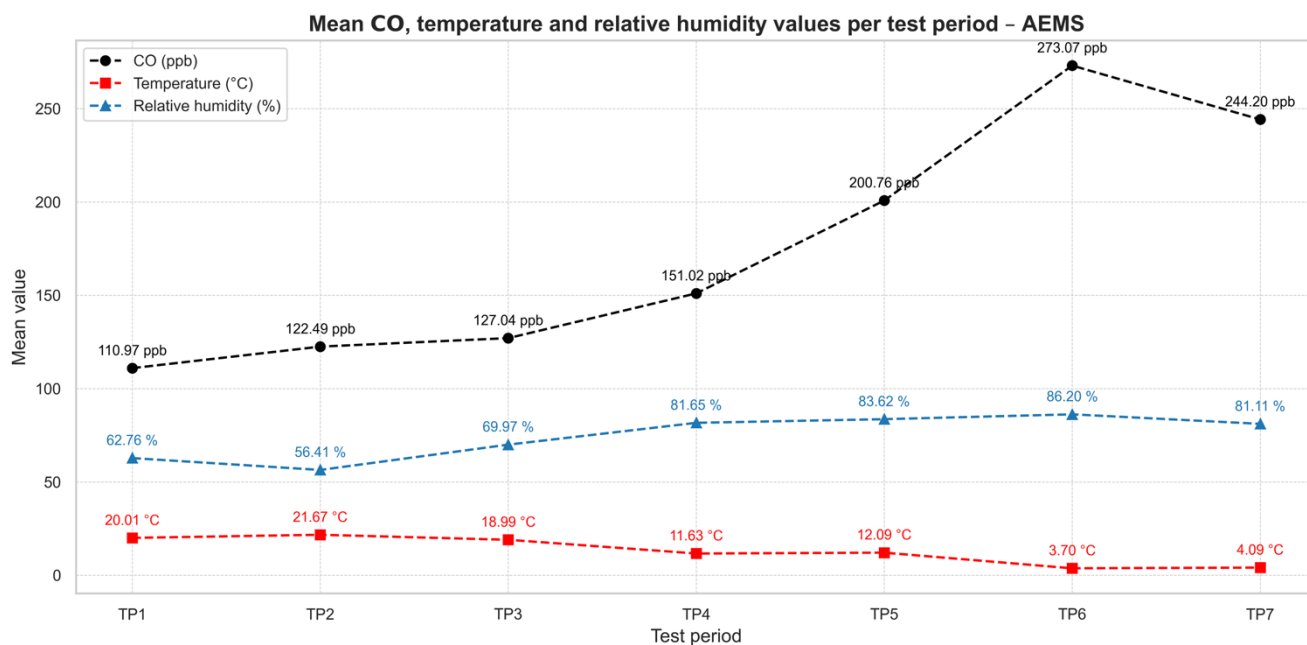
**Figure S1.** Test period (TP1–TP7) means of ambient temperature, relative humidity and O<sub>3</sub> given by the reference station AEMS (TP1 = 10 June – 10 July 2022, TP2 = 11 July – 11 August 2022, TP3 = 11 August – 10 September 2022, TP4 = 10 September – 11 October 2022, TP5 = 11 October – 12 November 2022, TP6 = 12 November – 12 December 2022, TP7 = 12 December 2022 – 11 January 2023).



**Figure S2.** Test period (TP1–TP7) means of ambient temperature, relative humidity and PM<sub>2.5</sub> given by the reference station AEMS (TP1 = 11 June – 10 July 2022, TP2 = 11 July – 9 August 2022, TP3 = 10 August – 8 September 2022, TP4 = 9 September – 8 October 2022, TP5 = 9 October – 7 November 2022, TP6 = 8 November – 7 December 2022, TP7 = 8 December 2022 – 6 January 2023).



**Figure S3.** Test period (TP1–TP7) means of ambient temperature, relative humidity and NO<sub>2</sub> given by the reference station AEMS (TP1 = 10 June – 10 July 2022, TP2 = 10 July – 10 August 2022, TP3 = 11 August – 10 September 2022, TP4 = 10 September – 10 October 2022, TP5 = 10 October – 11 November 2022, TP6 = 11 November – 11 December 2022, TP7 = 11 December 2022 – 10 January 2023).



**Figure S4.** Test period (TP1–TP7) means of ambient temperature, relative humidity and CO given by the reference station AEMS (TP1 = 10 June – 10 July 2022, TP2 = 10 July – 11 August 2022, TP3 = 11 August – 10 September 2022, TP4 = 10 September – 10 October 2022, TP5 = 10 October – 11 November 2022, TP6 = 11 November – 11 December 2022, TP7 = 11 December 2022 – 10 January 2023).

**Table S1.** Data quality objectives for indicative measurements and objective estimation set in the Air Quality Directive 2008/50/EC and in CEN/TS 17660-1:2021 and class 3 set in CEN/TS 17660-1:2021.

Pollutant	Averaging Period	LV	DQO of Class 1 sensor system	DQO of Class 2 sensor system	DQO of Class 3 sensor system
	h	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$ (% of LV)	$\mu\text{g m}^{-3}$ (% of LV)	$\mu\text{g m}^{-3}$ (% of LV)
NO <sub>2</sub>	1	200	50 (25 %)	150 (75 %)	400 (200 %)
O <sub>3</sub>	8 <sup>a</sup>	120	36 (30 %)	90 (75 %)	240 (200 %)
CO	8 <sup>b</sup>	10 <sup>c</sup>	2.5 <sup>c</sup> (25 %)	7.5 <sup>c</sup> (75 %)	20 <sup>c</sup> (200 %)

<sup>a</sup> For O<sub>3</sub>, an averaging period of 1 h instead of 8 h shall be used for the evaluation of the sensor system at the limit value (LV) to do the classification.

<sup>b</sup> For CO, an averaging period of 1 h instead of 8 h shall be used for the evaluation of the sensor system at the limit value (LV) to do the classification.

<sup>c</sup> In  $\text{mg m}^{-3}$ .

**Table S2.** Data quality objectives for indicative measurements and objective estimation set in the Air Quality Directive 2008/50/EC and in CEN/TS 17660-2:2024 and class 3 set in CEN/TS 17660-2:2024.

Pollutant	Averaging Period	LV	DQO of Class 1 sensor system	DQO of Class 2 sensor system	DQO of Class 3 sensor system
	h	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$ (% of LV)	$\mu\text{g m}^{-3}$ (% of LV)	$\mu\text{g m}^{-3}$ (% of LV)
PM <sub>2.5</sub>	24	30 <sup>a</sup>	15 (50 %)	30 (100 %)	60 (200 %)

<sup>a</sup> For PM<sub>2.5</sub> a concentration of 30  $\mu\text{g m}^{-3}$  shall be used as a substitute value for the daily limit value (LV).

**Table S3.** Hyperparameter-Tuning

Algorithm	Hyperparameters
Random Forest	mtree
	sample.fraction
	min.node.size
	num.trees
Extreme Gradient Boosting	nrounds
	eta
	max_depth
	lambda
	alpha
Ridge Regression	s

**Table S4.** Performances of LCS calibration models for NO<sub>2</sub> and CO for each AELCM box using hourly means. Results were observed on the NO<sub>2</sub> training dataset (11 January, 19:00:00–10 June 2022, 18:00:00) and NO<sub>2</sub> test dataset (10 June 2022, 19:00:00–10 January 2023, 13:00:00) as well as on the CO training dataset (11 January, 19:00:00–10 June 2022, 19:00:00) and CO test dataset (10 June 2022, 20:00:00–10 January 2023, 16:00:00).

Model target	Training R <sup>2</sup>	Training MAE (ppb)	Training RMSE (ppb)	Test R <sup>2</sup>	Test MAE (ppb)	Test RMSE (ppb)
NO <sub>2</sub> (MLR, 009)	0.86	1.88	2.56	0.70	2.37	3.20
NO <sub>2</sub> (MLR, 010)	0.86	1.99	2.62	0.71	2.84	3.63
NO <sub>2</sub> (RR, 009)	0.79	2.84	3.76	0.64	2.57	3.32
NO <sub>2</sub> (RR, 010)	0.78	2.82	3.71	0.63	2.83	3.55
NO <sub>2</sub> (XGB, 009)	0.94	1.23	1.74	0.78	2.09	3.09
NO <sub>2</sub> (XGB, 010)	0.91	1.69	2.51	0.76	2.01	2.84
NO <sub>2</sub> (RF, 009)	0.99	0.57	0.82	0.79	1.89	2.70
NO <sub>2</sub> (RF, 010)	0.92	1.42	2.02	0.75	2.33	3.09
CO (MLR, 009)	0.97	11.08	14.59	0.97	12.11	18.18
CO (MLR, 010)	0.97	12.56	15.93	0.96	14.80	21.85
CO (RR, 009)	0.94	14.80	22.04	0.93	18.81	28.62
CO (RR, 010)	0.93	16.30	23.52	0.89	23.04	35.16
CO (XGB, 009)	0.98	18.06	22.84	0.97	16.37	21.47
CO (XGB, 010)	0.99	24.73	28.52	0.96	25.66	33.72
CO (RF, 009)	1.00	3.62	5.36	0.96	16.01	25.17
CO (RF, 010)	0.99	4.48	6.50	0.97	13.94	19.88

## Performance Metrics NO<sub>2</sub>

**Table S5.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on extreme gradient boosting, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

1 month xgboost (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.76/0.77		0.80/0.83		0.81/0.86		0.95/0.95	0.85/0.88
R <sup>2</sup>	0.47/0.52		0.62/0.66		0.66/0.78		0.91/0.92	0.79/0.84
RMSE [ppb]	2.01/1.85		3.05/2.67		2.87/2.42		2.79/2.43	2.71/2.36
MAE [ppb]	1.30/1.29		2.06/1.83		2.19/1.82		2.20/1.77	1.94/1.68
Slope	0.53/0.62		0.58/0.62		0.81/0.72		0.90/0.83	0.89/0.80
Delta Slope	0.47/0.38		0.42/0.38		0.19/0.28		0.10/0.17	0.11/0.20
Intercept	1.10/1.31		0.83/1.24		1.40/1.28		2.52/2.05	0.54/0.93
Intercept	1.10/1.31		0.83/1.24		1.40/1.28		2.52/2.05	0.54/0.93
AELCM009								
Rs		0.77/0.81		0.87/0.88		0.86/0.92		0.87/0.89
R <sup>2</sup>		0.54/0.60		0.81/0.84		0.79/0.86		0.76/0.80
RMSE [ppb]		3.67/3.00		2.36/2.07		2.89/2.36		3.02/2.51
MAE [ppb]		2.37/1.87		1.52/1.52		2.30/1.77		2.06/1.72
Slope		0.39/0.51		0.77/0.88		0.69/0.81		0.70/0.77
Delta Slope		0.61/0.49		0.23/0.12		0.31/0.19		0.30/0.23
Intercept		0.98/1.23		0.63/0.89		1.34/0.43		0.60/0.76
Intercept		0.98/1.23		0.63/0.89		1.34/0.43		0.60/0.76

**Table S6.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on random forest, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

1 month random forest (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.69/0.76		0.77/0.81		0.82/0.85		0.94/0.95	0.83/0.87
R <sup>2</sup>	0.48/0.54		0.60/0.67		0.67/0.76		0.90/0.90	0.78/0.82
RMSE [ppb]	2.00/1.88		2.75/2.50		2.99/2.35		3.72/2.99	2.93/2.46
MAE [ppb]	1.45/1.38		1.88/1.74		2.32/1.84		3.14/2.44	2.20/1.85
Slope	0.64/0.66		0.67/0.66		0.86/0.78		0.87/0.82	0.91/0.84
Delta Slope	0.36/0.34		0.33/0.34		0.14/0.22		0.13/0.18	0.09/0.16
Intercept	1.66/1.66		1.72/1.70		1.70/1.59		3.93/3.23	1.51/1.50
Intercept	1.66/1.66		1.72/1.70		1.70/1.59		3.93/3.23	1.51/1.50
AELCM009								
Rs		0.71/0.79		0.86/0.88		0.87/0.91		0.86/0.89
R <sup>2</sup>		0.46/0.55		0.81/0.85		0.79/0.85		0.75/0.79
RMSE [ppb]		3.32/2.94		2.24/2.03		2.47/2.27		2.72/2.44
MAE [ppb]		2.10/1.79		1.65/1.56		1.90/1.75		1.88/1.70
Slope		0.43/0.53		0.74/0.82		0.70/0.79		0.70/0.75
Delta Slope		0.57/0.47		0.26/0.18		0.30/0.21		0.30/0.25
Intercept		1.77/1.69		1.35/1.39		2.26/1.01		1.39/1.28
Intercept		1.77/1.69		1.35/1.39		2.26/1.01		1.39/1.28

**Table S7.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on ridge regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

1 month ridge regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.72/0.73		0.78/0.78		0.79/0.79		0.93/0.93	0.82/0.82
R <sup>2</sup>	0.43/0.44		0.50/0.50		0.56/0.55		0.82/0.83	0.67/0.67
RMSE [ppb]	3.02/2.50		3.17/3.05		3.41/3.18		3.95/4.45	3.41/3.37
MAE [ppb]	2.43/2.01		2.41/2.30		2.56/2.45		3.37/3.74	2.69/2.63
Slope	1.01/0.78		0.64/0.49		0.69/0.52		0.64/0.49	0.76/0.58
Delta Slope	0.01/0.22		0.36/0.51		0.31/0.48		0.36/0.51	0.24/0.42
Intercept	0.20/1.54		1.89/2.86		3.45/4.17		4.84/5.30	2.22/3.16
Intercept	0.20/1.54		1.89/2.86		3.45/4.17		4.84/5.30	2.22/3.16
AELCM009								
Rs		0.72/0.74		0.83/0.81		0.81/0.81		0.84/0.84
R <sup>2</sup>		0.36/0.37		0.71/0.69		0.62/0.62		0.59/0.58
RMSE [ppb]		4.16/3.66		2.95/3.39		3.09/3.23		3.44/3.43
MAE [ppb]		3.18/2.73		2.42/2.87		2.37/2.49		2.66/2.70
Slope		0.67/0.55		0.54/0.41		0.63/0.47		0.69/0.55
Delta Slope		0.33/0.45		0.46/0.59		0.37/0.53		0.31/0.45
Intercept		0.81/1.85		3.17/4.28		3.87/5.05		2.07/3.19
Intercept		0.81/1.85		3.17/4.28		3.87/5.05		2.07/3.19

**Table S8.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on multiple linear regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

1 month multiple linear regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.45/0.49		0.69/0.69		0.82/0.82		0.93/0.93	0.77/0.76
R <sup>2</sup>	0.25/0.29		0.52/0.51		0.64/0.65		0.91/0.91	0.75/0.74
RMSE [ppb]	3.16/2.80		3.02/3.11		3.23/2.95		4.60/3.67	3.56/3.15
MAE [ppb]	2.46/2.23		2.28/2.39		2.35/2.18		3.97/3.08	2.77/2.47
Slope	0.61/0.64		0.59/0.58		0.88/0.79		1.02/0.92	0.98/0.90
Delta Slope	0.39/0.36		0.41/0.42		0.12/0.21		0.02/0.08	0.02/0.10
Intercept	2.44/1.53		2.47/1.84		1.48/1.19		3.57/3.57	1.56/1.15
Intercept	2.44/1.53		2.47/1.84		1.48/1.19		3.57/3.57	1.56/1.15
AELCM009								
Rs		0.43/0.55		0.84/0.81		0.87/0.88		0.78/0.81
R <sup>2</sup>		0.20/0.30		0.77/0.76		0.73/0.75		0.63/0.68
RMSE [ppb]		4.09/3.66		2.67/2.53		3.05/2.61		3.32/2.98
MAE [ppb]		3.02/2.65		1.96/1.94		2.29/1.93		2.42/2.17
Slope		0.35/0.40		0.74/0.70		0.95/0.84		0.74/0.71
Delta Slope		0.65/0.60		0.26/0.30		0.05/0.16		0.26/0.29
Intercept		3.50/3.22		0.44/1.64		-0.29/1.19		1.26/1.92
Intercept		3.50/3.22		0.44/1.64		0.29/1.19		1.26/1.92

**Table S9.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on extreme gradient boosting, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

2 month xgboost (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.76/0.76	0.76/0.77			0.81/0.84	0.88/0.84		0.86/0.87
R <sup>2</sup>	0.47/0.50	0.46/0.55			0.66/0.73	0.76/0.74		0.70/0.74
RMSE [ppb]	2.01/1.91	3.55/3.07			2.87/2.55	3.04/2.57		2.92/2.56
MAE [ppb]	1.30/1.29	2.25/1.94			2.19/1.93	2.44/1.97		2.04/1.78
Slope	0.53/0.60	0.42/0.51			0.81/0.73	0.87/0.77		0.88/0.78
Delta Slope	0.47/0.40	0.58/0.49			0.19/0.27	0.13/0.23		0.12/0.22
Intercept	1.10/1.22	1.25/1.37			1.40/1.45	2.95/2.47		0.62/1.02
Intercept	1.10/1.22	1.25/1.37			1.40/1.45	2.95/2.47		0.62/1.02
AELCM009								
Rs			0.81/0.84	0.87/0.87			0.95/0.95	0.88/0.89
R <sup>2</sup>			0.64/0.71	0.81/0.82			0.91/0.91	0.83/0.85
RMSE [ppb]			3.58/2.63	2.36/2.20			3.35/2.80	3.14/2.55
MAE [ppb]			2.47/1.79	1.52/1.65			2.36/2.10	2.12/1.85
Slope			0.43/0.57	0.77/0.84			0.70/0.75	0.70/0.76
Delta Slope			0.57/0.43	0.23/0.16			0.30/0.25	0.30/0.24
Intercept			0.96/1.38	0.63/1.25			1.17/1.74	0.58/1.25
Intercept			0.96/1.38	0.63/1.25			1.17/1.74	0.58/1.25

**Table S10.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on random forest, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

2 month random forest (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.69/0.72	0.69/0.73			0.82/0.84	0.85/0.85		0.84/0.86
R <sup>2</sup>	0.48/0.50	0.43/0.47			0.67/0.72	0.73/0.74		0.70/0.72
RMSE [ppb]	2.00/2.00	3.30/3.15			2.99/2.54	3.95/2.89		3.14/2.68
MAE [ppb]	1.45/1.46	2.21/2.08			2.32/1.98	3.35/2.26		2.33/1.95
Slope	0.64/0.66	0.52/0.55			0.86/0.79	0.86/0.82		0.91/0.82
Delta Slope	0.36/0.34	0.48/0.45			0.14/0.21	0.14/0.18		0.09/0.18
Intercept	1.66/1.68	2.49/2.35			1.70/1.57	4.24/2.97		1.59/1.60
Intercept	1.66/1.68	2.49/2.35			1.70/1.57	4.24/2.97		1.59/1.60
AELCM009								
Rs			0.80/0.83	0.86/0.85			0.95/0.95	0.86/0.88
R <sup>2</sup>			0.61/0.69	0.81/0.81			0.93/0.93	0.84/0.85
RMSE [ppb]			3.19/2.51	2.24/2.34			2.68/2.59	2.73/2.48
MAE [ppb]			2.15/1.75	1.65/1.87			1.96/1.98	1.92/1.87
Slope			0.49/0.60	0.74/0.79			0.74/0.75	0.73/0.75
Delta Slope			0.51/0.40	0.26/0.21			0.26/0.25	0.27/0.25
Intercept			1.24/1.60	1.35/2.02			1.78/2.24	1.07/1.73
Intercept			1.24/1.60	1.35/2.02			1.78/2.24	1.07/1.73

**Table S11.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on ridge regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

2 month ridge regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.72/0.73	0.72/0.73			0.79/0.78	0.79/0.79		0.83/0.84
R <sup>2</sup>	0.43/0.44	0.37/0.37			0.56/0.55	0.59/0.59		0.59/0.59
RMSE [ppb]	3.02/2.67	4.25/3.91			3.41/3.20	3.63/3.35		3.60/3.31
MAE [ppb]	2.43/2.13	3.34/3.00			2.56/2.44	2.90/2.68		2.81/2.56
Slope	1.01/0.89	0.72/0.63			0.69/0.60	0.64/0.55		0.85/0.75
Delta Slope	0.01/0.11	0.28/0.37			0.31/0.40	0.36/0.45		0.15/0.25
Intercept	0.20/0.64	0.94/1.25			3.45/3.64	5.25/5.37		1.58/1.89
Intercept	0.20/0.64	0.94/1.25			3.45/3.64	5.25/5.37		1.58/1.89
AELCM009								
Rs			0.75/0.77	0.83/0.82			0.94/0.94	0.85/0.84
R <sup>2</sup>			0.47/0.47	0.71/0.69			0.84/0.85	0.74/0.73
RMSE [ppb]			3.27/3.17	2.95/3.57			3.66/4.78	3.31/3.90
MAE [ppb]			2.52/2.41	2.42/3.01			2.89/3.87	2.61/3.10
Slope			0.57/0.40	0.54/0.36			0.63/0.43	0.63/0.44
Delta Slope			0.43/0.60	0.46/0.64			0.37/0.57	0.37/0.56
Intercept			1.76/3.38	3.17/4.65			3.31/4.83	2.45/4.05
Intercept			1.76/3.38	3.17/4.65			3.31/4.83	2.45/4.05

**Table S12.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on multiple linear regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

2 month multiple linear regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.45/0.47	0.50/0.52			0.82/0.83	0.85/0.85		0.77/0.77
R <sup>2</sup>	0.25/0.26	0.26/0.27			0.64/0.63	0.71/0.70		0.62/0.62
RMSE [ppb]	3.16/2.93	4.16/4.03			3.23/3.11	4.14/3.38		3.70/3.39
MAE [ppb]	2.46/2.30	3.25/3.11			2.35/2.24	3.40/2.61		2.87/2.57
Slope	0.61/0.62	0.46/0.46			0.88/0.83	0.89/0.84		0.87/0.82
Delta Slope	0.39/0.38	0.54/0.54			0.12/0.17	0.11/0.16		0.13/0.18
Intercept	2.44/1.94	3.79/3.24			1.48/1.10	4.05/3.39		2.26/1.85
Intercept	2.44/1.94	3.79/3.24			1.48/1.10	4.05/3.39		2.26/1.85
AELCM009								
Rs			0.64/0.73	0.84/0.80			0.94/0.94	0.84/0.85
R <sup>2</sup>			0.48/0.54	0.77/0.75			0.91/0.92	0.81/0.82
RMSE [ppb]			3.33/3.02	2.67/2.55			2.64/2.29	2.90/2.64
MAE [ppb]			2.51/2.21	1.96/1.98			1.93/1.73	2.13/1.97
Slope			0.47/0.53	0.74/0.69			1.02/0.91	0.88/0.82
Delta Slope			0.53/0.47	0.26/0.31			0.02/0.09	0.12/0.18
Intercept			1.72/1.84	0.44/1.70			-0.66/0.95	-0.11/0.98
Intercept			1.72/1.84	0.44/1.70			0.66/0.95	0.11/0.98

**Table S13.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on extreme gradient boosting, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

3 month xgboost (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.76/0.76	0.76/0.78	0.80/0.81				0.95/0.96	0.80/0.83
R <sup>2</sup>	0.47/0.49	0.46/0.53	0.62/0.64				0.91/0.92	0.75/0.79
RMSE [ppb]	2.01/1.94	3.55/3.15	3.05/2.73				2.79/2.41	2.91/2.60
MAE [ppb]	1.30/1.30	2.25/2.00	2.06/1.87				2.20/1.77	1.95/1.74
Slope	0.53/0.61	0.42/0.53	0.58/0.66				0.90/0.83	0.85/0.81
Delta Slope	0.47/0.39	0.58/0.47	0.42/0.34				0.10/0.17	0.15/0.19
Intercept	1.10/1.14	1.25/1.23	0.83/0.99				2.52/2.10	0.35/0.69
Intercept	1.10/1.14	1.25/1.23	0.83/0.99				2.52/2.10	0.35/0.69
AELCM009								
Rs				0.87/0.88	0.78/0.85	0.86/0.89		0.88/0.90
R <sup>2</sup>				0.81/0.83	0.61/0.73	0.79/0.81		0.76/0.81
RMSE [ppb]				2.36/2.11	3.30/2.44	2.89/2.32		2.88/2.30
MAE [ppb]				1.52/1.55	2.30/1.84	2.30/1.79		2.04/1.72
Slope				0.77/0.85	0.60/0.74	0.69/0.79		0.70/0.79
Delta Slope				0.23/0.15	0.40/0.26	0.31/0.21		0.30/0.21
Intercept				0.63/1.04	1.75/1.95	1.34/1.25		1.10/1.37
Intercept				0.63/1.04	1.75/1.95	1.34/1.25		1.10/1.37

**Table S14.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on random forest, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

3 month random forest (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.69/0.71	0.69/0.72	0.77/0.79				0.94/0.95	0.77/0.80
R <sup>2</sup>	0.48/0.49	0.43/0.46	0.60/0.62				0.90/0.91	0.75/0.77
RMSE [ppb]	2.00/2.10	3.30/3.25	2.75/2.69				3.72/2.98	3.01/2.79
MAE [ppb]	1.45/1.54	2.21/2.20	1.88/1.89				3.14/2.46	2.17/2.02
Slope	0.64/0.69	0.52/0.58	0.67/0.70				0.87/0.83	0.87/0.82
Delta Slope	0.36/0.31	0.48/0.42	0.33/0.30				0.13/0.17	0.13/0.18
Intercept	1.66/1.74	2.49/2.51	1.72/1.75				3.93/3.24	1.54/1.73
Intercept	1.66/1.74	2.49/2.51	1.72/1.75				3.93/3.24	1.54/1.73
AELCM009								
Rs			0.86/0.88	0.81/0.86	0.87/0.89			0.89/0.90
R <sup>2</sup>			0.81/0.83	0.68/0.75	0.79/0.81			0.78/0.81
RMSE [ppb]			2.24/2.14	2.78/2.38	2.47/2.23			2.51/2.25
MAE [ppb]			1.65/1.63	2.09/1.82	1.90/1.73			1.88/1.73
Slope			0.74/0.80	0.69/0.75	0.70/0.79			0.72/0.78
Delta Slope			0.26/0.20	0.31/0.25	0.30/0.21			0.28/0.22
Intercept			1.35/1.46	1.75/1.96	2.26/1.62			1.63/1.64
Intercept			1.35/1.46	1.75/1.96	2.26/1.62			1.63/1.64

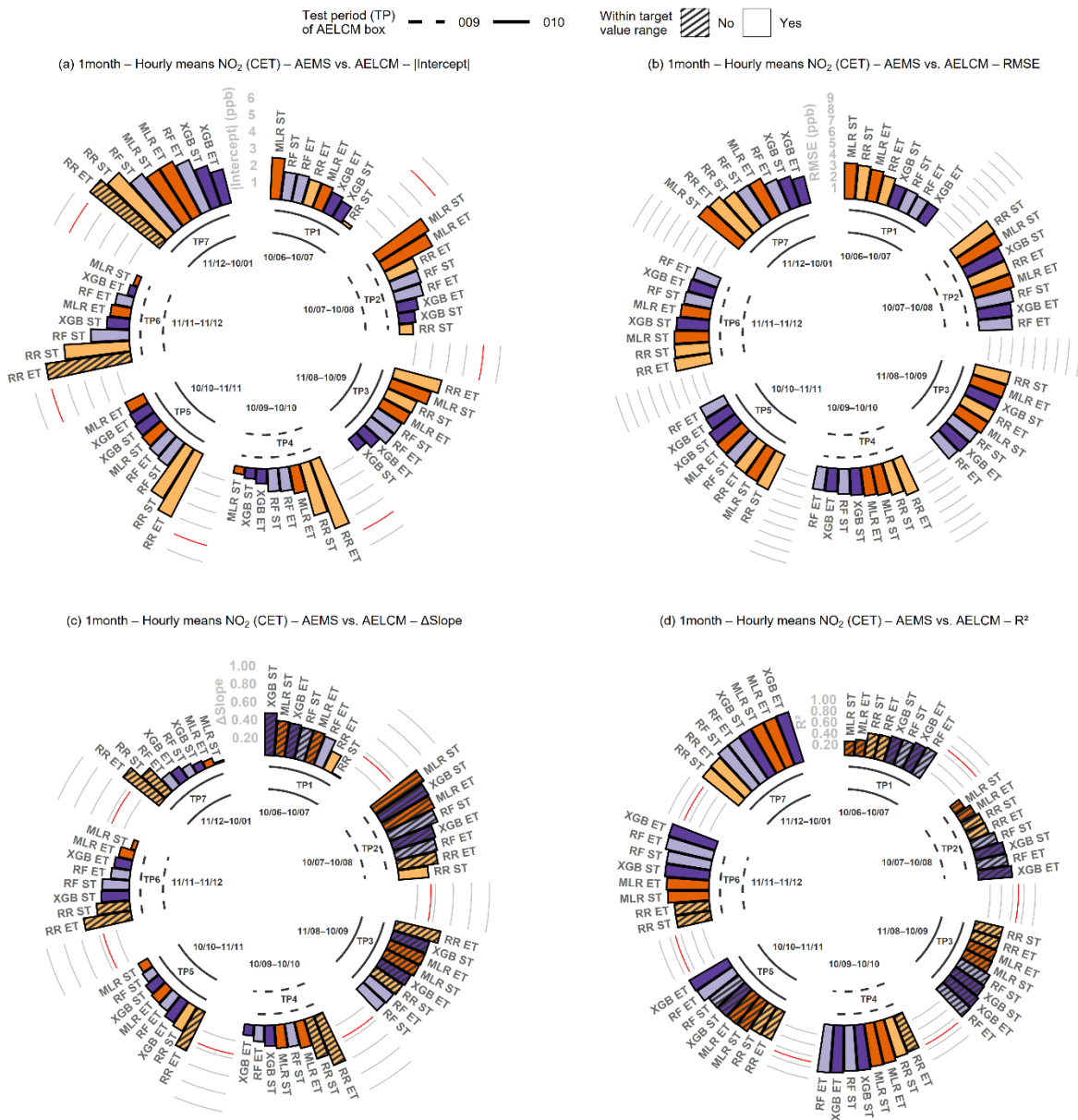
**Table S15.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on ridge regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

3 month ridge regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.72/0.72	0.72/0.72	0.78/0.77				0.93/0.93	0.78/0.77
R <sup>2</sup>	0.43/0.43	0.37/0.37	0.50/0.49				0.82/0.85	0.62/0.60
RMSE [ppb]	3.02/2.75	4.25/3.90	3.17/3.12				3.95/4.31	3.63/3.57
MAE [ppb]	2.43/2.21	3.34/3.01	2.41/2.35				3.37/3.65	2.89/2.80
Slope	1.01/0.90	0.72/0.63	0.64/0.56				0.64/0.50	0.77/0.65
Delta Slope	0.01/0.10	0.28/0.37	0.36/0.44				0.36/0.50	0.23/0.35
Intercept	0.20/0.60	0.94/1.29	1.89/2.28				4.84/5.34	1.65/2.12
Intercept	0.20/0.60	0.94/1.29	1.89/2.28				4.84/5.34	1.65/2.12
AELCM009								
Rs			0.83/0.83	0.80/0.78	0.81/0.79			0.86/0.85
R <sup>2</sup>			0.71/0.69	0.59/0.56	0.62/0.59			0.66/0.63
RMSE [ppb]			2.95/3.45	3.09/3.17	3.09/3.29			3.04/3.30
MAE [ppb]			2.42/2.91	2.30/2.44	2.37/2.55			2.36/2.63
Slope			0.54/0.40	0.69/0.52	0.63/0.49			0.65/0.50
Delta Slope			0.46/0.60	0.31/0.48	0.37/0.51			0.35/0.50
Intercept			3.17/4.40	2.61/4.13	3.87/5.13			3.05/4.38
Intercept			3.17/4.40	2.61/4.13	3.87/5.13			3.05/4.38

**Table S16.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on multiple linear regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

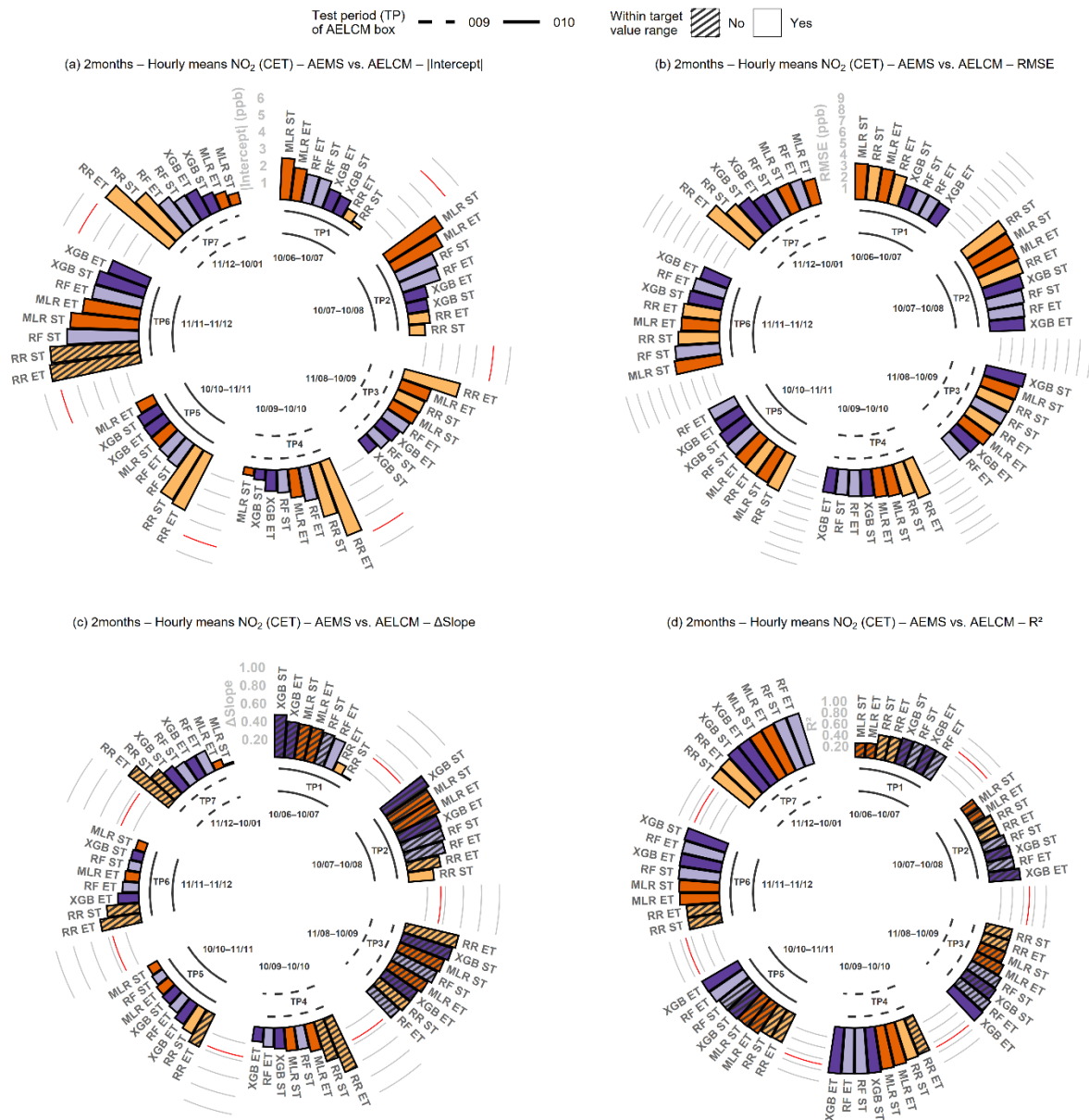
3 month multiple linear regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.45/0.38	0.50/0.43	0.69/0.62				0.93/0.93	0.67/0.63
R <sup>2</sup>	0.25/0.21	0.26/0.21	0.52/0.44				0.91/0.91	0.70/0.66
RMSE [ppb]	3.16/3.38	4.16/4.54	3.02/3.38				4.60/3.73	3.80/3.79
MAE [ppb]	2.46/2.70	3.25/3.65	2.28/2.62				3.97/3.16	2.99/3.03
Slope	0.61/0.58	0.46/0.42	0.59/0.57				1.02/0.91	0.93/0.84
Delta Slope	0.39/0.42	0.54/0.58	0.41/0.43				0.02/0.09	0.07/0.16
Intercept	2.44/2.64	3.79/4.31	2.47/2.88				3.57/3.75	1.93/2.45
Intercept	2.44/2.64	3.79/4.31	2.47/2.88				3.57/3.75	1.93/2.45
AELCM009								
Rs			0.84/0.82	0.83/0.82	0.87/0.87			0.88/0.87
R <sup>2</sup>			0.77/0.75	0.65/0.65	0.73/0.73			0.73/0.73
RMSE [ppb]			2.67/2.55	3.45/3.10	3.05/2.71			3.07/2.80
MAE [ppb]			1.96/1.94	2.63/2.30	2.29/2.01			2.29/2.08
Slope			0.74/0.70	0.91/0.84	0.95/0.85			0.88/0.82
Delta Slope			0.26/0.30	0.09/0.16	0.05/0.15			0.12/0.18
Intercept			0.44/1.53	-0.56/0.58	-0.29/1.34			-0.13/1.10
Intercept			0.44/1.53	0.56/0.58	0.29/1.34			0.13/1.10



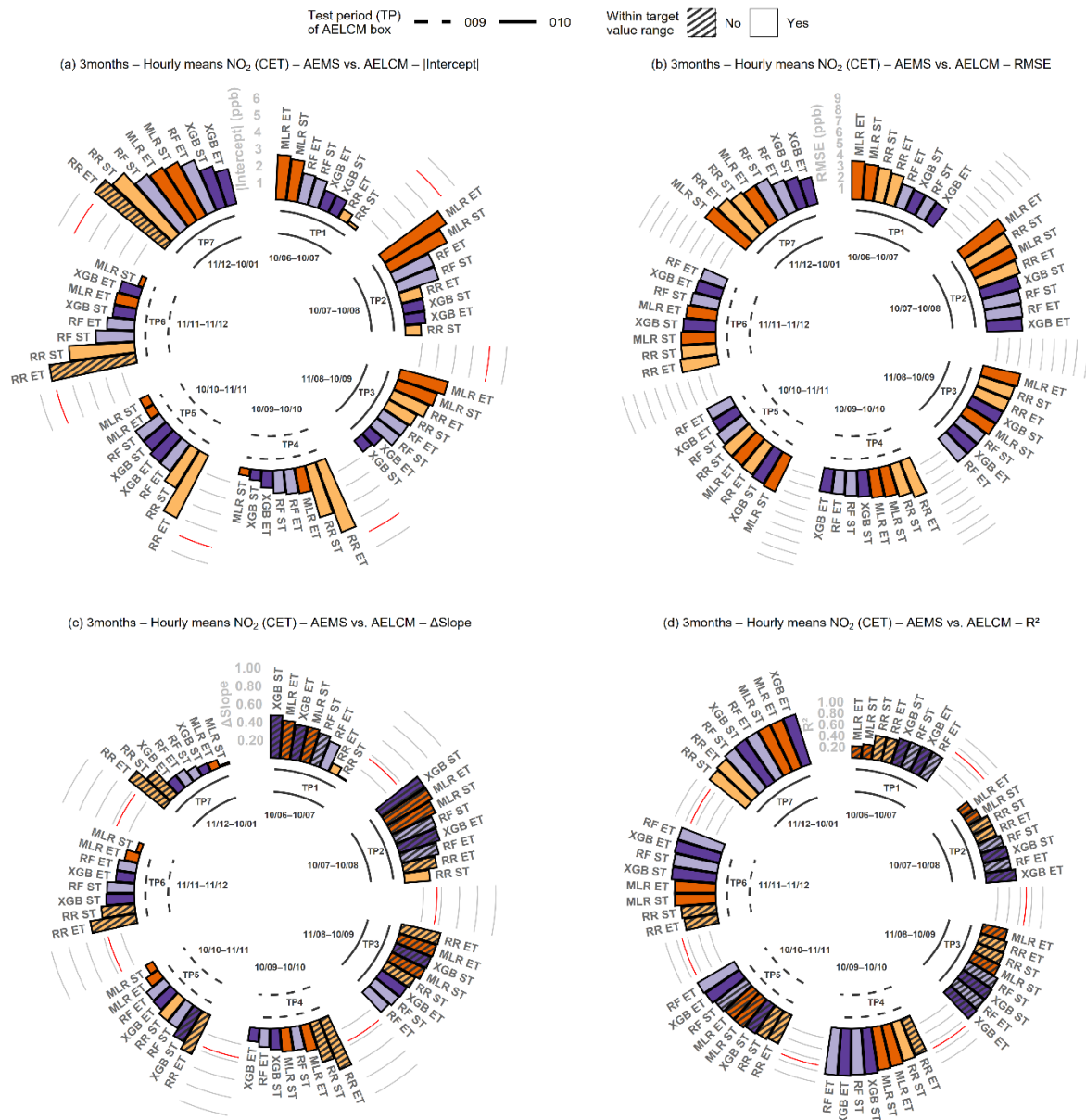


**Figure S5.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box, calculated from hourly mean values after calibration. Metrics are presented for each calibration model, test period (TP), and calibration variant (Single training (ST) and extended training (ET)). Models are ordered by performance from highest to lowest in each period. The extended training is characterized by the one-month variant for each AELCM box. Values highlighted in red describe the least accepted target value given by EPA for each performance metric (|Intercept| (a), RMSE (b),  $\Delta$ Slope (c), R<sup>2</sup> (d)).

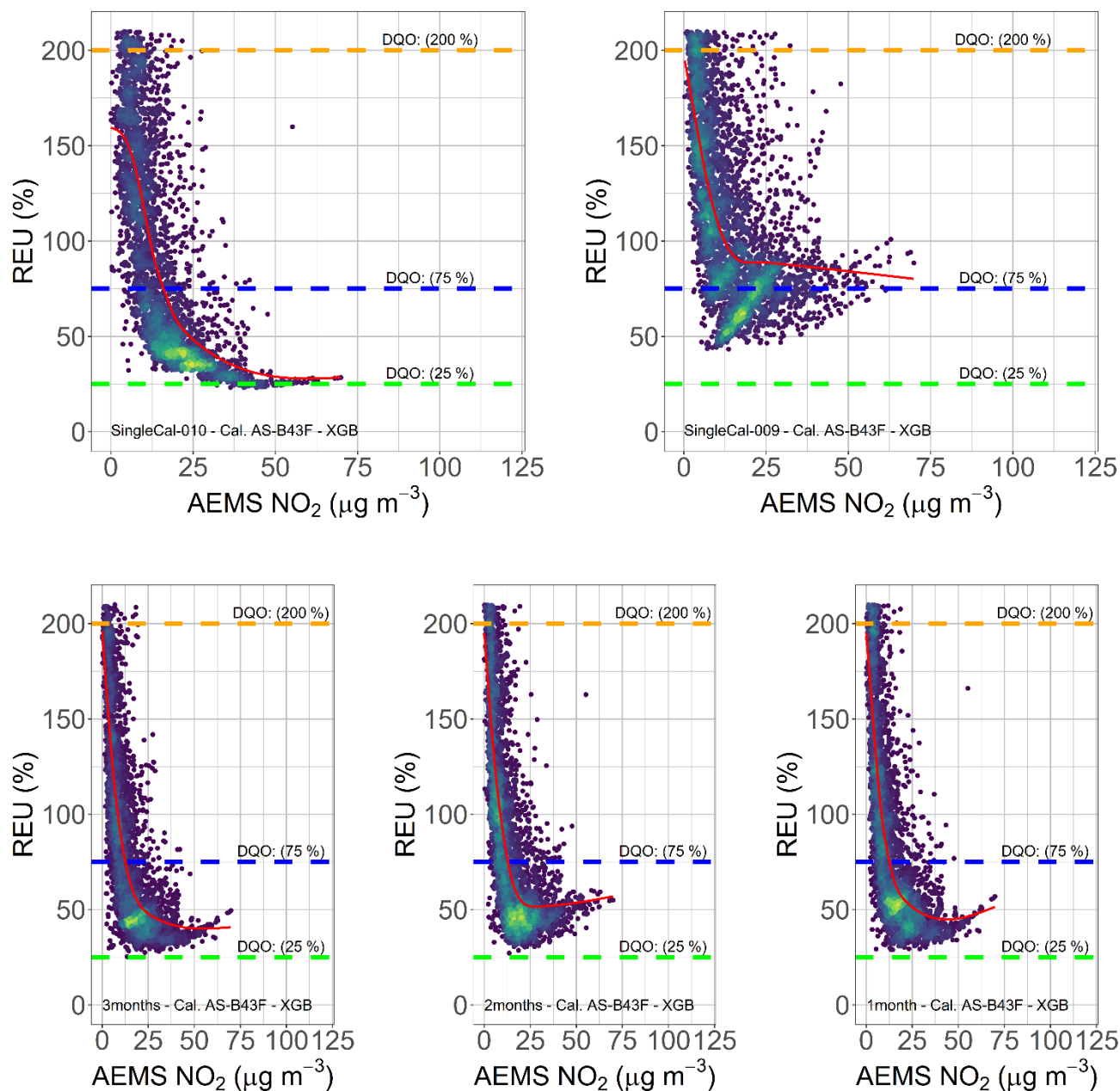




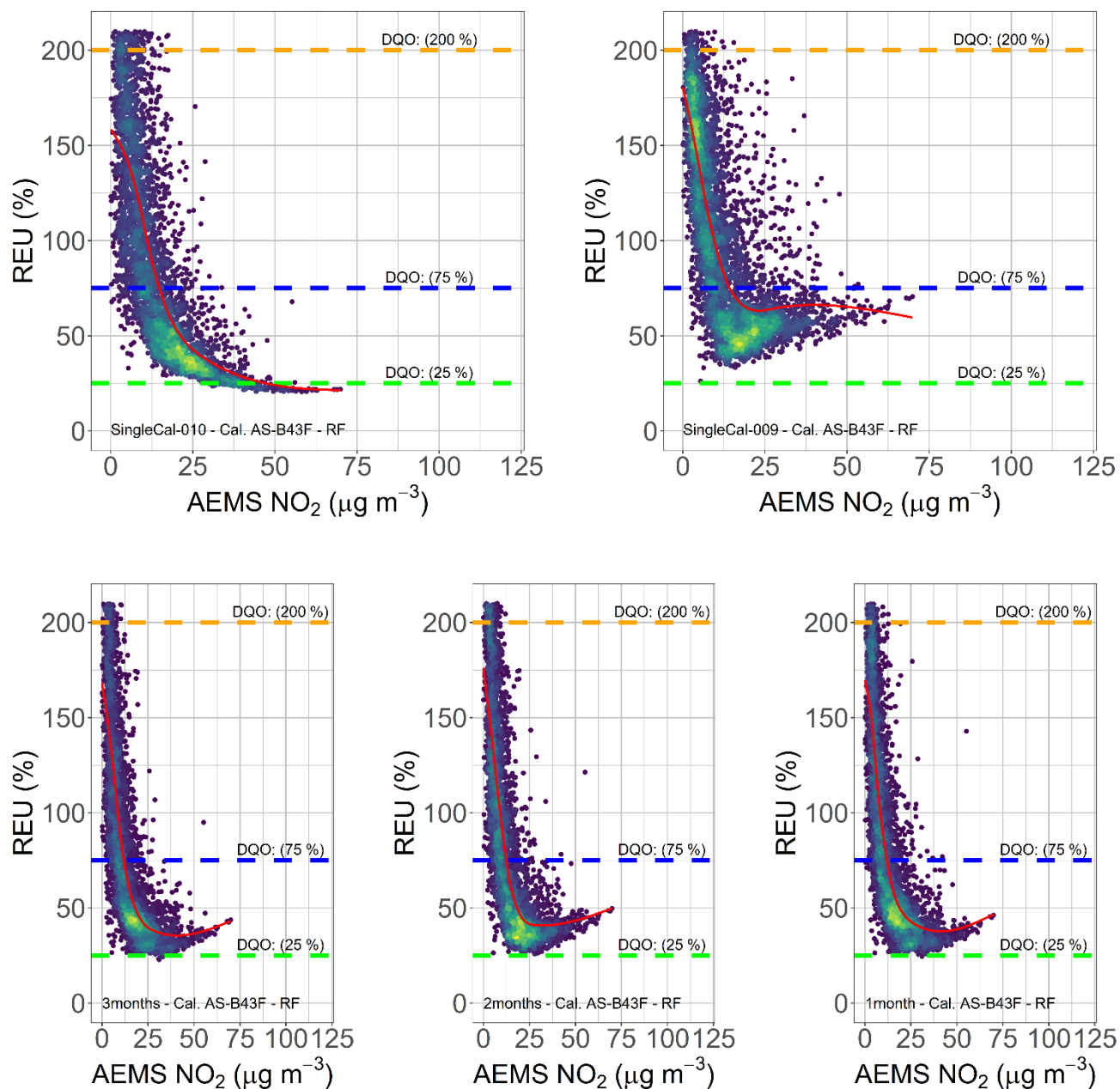
**Figure S6.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box, calculated from hourly mean values after calibration. Metrics are presented for each calibration model, test period (TP), and calibration variant (Single training (ST) and extended training (ET)). Models are ordered by performance from highest to lowest in each period. The extended training is characterized by the two-month variant for each AELCM box. Values highlighted in red describe the least accepted target value given by EPA for each performance metric (|Intercept| (a), RMSE (b),  $\Delta$ Slope (c), R<sup>2</sup> (d)).



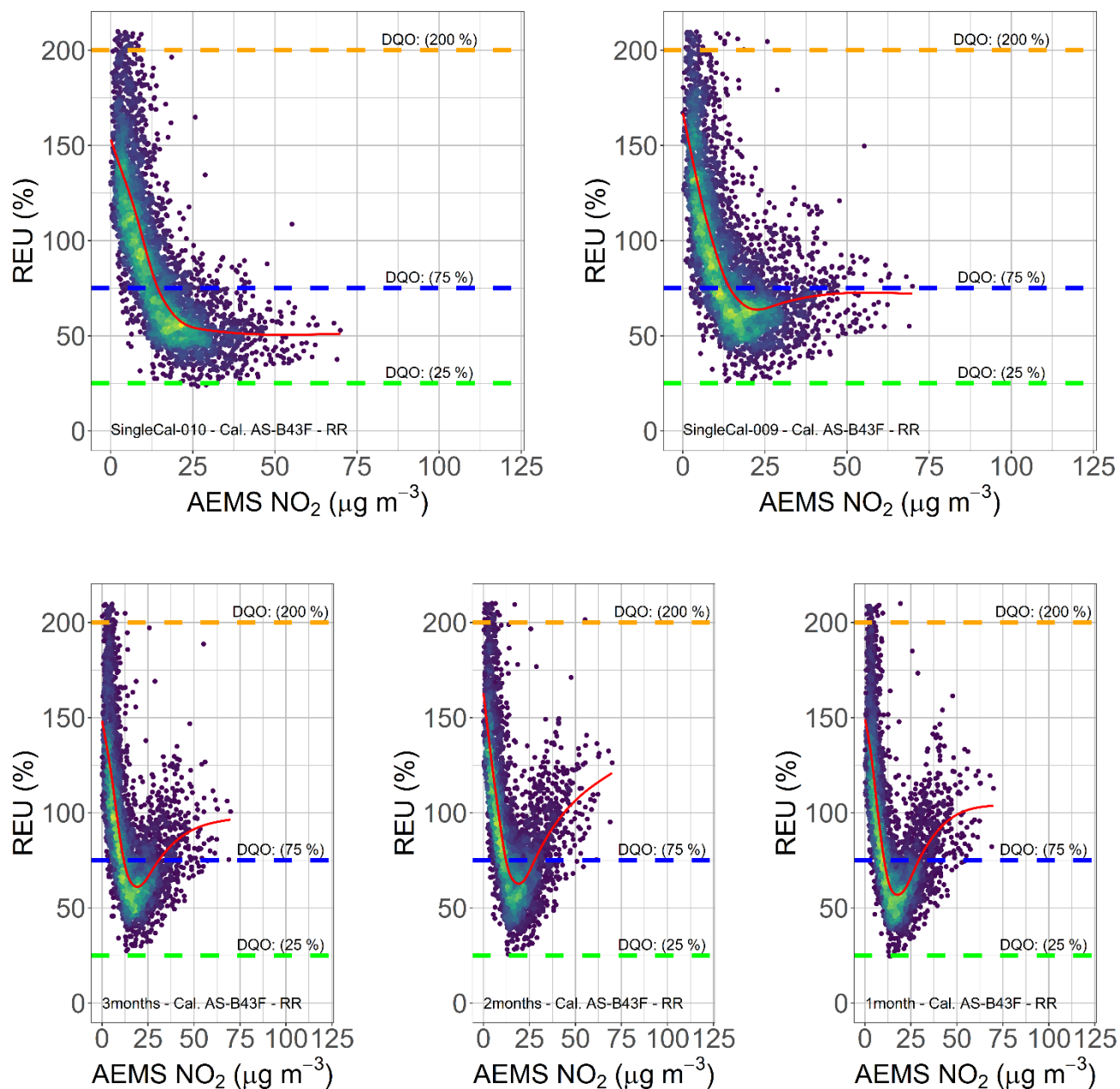
**Figure S7.** Performance metrics of the single NO<sub>2</sub> LCS in each AELCM box, calculated from hourly mean values after calibration. Metrics are presented for each calibration model, test period (TP), and calibration variant (Single training (ST) and extended training (ET)). Models are ordered by performance from highest to lowest in each period. The extended training is characterized by the three-month variant for each AELCM box. Values highlighted in red describe the least accepted target value given by EPA for each performance metric (|Intercept| (a), RMSE (b), ΔSlope (c), R<sup>2</sup> (d)).



**Figure S8.** Calculated REU values for XGB calibrated NO<sub>2</sub> LCS hourly data belonging to the test periods (TP1–TP7, 10 June 2022–10 January 2023) of AELCM009 and AELCM010. The calibration variants are single training (ST) (top row) and extended training (ET) (bottom row). The extended training is characterized by ET variants of 1, 2 and 3 months for each AELCM box. Horizontal dashed lines describe the data quality objectives (NO<sub>2</sub> Class 1 DQO = 25 %, Class 2 DQO = 75 % and Class 3 DQO = 200 %). The fitted smooth curve (red) is based on a generalized additive model (GAM). Data density is shown through colour, where darker colours express lower data density and brighter colours express higher data density.

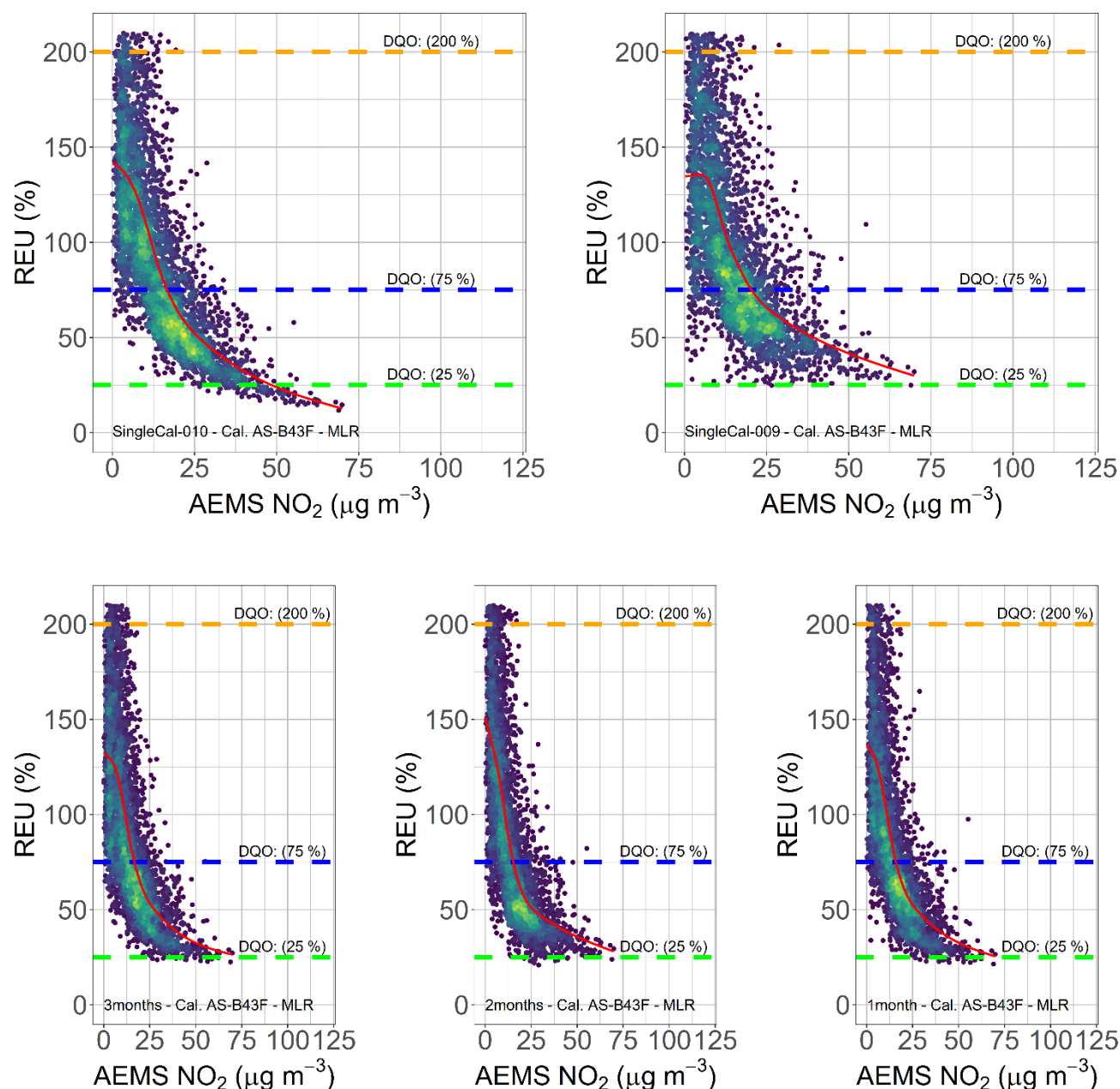


**Figure S9.** Calculated REU values for RF calibrated NO<sub>2</sub> LCS hourly data belonging to the test periods (TP1–TP7, 10 June 2022–10 January 2023) of AELCM009 and AELCM010. The calibration variants are single training (ST) (top row) and extended training (ET) (bottom row). The extended training is characterized by ET variants of 1, 2 and 3 months for each AELCM box. Horizontal dashed lines describe the data quality objectives (NO<sub>2</sub> Class 1 DQO = 25 %, Class 2 DQO = 75 % and Class 3 DQO = 200 %). The fitted smooth curve (red) is based on a generalized additive model (GAM). Data density is shown through colour, where darker colours express lower data density and brighter colours express higher data density.



**Figure S10.** Calculated REU values for RR calibrated NO<sub>2</sub> LCS hourly data belonging to the test periods (TP1–TP7, 10 June 2022–10 January 2023) of AELCM009 and AELCM010. The calibration variants are single training (ST) (top row) and extended training (ET) (bottom row). The extended training is characterized by ET variants of 1, 2 and 3 months for each AELCM box. Horizontal dashed lines describe the data quality objectives (NO<sub>2</sub> Class 1 DQO = 25 %, Class 2 DQO = 75 % and Class 3 DQO = 200 %). The fitted smooth curve (red) is based on a generalized additive model (GAM). Data density is shown through colour, where darker colours express lower data density and brighter colours express higher data density.





**Figure S11.** Calculated REU values for MLR calibrated NO<sub>2</sub> LCS hourly data belonging to the test periods (TP1–TP7, 10 June 2022–10 January 2023) of AELCM009 and AELCM010. The calibration variants are single training (ST) (top row) and extended training (ET) (bottom row). The extended training is characterized by ET variants of 1, 2 and 3 months for each AELCM box. Horizontal dashed lines describe the data quality objectives (NO<sub>2</sub> Class 1 DQO = 25 %, Class 2 DQO = 75 % and Class 3 DQO = 200 %). The fitted smooth curve (red) is based on a generalized additive model (GAM). Data density is shown through colour, where darker colours express lower data density and brighter colours express higher data density.

## Performance Metrics CO

**Table S17.** Performance metrics of the single CO LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on extreme gradient boosting, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

1 month xgboost (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.67/0.73		0.72/0.76		0.98/0.98		0.99/0.99	0.89/0.91
R <sup>2</sup>	0.48/0.58		0.61/0.70		0.95/0.97		0.98/0.99	0.96/0.97
RMSE [ppb]	16.09/13.85		26.76/24.42		37.40/30.76		43.64/42.49	32.70/29.75
MAE [ppb]	12.45/10.88		21.54/20.06		30.14/25.51		34.23/34.71	24.59/22.79
Slope	0.65/0.65		0.59/0.66		0.89/0.92		0.85/0.86	0.84/0.86
Delta Slope	0.35/0.35		0.41/0.34		0.11/0.08		0.15/0.14	0.16/0.14
Intercept	33.14/33.42		32.79/25.05		-6.88/-9.36		2.08/-0.68	4.34/3.46
Intercept	33.14/33.42		32.79/25.05		6.88/9.36		2.08/0.68	4.34/3.46
AELCM009								
Rs		0.66/0.72		0.92/0.96		1.00/1.00		0.93/0.95
R <sup>2</sup>		0.47/0.61		0.95/0.97		0.99/0.99		0.97/0.98
RMSE [ppb]		22.47/20.61		18.55/18.50		23.97/30.40		21.78/23.74
MAE [ppb]		16.80/15.77		13.56/13.53		20.69/25.73		17.02/18.34
Slope		0.49/0.61		0.90/0.86		0.97/0.89		0.93/0.88
Delta Slope		0.51/0.39		0.10/0.14		0.03/0.11		0.07/0.12
Intercept		52.66/37.26		4.06/9.50		-11.28/5.23		-1.19/5.53
Intercept		52.66/37.26		4.06/9.50		11.28/5.23		1.19/5.53

**Table S18.** Performance metrics of the single CO LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on random forest, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

1 month random forest (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.68/0.74		0.72/0.78		0.98/0.98		0.99/0.99	0.89/0.91
R <sup>2</sup>	0.52/0.60		0.62/0.73		0.97/0.98		0.99/0.99	0.97/0.98
RMSE [ppb]	19.77/17.06		18.02/15.11		18.30/15.01		16.97/15.77	18.29/15.76
MAE [ppb]	14.84/13.47		13.65/11.56		13.29/10.88		10.43/10.55	13.05/11.61
Slope	0.82/0.76		0.69/0.76		0.97/1.01		0.97/0.99	0.95/0.97
Delta Slope	0.18/0.24		0.31/0.24		0.03/0.01		0.03/0.01	0.05/0.03
Intercept	32.48/37.08		38.24/28.18		3.31/-1.60		6.05/-1.31	9.98/5.70
Intercept	32.48/37.08		38.24/28.18		3.31/1.60		6.05/1.31	9.98/5.70
AELCM009								
Rs		0.65/0.73		0.93/0.96		0.98/1.00		0.93/0.95
R <sup>2</sup>		0.48/0.61		0.93/0.95		0.97/0.99		0.96/0.98
RMSE [ppb]		21.44/17.82		17.84/15.57		28.66/11.74		23.09/15.25
MAE [ppb]		16.60/13.79		10.90/7.79		18.79/8.31		15.43/9.96
Slope		0.64/0.69		0.96/0.91		1.07/0.96		1.05/0.95
Delta Slope		0.36/0.31		0.04/0.09		0.07/0.04		0.05/0.05
Intercept		47.65/38.28		7.83/13.43		-6.99/6.26		-2.91/7.19
Intercept		47.65/38.28		7.83/13.43		6.99/6.26		2.91/7.19

**Table S19.** Performance metrics of the single CO LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on ridge regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

1 month ridge regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.67/0.67		0.78/0.78		0.99/0.99		0.99/0.99	0.90/0.90
R <sup>2</sup>	0.50/0.50		0.60/0.61		0.99/0.99		0.99/0.99	0.91/0.91
RMSE [ppb]	40.22/39.59		34.90/33.44		12.83/15.43		31.67/35.43	31.64/32.32
MAE [ppb]	32.27/32.46		25.45/24.85		9.09/11.51		17.00/18.81	20.95/21.91
Slope	1.84/1.77		1.41/1.35		0.92/0.89		0.83/0.80	0.89/0.85
Delta Slope	0.84/0.77		0.41/0.35		0.08/0.11		0.17/0.20	0.11/0.15
Intercept	-84.96/-73.30		-52.20/-41.62		18.05/26.71		26.38/34.49	18.51/26.86
Intercept	84.96/73.30		52.20/41.62		18.05/26.71		26.38/34.49	18.51/26.86
AELCM009								
Rs		0.67/0.67		0.98/0.98		1.00/1.00		0.93/0.93
R <sup>2</sup>		0.45/0.46		0.96/0.96		0.99/0.99		0.91/0.91
RMSE [ppb]		46.09/44.23		12.64/13.37		24.89/27.58		31.11/31.07
MAE [ppb]		36.06/35.02		6.85/7.83		16.50/18.27		19.80/20.38
Slope		1.44/1.40		0.95/0.92		0.85/0.82		0.90/0.87
Delta Slope		0.44/0.40		0.05/0.08		0.15/0.18		0.10/0.13
Intercept		-58.74/-49.92		9.49/15.90		26.51/31.88		12.23/18.93
Intercept		58.74/49.92		9.49/15.90		26.51/31.88		12.23/18.93



**Table S20.** Performance metrics of the single CO LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on multiple linear regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

1 month multiple linear regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.65/0.66		0.77/0.78		0.99/0.99		0.99/0.99	0.90/0.91
R <sup>2</sup>	0.54/0.56		0.68/0.70		0.98/0.99		0.98/0.99	0.97/0.97
RMSE [ppb]	20.04/20.53		16.64/16.56		23.18/15.92		19.57/19.95	19.99/18.35
MAE [ppb]	16.22/16.75		12.86/12.83		15.16/11.40		12.49/11.81	14.18/13.20
Slope	0.90/0.98		0.79/0.85		0.82/0.89		0.99/1.05	0.92/0.98
Delta Slope	0.10/0.02		0.21/0.15		0.18/0.11		0.01/0.05	0.08/0.02
Intercept	22.63/13.76		27.72/20.55		27.03/18.01		-1.97/-12.39	13.46/6.09
Intercept	22.63/13.76		27.72/20.55		27.03/18.01		1.97/12.39	13.46/6.09
AELCM009								
Rs		0.63/0.66		0.98/0.99		1.00/1.00		0.94/0.94
R <sup>2</sup>		0.50/0.52		0.91/0.93		0.99/0.99		0.97/0.97
RMSE [ppb]		21.45/22.53		21.78/18.05		17.68/13.40		20.39/18.37
MAE [ppb]		17.16/18.17		7.38/6.08		12.37/9.89		12.30/11.38
Slope		0.70/0.82		0.80/0.84		0.94/0.96		0.91/0.93
Delta Slope		0.30/0.18		0.20/0.16		0.06/0.04		0.09/0.07
Intercept		34.74/22.65		26.25/23.75		5.48/0.88		10.14/9.08
Intercept		34.74/22.65		26.25/23.75		5.48/0.88		10.14/9.08

**Table S21.** Performance metrics of the single CO LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on extreme gradient boosting, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

2 month xgboost (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.67/0.74	0.57/0.66			0.98/0.99	0.99/0.99		0.90/0.92
R <sup>2</sup>	0.48/0.62	0.36/0.47			0.95/0.98	0.98/0.99		0.95/0.97
RMSE [ppb]	16.09/13.25	25.92/23.00			37.40/31.82	47.78/45.91		33.96/30.92
MAE [ppb]	12.45/10.49	19.16/17.03			30.14/26.30	41.55/40.76		25.83/23.65
Slope	0.65/0.77	0.49/0.62			0.89/0.87	0.85/0.85		0.83/0.82
Delta Slope	0.35/0.23	0.51/0.38			0.11/0.13	0.15/0.15		0.17/0.18
Intercept	33.14/21.59	50.13/38.49			-6.88/-0.61	-1.36/-0.77		8.53/11.70
Intercept	33.14/21.59	50.13/38.49			6.88/0.61	1.36/0.77		8.53/11.70
AELCM009								
Rs			0.79/0.85	0.92/0.96			0.99/0.99	0.93/0.96
R <sup>2</sup>			0.72/0.82	0.95/0.96			0.99/0.99	0.98/0.98
RMSE [ppb]			22.01/20.41	18.55/20.21			24.22/31.43	21.72/24.58
MAE [ppb]			17.72/17.02	13.56/14.22			19.33/24.27	16.87/18.51
Slope			0.63/0.71	0.90/0.87			0.96/0.90	0.95/0.90
Delta Slope			0.37/0.29	0.10/0.13			0.04/0.10	0.05/0.10
Intercept			31.73/20.74	4.06/6.32			-8.20/0.12	-5.45/0.21
Intercept			31.73/20.74	4.06/6.32			8.20/0.12	5.45/0.21

**Table S22.** Performance metrics of the single CO LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on random forest, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

2 month random forest (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.68/0.73	0.57/0.66			0.98/0.99	0.99/0.99		0.90/0.92
R <sup>2</sup>	0.52/0.57	0.39/0.44			0.97/0.98	0.98/0.99		0.96/0.96
RMSE [ppb]	19.77/21.14	26.39/28.06			18.30/13.25	18.96/16.12		21.11/20.43
MAE [ppb]	14.84/15.61	20.04/19.46			13.29/9.47	12.67/11.11		15.21/13.91
Slope	0.82/0.95	0.64/0.79			0.97/0.98	0.93/0.95		0.91/0.92
Delta Slope	0.18/0.05	0.36/0.21			0.03/0.02	0.07/0.05		0.09/0.08
Intercept	32.48/19.82	52.92/36.99			3.31/3.39	12.41/6.53		18.56/18.05
Intercept	32.48/19.82	52.92/36.99			3.31/3.39	12.41/6.53		18.56/18.05
AELCM009								
Rs			0.78/0.83	0.93/0.97			0.99/0.99	0.93/0.96
R <sup>2</sup>			0.73/0.81	0.93/0.94			0.97/0.99	0.96/0.98
RMSE [ppb]			15.80/13.57	17.84/16.74			43.65/15.47	28.71/15.32
MAE [ppb]			12.26/10.25	10.90/7.43			28.53/10.67	17.23/9.45
Slope			0.75/0.82	0.96/0.92			1.13/1.00	1.13/0.99
Delta Slope			0.25/0.18	0.04/0.08			0.13/0.00	0.13/0.01
Intercept			26.29/17.81	7.83/9.14			-8.66/-2.65	-15.12/-1.76
Intercept			26.29/17.81	7.83/9.14			8.66/2.65	15.12/1.76

**Table S23.** Performance metrics of the single CO LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on ridge regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

2 month ridge regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.67/0.67	0.63/0.63			0.99/0.99	1.00/1.00		0.89/0.89
R <sup>2</sup>	0.50/0.51	0.37/0.38			0.99/0.99	0.99/0.99		0.86/0.85
RMSE [ppb]	40.22/40.77	59.93/60.17			12.83/13.43	29.40/28.21		39.49/39.56
MAE [ppb]	32.27/32.92	47.63/48.17			9.09/10.10	21.05/20.07		27.51/27.81
Slope	1.84/1.85	1.59/1.59			0.92/0.93	0.83/0.83		0.88/0.88
Delta Slope	0.84/0.85	0.59/0.59			0.08/0.07	0.17/0.17		0.12/0.12
Intercept	-84.96/-83.17	-66.93/-64.70			18.05/19.68	27.04/27.12		19.94/22.62
Intercept	84.96/83.17	66.93/64.70			18.05/19.68	27.04/27.12		19.94/22.62
AELCM009								
Rs			0.82/0.82	0.98/0.99			1.00/1.00	0.95/0.95
R <sup>2</sup>			0.70/0.70	0.96/0.96			0.99/0.99	0.96/0.96
RMSE [ppb]			27.92/25.02	12.64/13.97			29.38/35.14	24.51/26.18
MAE [ppb]			20.09/18.17	6.85/8.46			15.74/18.30	14.23/14.97
Slope			1.33/1.26	0.95/0.90			0.85/0.80	0.89/0.84
Delta Slope			0.33/0.26	0.05/0.10			0.15/0.20	0.11/0.16
Intercept			-49.10/-34.90	9.49/20.00			22.82/32.21	13.29/23.98
Intercept			49.10/34.90	9.49/20.00			22.82/32.21	13.29/23.98

**Table S24.** Performance metrics of the single CO LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on multiple linear regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

2 month multiple linear regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.65/0.66	0.60/0.62			0.99/0.99	0.99/0.99		0.90/0.90
R <sup>2</sup>	0.54/0.56	0.45/0.46			0.98/0.99	0.98/0.99		0.96/0.96
RMSE [ppb]	20.04/23.03	24.57/29.21			23.18/14.61	24.67/20.48		23.19/22.45
MAE [ppb]	16.22/18.85	19.86/23.97			15.16/10.63	16.95/15.58		17.05/17.26
Slope	0.90/1.11	0.71/0.91			0.82/0.89	0.90/0.94		0.85/0.89
Delta Slope	0.10/0.11	0.29/0.09			0.18/0.11	0.10/0.06		0.15/0.11
Intercept	22.63/0.18	42.83/19.77			27.03/18.08	11.38/2.28		25.31/20.64
Intercept	22.63/0.18	42.83/19.77			27.03/18.08	11.38/2.28		25.31/20.64
AELCM009								
Rs			0.81/0.82	0.98/0.99			0.99/0.99	0.95/0.95
R <sup>2</sup>			0.76/0.78	0.91/0.93			0.99/0.99	0.97/0.98
RMSE [ppb]			15.86/14.44	21.78/18.82			16.15/17.90	18.14/17.16
MAE [ppb]			12.39/11.14	7.38/6.04			12.04/11.54	10.60/9.58
Slope			0.80/0.84	0.80/0.84			1.02/1.07	0.98/1.03
Delta Slope			0.20/0.16	0.20/0.16			0.02/0.07	0.02/0.03
Intercept			18.84/15.79	26.25/22.84			-10.14/-18.82	-2.66/-7.06
Intercept			18.84/15.79	26.25/22.84			10.14/18.82	2.66/7.06

**Table S25.** Performance metrics of the single CO LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on extreme gradient boosting, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

3 month xgboost (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.67/0.66	0.57/0.60	0.72/0.74				0.99/0.99	0.78/0.78
R <sup>2</sup>	0.48/0.51	0.36/0.42	0.61/0.69				0.98/0.99	0.95/0.96
RMSE [ppb]	16.09/15.92	25.92/24.55	26.76/23.80				43.64/43.30	29.80/28.71
MAE [ppb]	12.45/12.57	19.16/18.27	21.54/19.54				34.23/35.27	21.84/21.41
Slope	0.65/0.75	0.49/0.64	0.59/0.75				0.85/0.85	0.82/0.83
Delta Slope	0.35/0.25	0.51/0.36	0.41/0.25				0.15/0.15	0.18/0.17
Intercept	33.14/22.59	50.13/35.96	32.79/14.32				2.08/0.41	8.68/9.98
Intercept	33.14/22.59	50.13/35.96	32.79/14.32				2.08/0.41	8.68/9.98
AELCM009								
Rs			0.92/0.94	0.98/0.99	1.00/1.00			0.98/0.99
R <sup>2</sup>			0.95/0.96	0.96/0.98	0.99/0.99			0.97/0.99
RMSE [ppb]			18.55/16.94	23.84/20.64	23.97/27.49			22.26/22.13
MAE [ppb]			13.56/12.33	16.68/14.31	20.69/22.65			16.98/16.43
Slope			0.90/0.88	1.01/0.90	0.97/0.89			0.96/0.89
Delta Slope			0.10/0.12	0.01/0.10	0.03/0.11			0.04/0.11
Intercept			4.06/7.72	-12.05/7.37	-11.28/7.92			-5.70/7.28
Intercept			4.06/7.72	12.05/7.37	11.28/7.92			5.70/7.28

**Table S26.** Performance metrics of the single CO LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on random forest, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

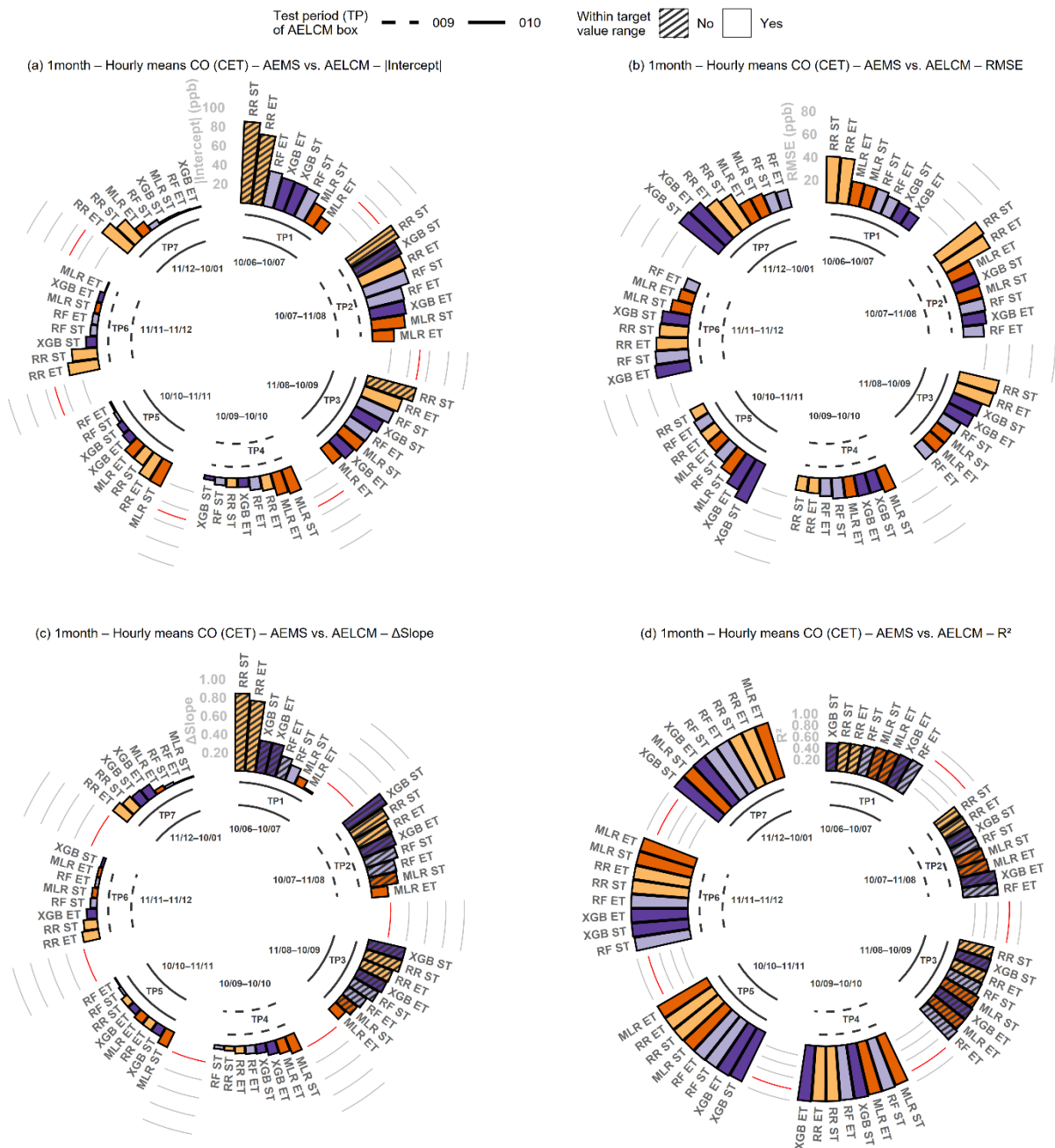
3 month random forest (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.68/0.68	0.57/0.61	0.72/0.73				0.99/0.99	0.78/0.78
R <sup>2</sup>	0.52/0.54	0.39/0.41	0.62/0.69				0.99/0.99	0.95/0.95
RMSE [ppb]	19.77/22.12	26.39/30.77	18.02/17.18				16.97/15.61	20.62/22.22
MAE [ppb]	14.84/16.23	20.04/22.16	13.65/13.29				10.43/10.24	14.74/15.48
Slope	0.82/0.99	0.64/0.81	0.69/0.87				0.97/0.99	0.94/0.95
Delta Slope	0.18/0.01	0.36/0.19	0.31/0.13				0.03/0.01	0.06/0.05
Intercept	32.48/14.27	52.92/36.32	38.24/17.00				6.05/-0.21	14.05/13.62
Intercept	32.48/14.27	52.92/36.32	38.24/17.00				6.05/0.21	14.05/13.62
AELCM009								
Rs				0.93/0.95	0.99/0.99	0.98/1.00		0.98/0.99
R <sup>2</sup>				0.93/0.93	0.97/0.98	0.97/0.99		0.97/0.98
RMSE [ppb]				17.84/17.06	21.11/15.73	28.66/12.48		22.99/15.21
MAE [ppb]				10.90/8.83	13.59/11.36	18.79/7.40		14.43/9.19
Slope				0.96/0.92	1.08/0.94	1.07/0.96		1.07/0.95
Delta Slope				0.04/0.08	0.08/0.06	0.07/0.04		0.07/0.05
Intercept				7.83/13.74	-8.51/16.46	-6.99/10.77		-6.32/11.94
Intercept				7.83/13.74	8.51/16.46	6.99/10.77		6.32/11.94

**Table S27.** Performance metrics of the single CO LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on ridge regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

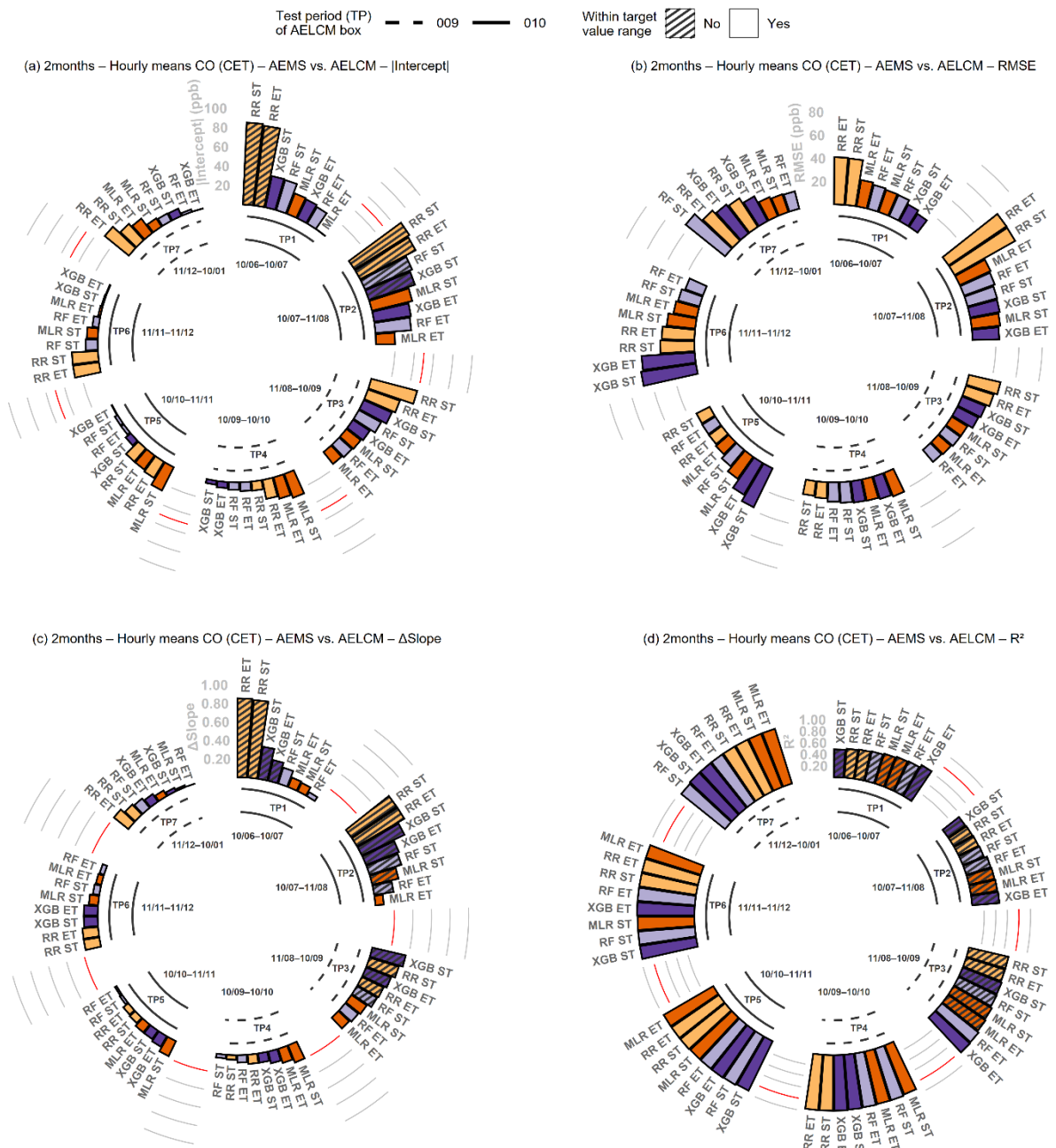
3 month ridge regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.67/0.67	0.63/0.63	0.78/0.78				0.99/0.99	0.79/0.79
R <sup>2</sup>	0.50/0.50	0.37/0.37	0.60/0.60				0.99/0.99	0.80/0.80
RMSE [ppb]	40.22/41.46	59.93/61.67	34.90/36.26				31.67/28.55	43.10/43.74
MAE [ppb]	32.27/33.34	47.63/48.98	25.45/26.41				17.00/15.04	30.59/30.94
Slope	1.84/1.88	1.59/1.63	1.41/1.44				0.83/0.85	0.88/0.90
Delta Slope	0.84/0.88	0.59/0.63	0.41/0.44				0.17/0.15	0.12/0.10
Intercept	-84.96/-90.91	-66.93/-73.03	-52.20/-57.34				26.38/25.41	17.78/14.60
Intercept	84.96/90.91	66.93/73.03	52.20/57.34				26.38/25.41	17.78/14.60
AELCM009								
Rs				0.98/0.99	0.99/0.99	1.00/1.00		0.99/0.99
R <sup>2</sup>				0.96/0.97	0.99/0.99	0.99/0.99		0.98/0.98
RMSE [ppb]				12.64/14.33	14.98/18.35	24.89/30.89		18.29/22.33
MAE [ppb]				6.85/9.04	11.80/14.98	16.50/20.80		11.72/14.94
Slope				0.95/0.89	0.93/0.88	0.85/0.80		0.88/0.83
Delta Slope				0.05/0.11	0.07/0.12	0.15/0.20		0.12/0.17
Intercept				9.49/21.56	21.05/32.75	26.51/35.86		22.24/33.61
Intercept				9.49/21.56	21.05/32.75	26.51/35.86		22.24/33.61

**Table S28.** Performance metrics of the single CO LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on multiple linear regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

3 month multiple linear regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.65/0.67	0.60/0.63	0.77/0.78				0.99/0.99	0.79/0.79
R <sup>2</sup>	0.54/0.55	0.45/0.44	0.68/0.68				0.98/0.99	0.95/0.93
RMSE [ppb]	20.04/26.68	24.57/36.24	16.64/21.98				19.57/15.82	20.40/26.26
MAE [ppb]	16.22/21.83	19.86/29.97	12.86/16.93				12.49/9.88	15.36/19.65
Slope	0.90/1.35	0.71/1.12	0.79/1.09				0.99/1.03	0.95/1.01
Delta Slope	0.10/0.35	0.29/0.12	0.21/0.09				0.01/0.03	0.05/0.01
Intercept	22.63/-28.13	42.83/-7.59	27.72/-10.99				-1.97/-9.76	11.46/3.33
Intercept	22.63/28.13	42.83/7.59	27.72/10.99				1.97/9.76	11.46/3.33
AELCM009								
Rs				0.98/0.99	0.99/0.99	1.00/1.00		0.99/0.99
R <sup>2</sup>				0.91/0.91	0.99/0.99	0.99/0.99		0.98/0.98
RMSE [ppb]				21.78/21.45	18.10/17.52	17.68/16.44		19.27/18.60
MAE [ppb]				7.38/7.21	11.68/11.95	12.37/11.23		10.48/10.13
Slope				0.80/0.79	0.86/0.85	0.94/0.94		0.90/0.89
Delta Slope				0.20/0.21	0.14/0.15	0.06/0.06		0.10/0.11
Intercept				26.25/30.52	23.14/27.00	5.48/6.34		14.06/17.51
Intercept				26.25/30.52	23.14/27.00	5.48/6.34		14.06/17.51

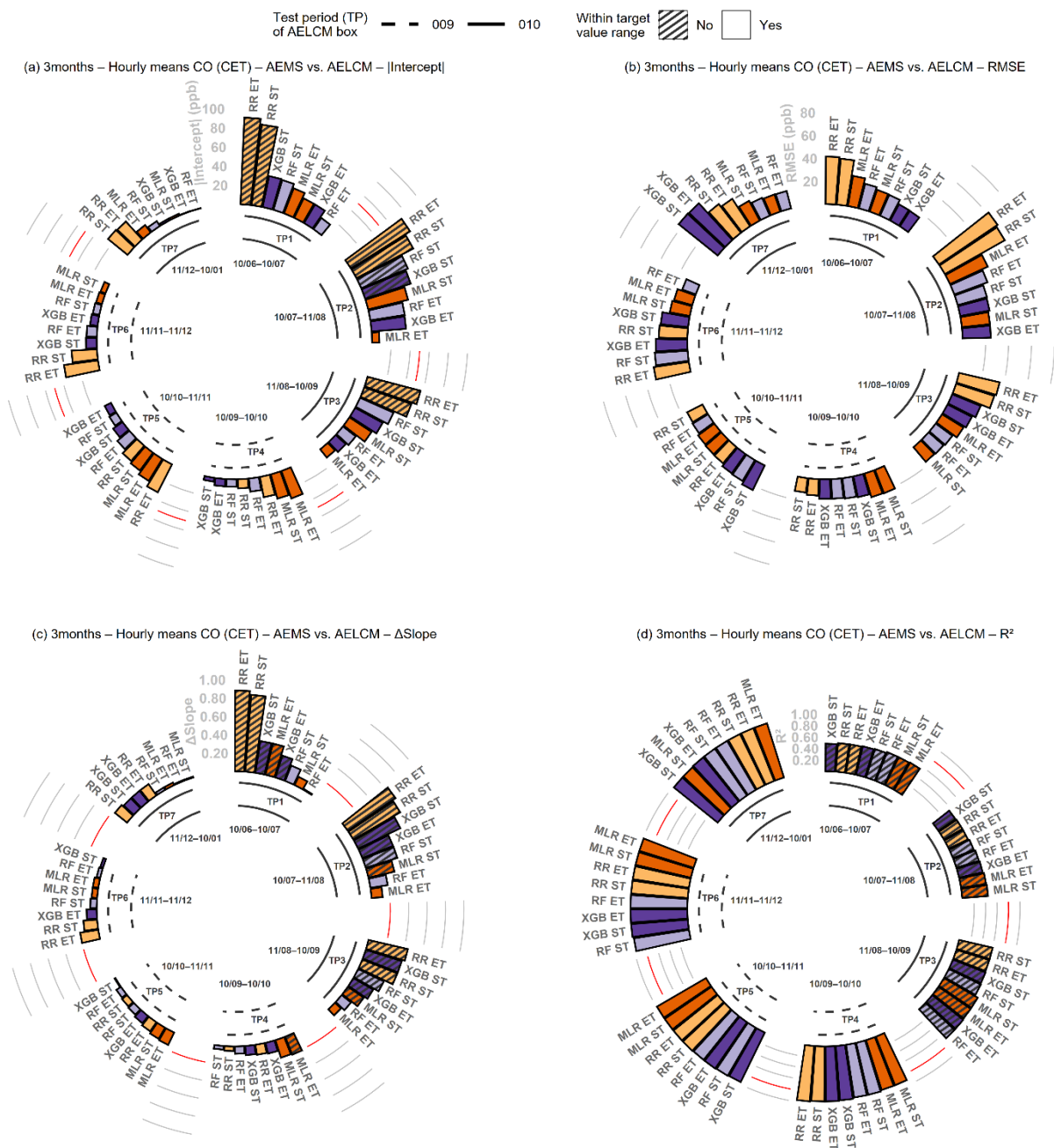


**Figure S12.** Performance metrics of the single CO LCS in each AELCM box, calculated from hourly mean values after calibration. Metrics are presented for each calibration model, test period (TP), and calibration variant (Single training (ST) and extended training (ET)). Models are ordered by performance from highest to lowest in each period. The extended training is characterized by the one-month variant for each AELCM box. Values highlighted in red describe the least accepted target value given by EPA for each performance metric (|Intercept| (a), RMSE (b),  $\Delta$ Slope (c),  $R^2$  (d)).

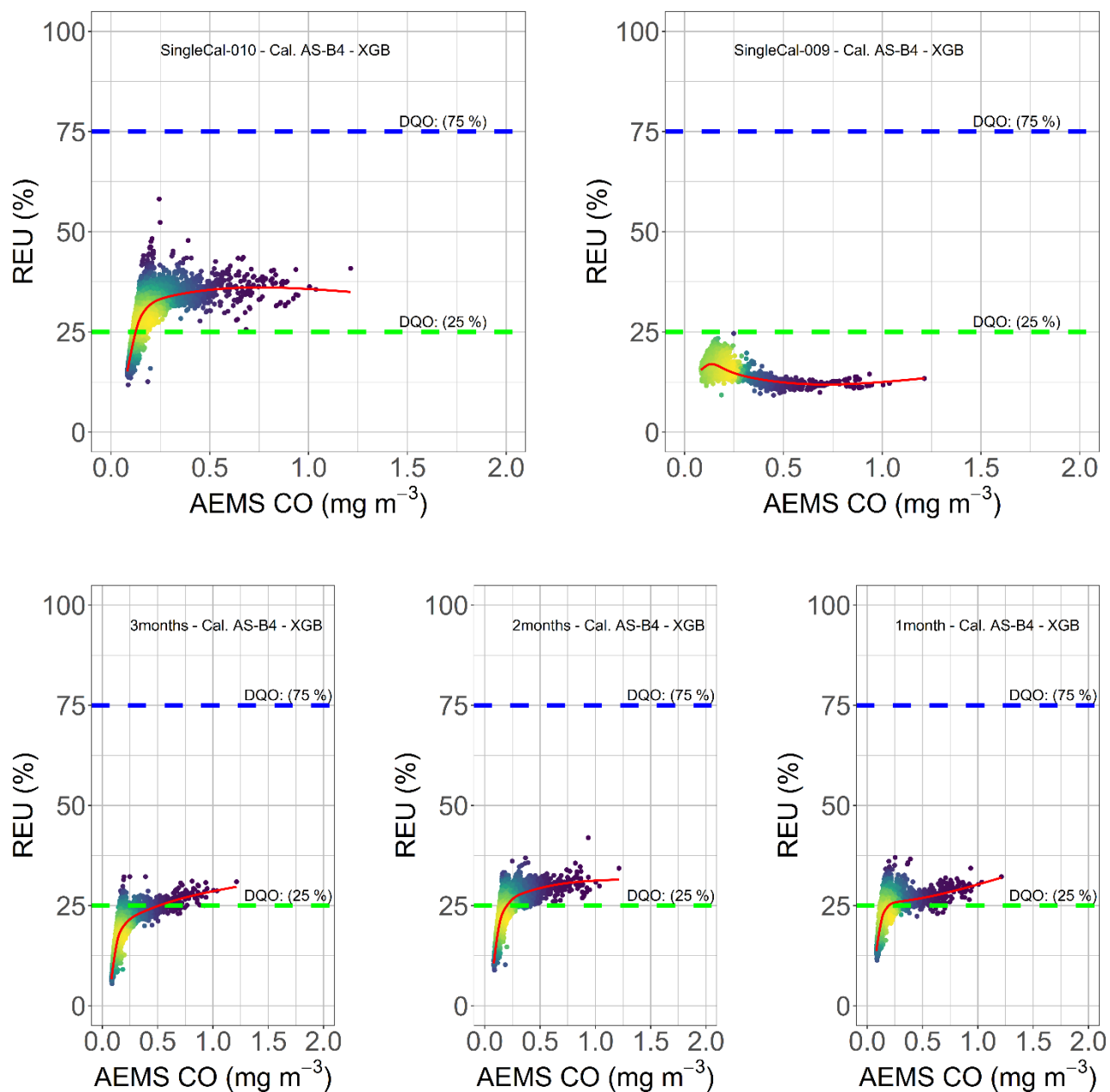


**Figure S13.** Performance metrics of the single CO LCS in each AELCM box, calculated from hourly mean values after calibration. Metrics are presented for each calibration model, test period (TP), and calibration variant (Single training (ST) and extended training (ET)). Models are ordered by performance from highest to lowest in each period. The extended training is characterized by the two-month variant for each AELCM box. Values highlighted in red describe the least accepted target value given by EPA for each performance metric (|Intercept| (a), RMSE (b),  $\Delta$ Slope (c),  $R^2$  (d)).



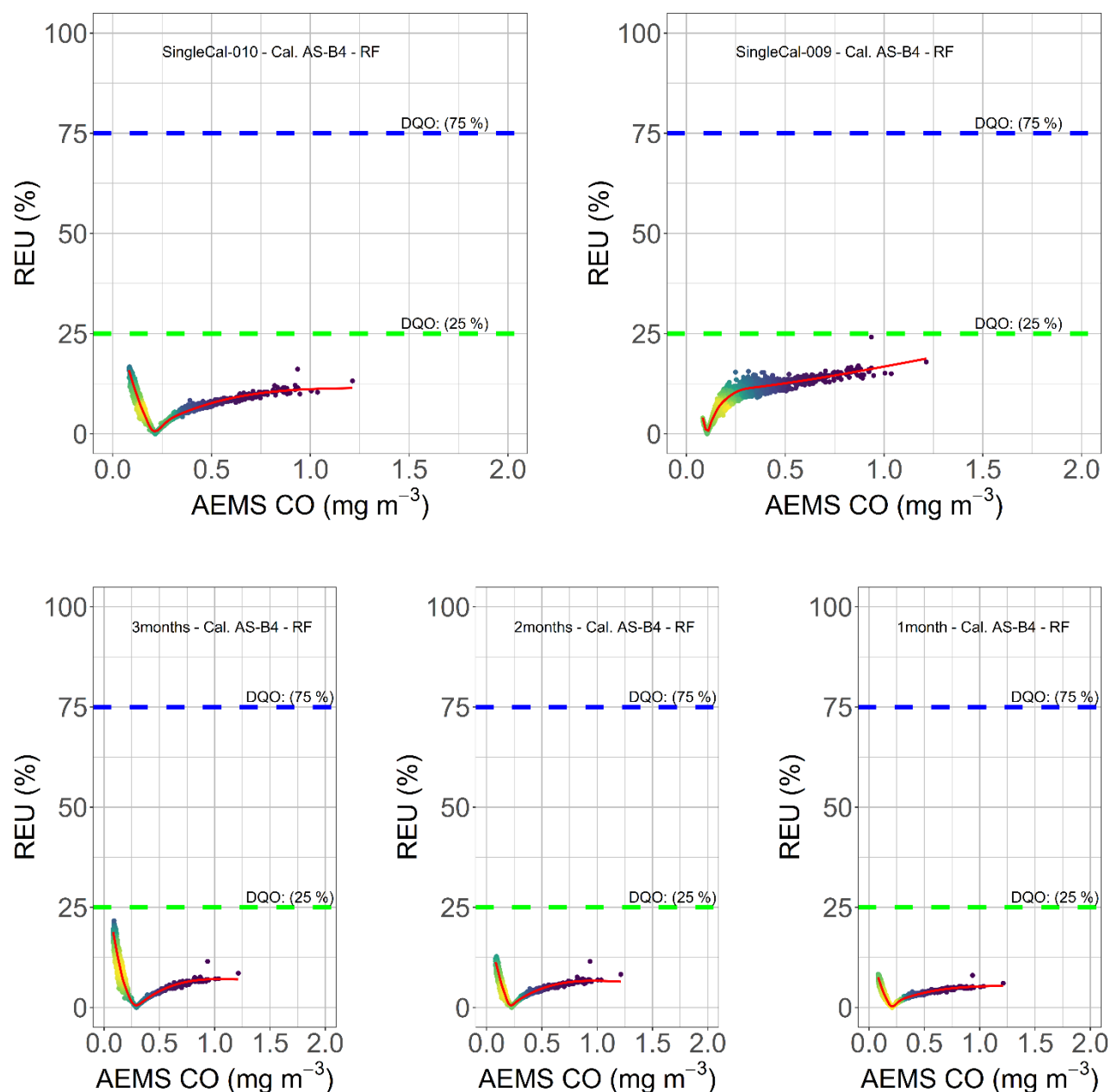


**Figure S14.** Performance metrics of the single CO LCS in each AELCM box, calculated from hourly mean values after calibration. Metrics are presented for each calibration model, test period (TP), and calibration variant (Single training (ST) and extended training (ET)). Models are ordered by performance from highest to lowest in each period. The extended training is characterized by the three-month variant for each AELCM box. Values highlighted in red describe the least accepted target value given by EPA for each performance metric ( $|Intercept|$  (a), RMSE (b),  $\Delta$ Slope (c),  $R^2$  (d)).

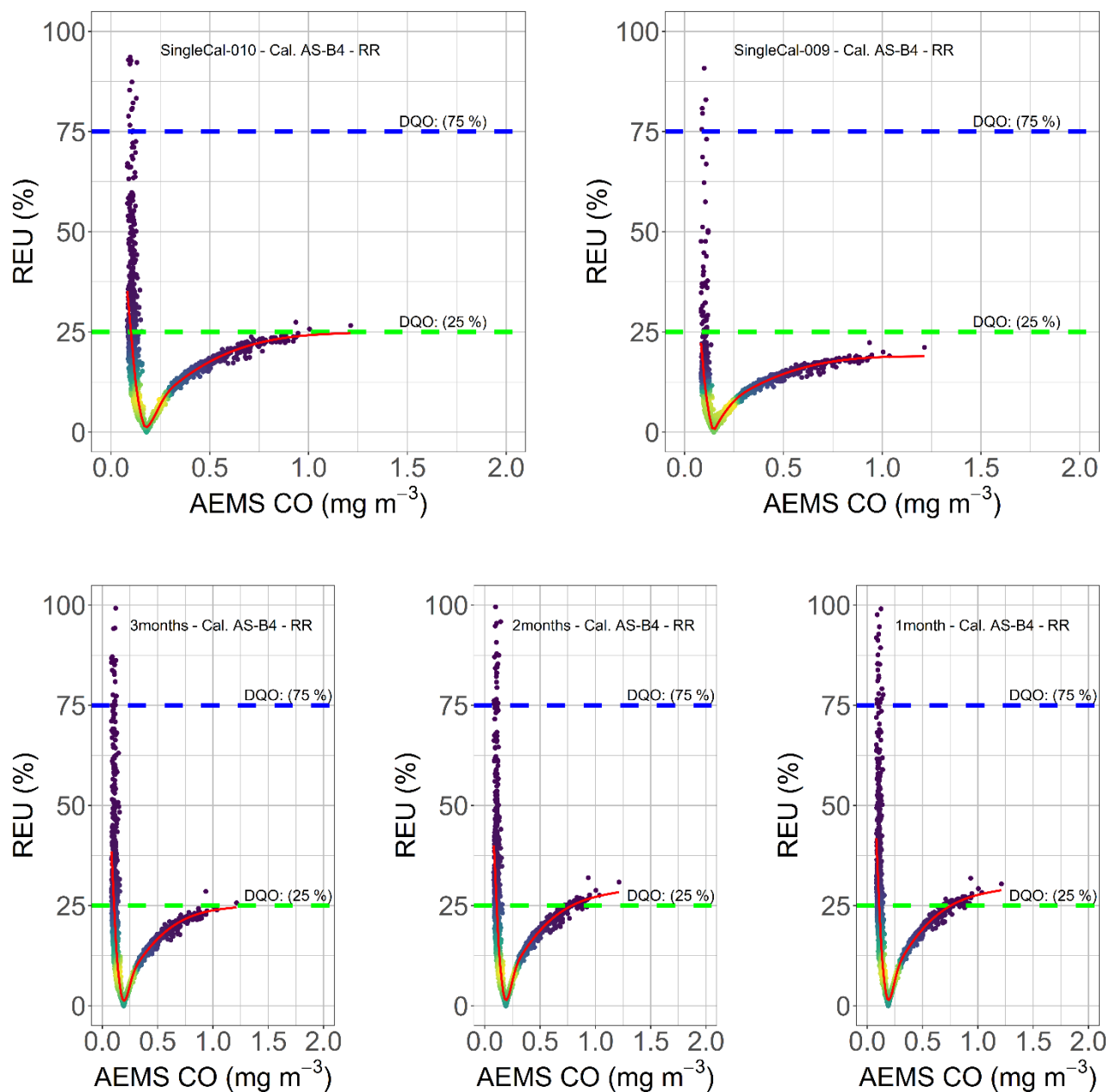


**Figure S15.** Calculated REU values for XGB calibrated CO LCS hourly data belonging to the test periods (TP1–TP7, 10 June 2022–10 January 2023) of AELCM009 and AELCM010. The calibration variants are single training (ST) (top row) and extended training (ET) (bottom row). The extended training is characterized by ET variants of 1, 2 and 3 months for each AELCM box. Horizontal dashed lines describe the data quality objectives (CO Class 1 DQO = 25 %, Class 2 DQO = 75 % and Class 3 DQO = 200 %). The fitted smooth curve (red) is based on a generalized additive model (GAM). Data density is shown through colour, where darker colours express lower data density and brighter colours express higher data density.

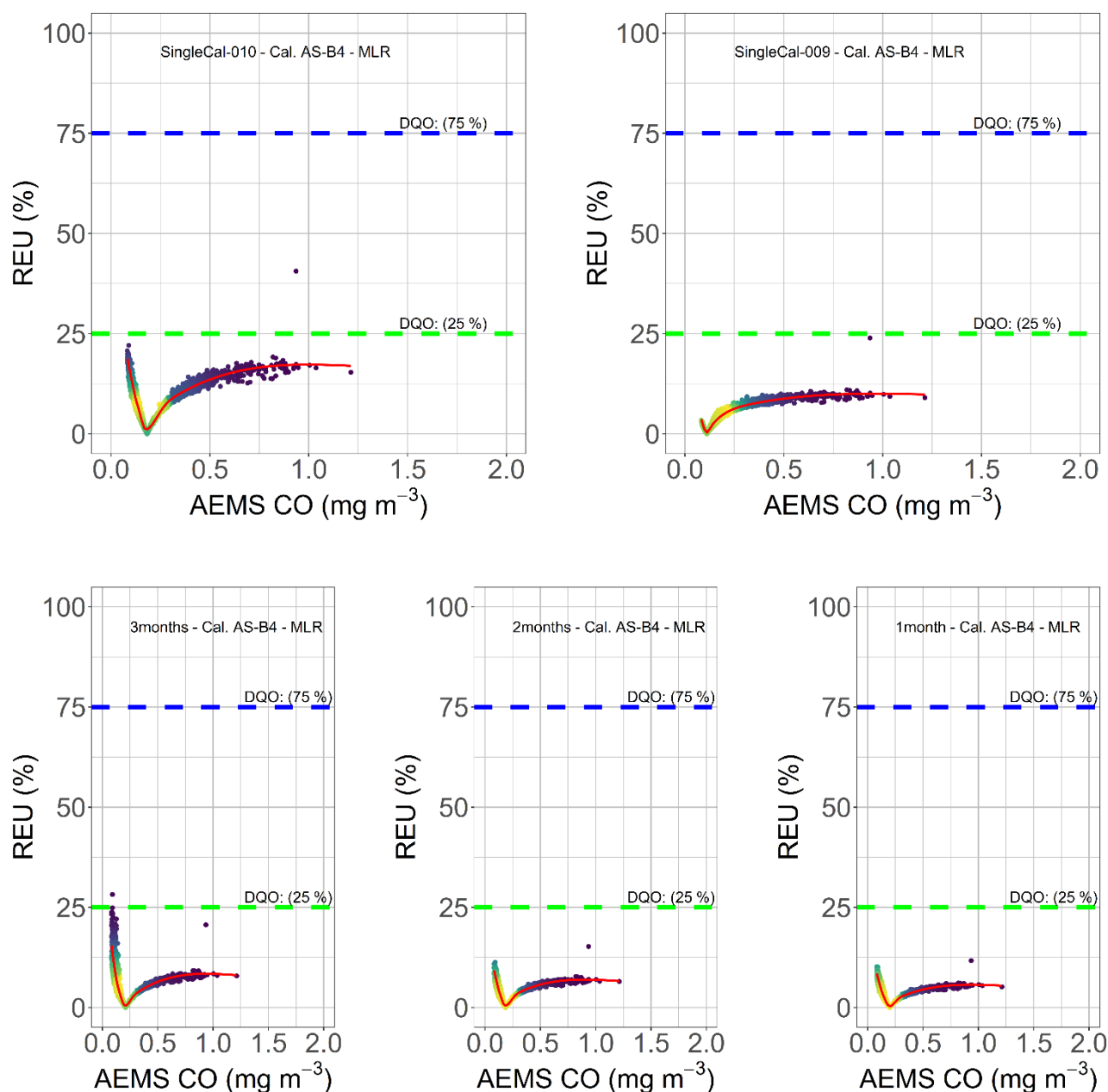




**Figure S16.** Calculated REU values for RF calibrated CO LCS hourly data belonging to the test periods (TP1–TP7, 10 June 2022–10 January 2023) of AELCM009 and AELCM010. The calibration variants are single training (ST) (top row) and extended training (ET) (bottom row). The extended training is characterized by ET variants of 1, 2 and 3 months for each AELCM box. Horizontal dashed lines describe the data quality objectives (CO Class 1 DQO = 25 %, Class 2 DQO = 75 % and Class 3 DQO = 200 %). The fitted smooth curve (red) is based on a generalized additive model (GAM). Data density is shown through colour, where darker colours express lower data density and brighter colours express higher data density.



**Figure S17.** Calculated REU values for RR calibrated CO LCS hourly data belonging to the test periods (TP1–TP7, 10 June 2022–10 January 2023) of AELCM009 and AELCM010. The calibration variants are single training (ST) (top row) and extended training (ET) (bottom row). The extended training is characterized by ET variants of 1, 2 and 3 months for each AELCM box. Horizontal dashed lines describe the data quality objectives (CO Class 1 DQO = 25 %, Class 2 DQO = 75 % and Class 3 DQO = 200 %). The fitted smooth curve (red) is based on a generalized additive model (GAM). Data density is shown through colour, where darker colours express lower data density and brighter colours express higher data density.



**Figure S18.** Calculated REU values for MLR calibrated CO LCS hourly data belonging to the test periods (TP1–TP7, 10 June 2022–10 January 2023) of AELCM009 and AELCM010. The calibration variants are single training (ST) (top row) and extended training (ET) (bottom row). The extended training is characterized by ET variants of 1, 2 and 3 months for each AELCM box. Horizontal dashed lines describe the data quality objectives (CO Class 1 DQO = 25 %, Class 2 DQO = 75 % and Class 3 DQO = 200 %). The fitted smooth curve (red) is based on a generalized additive model (GAM). Data density is shown through colour, where darker colours express lower data density and brighter colours express higher data density.

## Performance Metrics O<sub>3</sub>

**Table S29.** Performance metrics of the single O<sub>3</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on extreme gradient boosting, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

1 month xgboost (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.95/0.97		0.97/0.98		0.88/0.92		0.96/0.97	0.96/0.97
R <sup>2</sup>	0.89/0.93		0.93/0.95		0.83/0.90		0.90/0.95	0.92/0.95
RMSE [ppb]	6.10/4.42		7.39/5.69		4.33/3.33		4.93/3.53	5.81/4.35
MAE [ppb]	4.60/3.42		5.64/4.50		3.06/2.22		4.02/2.80	4.33/3.24
Slope	0.73/0.87		0.77/0.85		0.90/0.95		0.84/0.90	0.84/0.91
Delta Slope	0.27/0.13		0.23/0.15		0.10/0.05		0.16/0.10	0.16/0.09
Intercept	9.09/5.18		2.93/1.83		1.68/1.31		-0.90/-0.73	1.64/1.00
Intercept	9.09/5.18		2.93/1.83		1.68/1.31		0.90/0.73	1.64/1.00
AELCM009								
Rs		0.98/0.99		0.98/0.98		0.94/0.95		0.99/0.99
R <sup>2</sup>		0.95/0.97		0.98/0.97		0.97/0.98		0.98/0.98
RMSE [ppb]		4.43/3.42		2.44/2.09		3.70/1.46		3.62/2.46
MAE [ppb]		3.17/2.51		2.05/1.64		3.37/1.14		2.86/1.76
Slope		0.87/0.95		0.96/1.00		1.02/1.06		0.90/1.00
Delta Slope		0.13/0.05		0.04/0.00		0.02/0.06		0.10/0.00
Intercept		5.55/2.86		2.40/-0.53		3.19/-0.43		3.84/0.05
Intercept		5.55/2.86		2.40/0.53		3.19/0.43		3.84/0.05

**Table S30.** Performance metrics of the single O<sub>3</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on random forest, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

1 month random forest (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.96/0.97		0.98/0.98		0.84/0.91		0.96/0.97	0.96/0.97
R <sup>2</sup>	0.91/0.93		0.94/0.96		0.79/0.88		0.92/0.95	0.93/0.95
RMSE [ppb]	5.60/4.80		5.80/4.54		5.56/3.95		3.55/3.03	5.21/4.14
MAE [ppb]	4.52/3.84		4.48/3.57		4.26/2.71		2.82/2.39	4.02/3.13
Slope	0.76/0.88		0.76/0.85		0.87/0.96		0.92/0.92	0.86/0.93
Delta Slope	0.24/0.12		0.24/0.15		0.13/0.04		0.08/0.08	0.14/0.07
Intercept	10.71/6.67		6.47/3.70		4.31/2.04		-0.24/-0.35	3.71/1.80
Intercept	10.71/6.67		6.47/3.70		4.31/2.04		0.24/0.35	3.71/1.80
AELCM009								
Rs		0.96/0.97		0.98/0.98		0.91/0.94		0.98/0.99
R <sup>2</sup>		0.91/0.95		0.96/0.97		0.95/0.98		0.96/0.98
RMSE [ppb]		6.31/4.54		2.89/2.02		3.57/1.51		4.51/3.00
MAE [ppb]		4.76/3.32		2.33/1.60		3.05/1.14		3.38/2.02
Slope		0.75/0.89		0.91/0.99		0.91/1.05		0.86/0.98
Delta Slope		0.25/0.11		0.09/0.01		0.09/0.05		0.14/0.02
Intercept		9.93/5.46		3.39/-0.11		3.90/-0.57		4.80/0.53
Intercept		9.93/5.46		3.39/0.11		3.90/0.57		4.80/0.53

**Table S31.** Performance metrics of the single O<sub>3</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on ridge regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

1 month ridge regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.97/0.97		0.98/0.98		0.92/0.91		0.97/0.97	0.97/0.97
R <sup>2</sup>	0.94/0.94		0.95/0.95		0.88/0.89		0.89/0.90	0.93/0.94
RMSE [ppb]	5.74/5.12		4.85/4.83		4.68/4.37		5.00/4.64	5.08/4.75
MAE [ppb]	4.76/4.16		3.95/3.90		3.79/3.54		3.57/3.60	4.02/3.80
Slope	0.87/0.87		0.83/0.82		0.98/0.92		1.06/0.98	0.97/0.95
Delta Slope	0.13/0.13		0.17/0.18		0.02/0.08		0.06/0.02	0.03/0.05
Intercept	9.08/8.21		6.75/6.08		3.00/3.54		-3.60/-2.45	1.95/2.09
Intercept	9.08/8.21		6.75/6.08		3.00/3.54		3.60/2.45	1.95/2.09
AELCM009								
Rs		0.98/0.98		0.98/0.98		0.95/0.95		0.99/0.99
R <sup>2</sup>		0.95/0.95		0.97/0.97		0.93/0.93		0.97/0.97
RMSE [ppb]		5.94/4.81		2.45/2.28		2.95/2.49		4.08/3.39
MAE [ppb]		4.44/3.55		1.97/1.78		2.47/1.97		2.96/2.43
Slope		1.04/1.01		0.92/0.89		0.99/0.95		1.04/1.01
Delta Slope		0.04/0.01		0.08/0.11		0.01/0.05		0.04/0.01
Intercept		2.13/1.73		2.80/2.22		1.83/1.56		1.41/0.93
Intercept		2.13/1.73		2.80/2.22		1.83/1.56		1.41/0.93

**Table S32.** Performance metrics of the single O<sub>3</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on multiple linear regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

1 month multiple linear regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.97/0.98		0.98/0.98		0.91/0.91		0.97/0.97	0.97/0.97
R <sup>2</sup>	0.92/0.95		0.94/0.95		0.89/0.90		0.94/0.94	0.93/0.94
RMSE [ppb]	5.32/5.09		5.32/4.45		3.80/3.50		6.07/4.87	5.19/4.52
MAE [ppb]	4.37/4.22		4.16/3.60		2.82/2.65		5.33/4.21	4.17/3.67
Slope	0.87/0.91		0.81/0.86		1.03/0.95		1.10/0.99	0.99/0.98
Delta Slope	0.13/0.09		0.19/0.14		0.03/0.05		0.10/0.01	0.01/0.02
Intercept	7.93/6.91		4.80/3.99		0.28/1.79		-6.74/-3.83	-0.47/0.35
Intercept	7.93/6.91		4.80/3.99		0.28/1.79		6.74/3.83	0.47/0.35
AELCM009								
Rs		0.99/0.99		0.99/0.99		0.96/0.97		0.99/0.99
R <sup>2</sup>		0.95/0.96		0.98/0.98		0.98/0.98		0.97/0.98
RMSE [ppb]		6.41/5.27		1.60/1.79		2.74/1.56		4.13/3.34
MAE [ppb]		3.92/2.89		1.31/1.38		2.45/1.28		2.56/1.85
Slope		1.12/1.10		0.99/1.01		0.98/1.03		1.06/1.06
Delta Slope		0.12/0.10		0.01/0.01		0.02/0.03		0.06/0.06
Intercept		-1.57/-2.17		0.66/-0.95		2.54/0.72		0.70/-0.61
Intercept		1.57/2.17		0.66/0.95		2.54/0.72		0.70/0.61

**Table S33.** Performance metrics of the single O<sub>3</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on extreme gradient boosting, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

2 month xgboost (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.95/0.96	0.93/0.94			0.88/0.93	0.93/0.93		0.97/0.98
R <sup>2</sup>	0.89/0.92	0.86/0.88			0.83/0.89	0.92/0.96		0.93/0.95
RMSE [ppb]	6.10/4.96	8.58/7.02			4.33/3.64	2.95/1.85		5.88/4.76
MAE [ppb]	4.60/3.89	6.08/5.16			3.06/2.35	2.28/1.41		4.01/3.21
Slope	0.73/0.82	0.68/0.74			0.90/0.99	0.82/0.99		0.84/0.92
Delta Slope	0.27/0.18	0.32/0.26			0.10/0.01	0.18/0.01		0.16/0.08
Intercept	9.09/8.07	9.90/10.22			1.68/1.07	0.21/-0.50		2.47/2.26
Intercept	9.09/8.07	9.90/10.22			1.68/1.07	0.21/0.50		2.47/2.26
AELCM009								
Rs			0.99/0.99	0.98/0.98			0.98/0.98	0.99/0.99
R <sup>2</sup>			0.97/0.98	0.98/0.97			0.98/0.98	0.97/0.98
RMSE [ppb]			3.89/3.19	2.44/2.39			2.95/2.03	3.15/2.58
MAE [ppb]			2.94/2.39	2.05/1.88			2.42/1.61	2.47/1.96
Slope			0.86/0.95	0.96/1.00			1.11/1.06	0.91/0.97
Delta Slope			0.14/0.05	0.04/0.00			0.11/0.06	0.09/0.03
Intercept			3.95/0.30	2.40/-0.85			-0.01/-1.26	2.80/-0.27
Intercept			3.95/0.30	2.40/0.85			0.01/1.26	2.80/0.27

**Table S34.** Performance metrics of the single O<sub>3</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on random forest, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

2 month random forest (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.96/0.96	0.94/0.96			0.84/0.91	0.88/0.93		0.96/0.98
R <sup>2</sup>	0.91/0.92	0.89/0.92			0.79/0.88	0.92/0.96		0.94/0.95
RMSE [ppb]	5.60/5.39	7.37/6.06			5.56/4.19	2.46/1.83		5.54/4.66
MAE [ppb]	4.52/4.42	5.76/4.79			4.26/2.77	2.06/1.44		4.15/3.35
Slope	0.76/0.85	0.69/0.80			0.87/1.00	0.87/1.00		0.87/0.96
Delta Slope	0.24/0.15	0.31/0.20			0.13/0.00	0.13/0.00		0.13/0.04
Intercept	10.71/8.66	12.41/10.02			4.31/1.73	1.13/-0.27		4.22/2.42
Intercept	10.71/8.66	12.41/10.02			4.31/1.73	1.13/0.27		4.22/2.42
AELCM009								
Rs			0.98/0.99	0.98/0.98			0.98/0.98	0.98/0.99
R <sup>2</sup>			0.96/0.98	0.96/0.97			0.97/0.97	0.96/0.98
RMSE [ppb]			5.04/3.30	2.89/2.19			2.45/1.95	3.64/2.55
MAE [ppb]			3.85/2.40	2.33/1.72			1.79/1.45	2.66/1.86
Slope			0.79/0.92	0.91/0.98			1.03/1.02	0.87/0.95
Delta Slope			0.21/0.08	0.09/0.02			0.03/0.02	0.13/0.05
Intercept			6.55/1.64	3.39/-0.17			0.74/-0.57	3.76/0.48
Intercept			6.55/1.64	3.39/0.17			0.74/0.57	3.76/0.48

**Table S35.** Performance metrics of the single O<sub>3</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on ridge regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

2 month ridge regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.97/0.97	0.97/0.97			0.92/0.91	0.94/0.94		0.98/0.98
R <sup>2</sup>	0.94/0.94	0.93/0.94			0.88/0.89	0.87/0.89		0.95/0.96
RMSE [ppb]	5.74/5.53	5.92/5.74			4.68/4.69	3.37/2.81		5.03/4.84
MAE [ppb]	4.76/4.57	4.85/4.70			3.79/3.84	2.22/2.16		3.90/3.82
Slope	0.87/0.87	0.82/0.81			0.98/0.92	1.00/0.91		0.98/0.96
Delta Slope	0.13/0.13	0.18/0.19			0.02/0.08	0.00/0.09		0.02/0.04
Intercept	9.08/8.86	10.11/10.15			3.00/4.12	-0.33/1.17		2.79/3.53
Intercept	9.08/8.86	10.11/10.15			3.00/4.12	0.33/1.17		2.79/3.53
AELCM009								
Rs			0.99/0.98	0.98/0.98			0.98/0.98	0.99/0.98
R <sup>2</sup>			0.97/0.96	0.97/0.96			0.94/0.93	0.97/0.96
RMSE [ppb]			3.59/4.11	2.45/2.59			3.03/3.27	3.06/3.38
MAE [ppb]			2.89/3.27	1.97/2.02			2.15/2.42	2.34/2.57
Slope			0.94/0.89	0.92/0.87			1.06/1.00	0.98/0.92
Delta Slope			0.06/0.11	0.08/0.13			0.06/0.00	0.02/0.08
Intercept			3.37/2.85	2.80/2.41			-0.82/-1.09	1.43/0.98
Intercept			3.37/2.85	2.80/2.41			0.82/1.09	1.43/0.98

**Table S36.** Performance metrics of the single O<sub>3</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on multiple linear regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

2 month multiple linear regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.97/0.98	0.95/0.97			0.91/0.91	0.95/0.95		0.97/0.98
R <sup>2</sup>	0.92/0.95	0.88/0.94			0.89/0.90	0.95/0.95		0.94/0.96
RMSE [ppb]	5.32/5.54	6.81/5.67			3.80/3.95	4.23/2.40		5.17/4.59
MAE [ppb]	4.37/4.69	5.12/4.56			2.82/3.03	3.73/1.77		4.01/3.51
Slope	0.87/0.88	0.76/0.80			1.03/0.97	1.07/0.98		0.99/0.98
Delta Slope	0.13/0.12	0.24/0.20			0.03/0.03	0.07/0.02		0.01/0.02
Intercept	7.93/8.54	10.05/10.24			0.28/2.46	-4.25/-1.12		0.27/2.08
Intercept	7.93/8.54	10.05/10.24			0.28/2.46	4.25/1.12		0.27/2.08
AELCM009								
Rs			0.99/0.99	0.99/0.99			0.99/0.99	0.99/0.99
R <sup>2</sup>			0.98/0.98	0.98/0.98			0.98/0.98	0.98/0.98
RMSE [ppb]			2.80/3.12	1.60/2.04			2.09/1.78	2.22/2.39
MAE [ppb]			2.02/2.39	1.31/1.60			1.59/1.30	1.64/1.76
Slope			0.99/0.96	0.99/0.99			1.05/1.06	1.00/0.98
Delta Slope			0.01/0.04	0.01/0.01			0.05/0.06	0.00/0.02
Intercept			0.79/0.00	0.66/-0.83			0.29/-1.22	0.72/-0.40
Intercept			0.79/0.00	0.66/0.83			0.29/1.22	0.72/0.40

**Table S37.** Performance metrics of the single O<sub>3</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on extreme gradient boosting, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

3 month xgboost (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.95/0.95	0.93/0.93	0.97/0.97				0.96/0.97	0.96/0.97
R <sup>2</sup>	0.89/0.90	0.86/0.86	0.93/0.93				0.90/0.95	0.91/0.92
RMSE [ppb]	6.10/6.01	8.58/8.82	7.39/7.24				4.93/3.55	6.89/6.69
MAE [ppb]	4.60/4.60	6.08/6.30	5.64/5.44				4.02/2.83	5.09/4.79
Slope	0.73/0.73	0.68/0.67	0.77/0.75				0.84/0.89	0.82/0.80
Delta Slope	0.27/0.27	0.32/0.33	0.23/0.25				0.16/0.11	0.18/0.20
Intercept	9.09/9.27	9.90/10.20	2.93/4.22				-0.90/-0.64	2.68/3.59
Intercept	9.09/9.27	9.90/10.20	2.93/4.22				0.90/0.64	2.68/3.59
AELCM009								
Rs			0.98/0.99	0.92/0.94	0.94/0.96			0.95/0.96
R <sup>2</sup>			0.98/0.98	0.95/0.95	0.97/0.98			0.96/0.97
RMSE [ppb]			2.44/1.78	4.93/3.10	3.70/1.79			3.83/2.31
MAE [ppb]			2.05/1.41	4.36/2.40	3.37/1.41			3.26/1.74
Slope			0.96/0.98	0.91/0.95	1.02/1.02			0.93/0.96
Delta Slope			0.04/0.02	0.09/0.05	0.02/0.02			0.07/0.04
Intercept			2.40/0.25	5.29/2.79	3.19/0.98			4.04/1.69
Intercept			2.40/0.25	5.29/2.79	3.19/0.98			4.04/1.69

**Table S38.** Performance metrics of the single O<sub>3</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on random forest, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

3 month random forest (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.96/0.96	0.94/0.94	0.98/0.98				0.96/0.97	0.97/0.97
R <sup>2</sup>	0.91/0.92	0.89/0.88	0.94/0.94				0.92/0.95	0.92/0.92
RMSE [ppb]	5.60/5.41	7.37/7.34	5.80/5.80				3.55/2.96	5.74/5.60
MAE [ppb]	4.52/4.38	5.76/5.63	4.48/4.37				2.82/2.34	4.39/4.18
Slope	0.76/0.76	0.69/0.71	0.76/0.77				0.92/0.93	0.84/0.84
Delta Slope	0.24/0.24	0.31/0.29	0.24/0.23				0.08/0.07	0.16/0.16
Intercept	10.71/10.24	12.41/11.51	6.47/5.92				-0.24/-0.38	4.59/4.26
Intercept	10.71/10.24	12.41/11.51	6.47/5.92				0.24/0.38	4.59/4.26
AELCM009								
Rs			0.98/0.98	0.91/0.94	0.91/0.95			0.94/0.96
R <sup>2</sup>			0.96/0.98	0.91/0.94	0.95/0.98			0.94/0.96
RMSE [ppb]			2.89/1.92	5.54/3.65	3.57/1.72			4.15/2.58
MAE [ppb]			2.33/1.55	4.67/2.82	3.05/1.37			3.35/1.92
Slope			0.91/0.96	0.85/0.93	0.91/0.99			0.87/0.94
Delta Slope			0.09/0.04	0.15/0.07	0.09/0.01			0.13/0.06
Intercept			3.39/1.10	6.21/3.37	3.90/1.32			4.75/2.18
Intercept			3.39/1.10	6.21/3.37	3.90/1.32			4.75/2.18

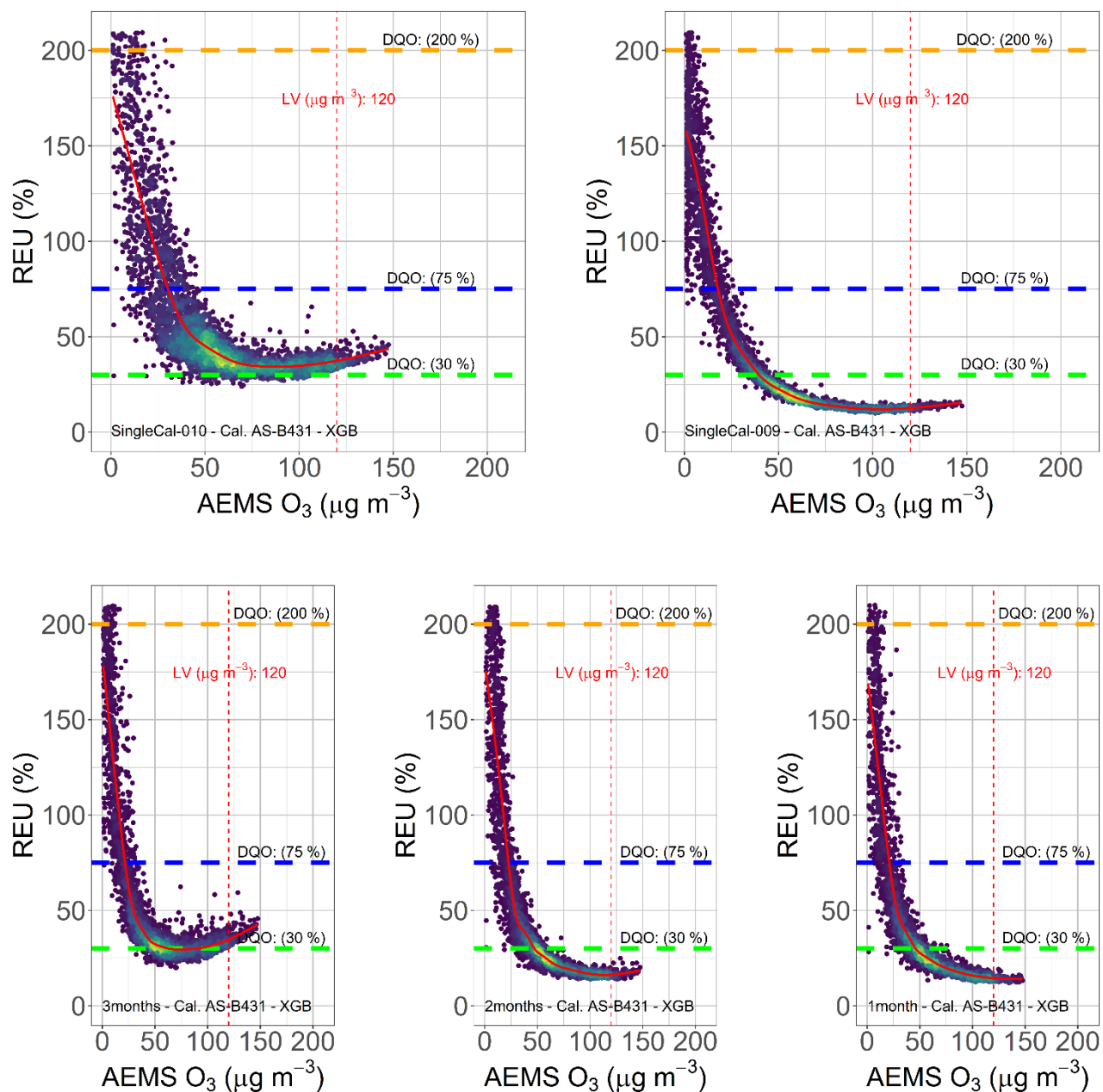
**Table S39.** Performance metrics of the single O<sub>3</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on ridge regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

3 month ridge regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.97/0.97	0.97/0.97	0.98/0.98				0.97/0.97	0.97/0.97
R <sup>2</sup>	0.94/0.94	0.93/0.94	0.95/0.95				0.89/0.91	0.93/0.93
RMSE [ppb]	5.74/5.18	5.92/5.38	4.85/4.63				5.00/4.73	5.40/4.99
MAE [ppb]	4.76/4.22	4.85/4.36	3.95/3.75				3.57/3.70	4.28/4.01
Slope	0.87/0.89	0.82/0.84	0.83/0.85				1.06/0.99	0.97/0.97
Delta Slope	0.13/0.11	0.18/0.16	0.17/0.15				0.06/0.01	0.03/0.03
Intercept	9.08/7.49	10.11/8.78	6.75/5.12				-3.60/-2.96	2.39/1.56
Intercept	9.08/7.49	10.11/8.78	6.75/5.12				3.60/2.96	2.39/1.56
AELCM009								
Rs			0.98/0.98	0.93/0.93	0.93/0.95			0.96/0.96
R <sup>2</sup>			0.97/0.97	0.93/0.93	0.93/0.93			0.95/0.95
RMSE [ppb]			2.45/2.69	4.40/4.39	2.95/3.01			3.37/3.44
MAE [ppb]			1.97/2.11	3.78/3.69	2.47/2.53			2.74/2.78
Slope			0.92/0.85	0.92/0.84	0.99/0.92			0.93/0.86
Delta Slope			0.08/0.15	0.08/0.16	0.01/0.08			0.07/0.14
Intercept			2.80/3.74	4.45/5.07	1.83/2.66			3.15/3.89
Intercept			2.80/3.74	4.45/5.07	1.83/2.66			3.15/3.89

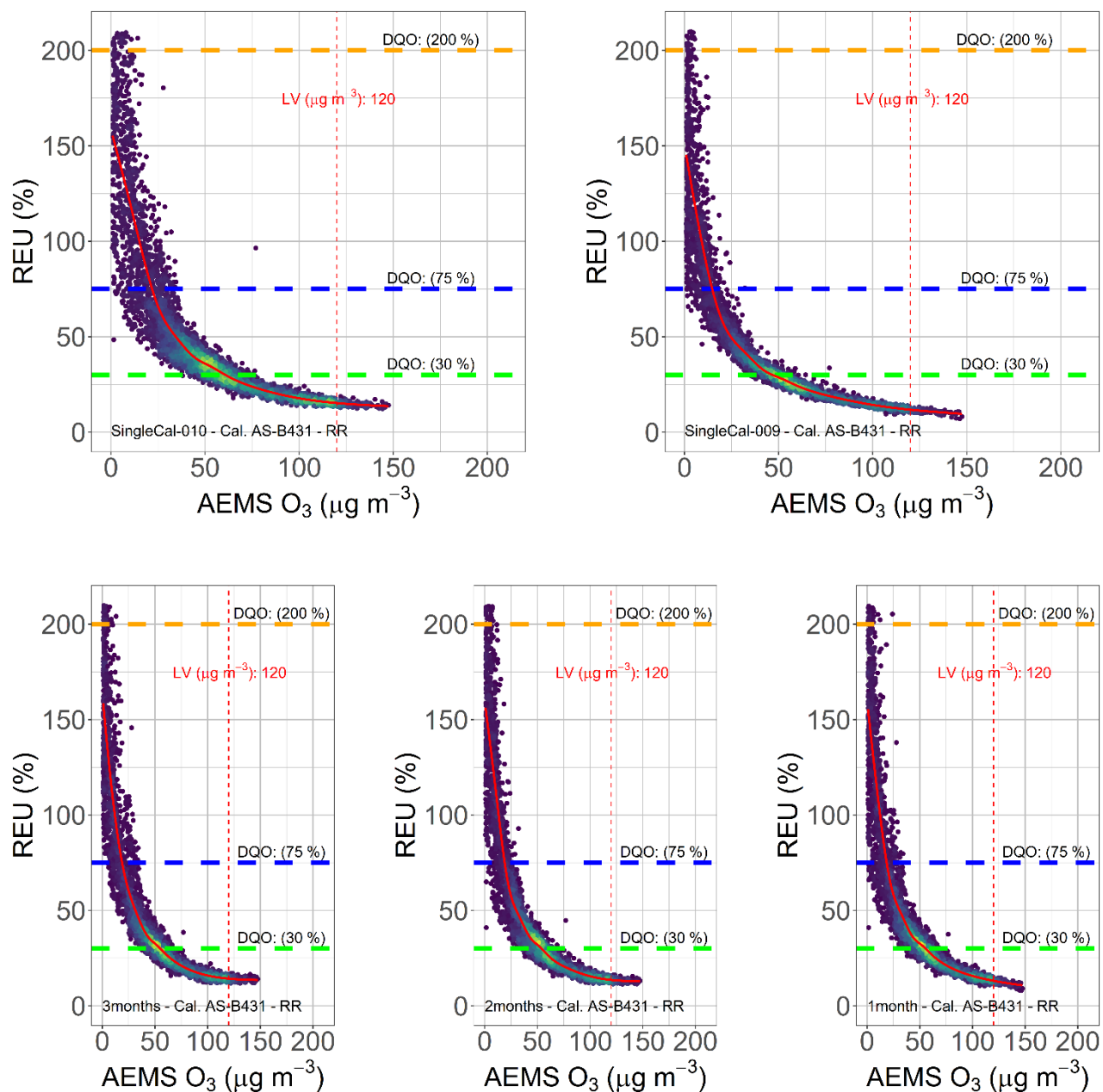
**Table S40.** Performance metrics of the single O<sub>3</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on multiple linear regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from hourly mean values.

3 month multiple linear regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.97/0.97	0.95/0.96	0.98/0.98				0.97/0.97	0.96/0.97
R <sup>2</sup>	0.92/0.94	0.88/0.92	0.94/0.95				0.94/0.94	0.91/0.93
RMSE [ppb]	5.32/4.96	6.81/5.94	5.32/4.98				6.07/4.89	5.91/5.21
MAE [ppb]	4.37/4.09	5.12/4.60	4.16/4.01				5.33/4.20	4.74/4.22
Slope	0.87/0.87	0.76/0.78	0.81/0.82				1.10/1.03	0.95/0.94
Delta Slope	0.13/0.13	0.24/0.22	0.19/0.18				0.10/0.03	0.05/0.06
Intercept	7.93/8.00	10.05/9.69	4.80/4.97				-6.74/-4.36	0.52/1.41
Intercept	7.93/8.00	10.05/9.69	4.80/4.97				6.74/4.36	0.52/1.41
AELCM009								
Rs			0.99/0.99	0.93/0.94	0.96/0.97			0.96/0.96
R <sup>2</sup>			0.98/0.98	0.96/0.97	0.98/0.98			0.97/0.97
RMSE [ppb]			1.60/1.63	4.05/3.23	2.74/1.95			2.97/2.37
MAE [ppb]			1.31/1.28	3.53/2.70	2.45/1.71			2.43/1.90
Slope			0.99/0.97	0.92/0.90	0.98/1.00			0.93/0.93
Delta Slope			0.01/0.03	0.08/0.10	0.02/0.00			0.07/0.07
Intercept			0.66/0.40	4.38/3.66	2.54/1.56			3.00/2.30
Intercept			0.66/0.40	4.38/3.66	2.54/1.56			3.00/2.30





**Figure S19.** Calculated REU values for XGB calibrated O<sub>3</sub> LCS hourly data belonging to the test periods (TP1–TP7, 10 June 2022–11 January 2023) of AELCM009 and AELCM010. The calibration variants are single training (ST) (top row) and extended training (ET) (bottom row). The extended training is characterized by ET variants of 1, 2 and 3 months for each AELCM box. Horizontal dashed lines describe the data quality objectives (O<sub>3</sub> Class 1 DQO = 30 %, Class 2 DQO = 75 % and Class 3 DQO = 200 %). The vertical dashed line describes the limit value for O<sub>3</sub> (LV = 120 μg m<sup>-3</sup>). The fitted smooth curve (red) is based on a generalized additive model (GAM). Data density is shown through colour, where darker colours express lower data density and brighter colours express higher data density.



**Figure S20.** Calculated REU values for RR calibrated O<sub>3</sub> LCS hourly data belonging to the test periods (TP1–TP7, 10 June 2022–11 January 2023) of AELCM009 and AELCM010. The calibration variants are single training (ST) (top row) and extended training (ET) (bottom row). The extended training is characterized by ET variants of 1, 2 and 3 months for each AELCM box. Horizontal dashed lines describe the data quality objectives (O<sub>3</sub> Class 1 DQO = 30 %, Class 2 DQO = 75 % and Class 3 DQO = 200 %). The vertical dashed line describes the limit value for O<sub>3</sub> (LV = 120 μg m<sup>-3</sup>). The fitted smooth curve (red) is based on a generalized additive model (GAM). Data density is shown through colour, where darker colours express lower data density and brighter colours express higher data density.

## Performance Metrics PM<sub>2.5</sub>

**Table S41.** Performance metrics of the single PM<sub>2.5</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on extreme gradient boosting, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from daily mean values.

1 month xgboost (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.94/0.95		0.92/0.92		0.90/0.90		0.97/0.97	0.96/0.96
R <sup>2</sup>	0.86/0.86		0.86/0.87		0.89/0.89		0.95/0.95	0.93/0.93
RMSE (µg m <sup>-3</sup> )	2.12/1.93		1.30/1.12		2.53/2.42		3.28/3.23	2.42/2.30
MAE (µg m <sup>-3</sup> )	1.28/1.12		0.92/0.77		2.07/1.97		1.88/1.79	1.53/1.41
Slope	0.52/0.55		0.80/0.83		0.76/0.78		0.81/0.81	0.79/0.80
Delta Slope	0.48/0.45		0.20/0.17		0.24/0.22		0.19/0.19	0.21/0.20
Intercept	2.01/2.02		0.76/0.78		0.07/0.05		0.69/0.79	0.42/0.56
Intercept	2.01/2.02		0.76/0.78		0.07/0.05		0.69/0.79	0.42/0.56
AELCM009								
Rs		0.94/0.93		0.96/0.97		0.95/0.95		0.96/0.95
R <sup>2</sup>		0.92/0.92		0.95/0.96		0.93/0.94		0.93/0.92
RMSE (µg m <sup>-3</sup> )		1.53/1.34		0.79/0.86		1.34/1.37		1.26/1.21
MAE (µg m <sup>-3</sup> )		1.25/1.10		0.68/0.75		1.06/1.07		0.99/0.98
Slope		0.71/0.71		0.87/0.90		0.89/0.93		0.87/0.91
Delta Slope		0.29/0.29		0.13/0.10		0.11/0.07		0.13/0.09
Intercept		1.13/1.41		0.72/1.04		0.98/1.27		0.57/0.81
Intercept		1.13/1.41		0.72/1.04		0.98/1.27		0.57/0.81

**Table S42.** Performance metrics of the single PM<sub>2.5</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on random forest, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from daily mean values.

1 month random forest (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.95/0.96		0.93/0.93		0.89/0.89		0.97/0.97	0.95/0.95
R <sup>2</sup>	0.88/0.88		0.87/0.88		0.89/0.89		0.98/0.98	0.95/0.95
RMSE (µg m <sup>-3</sup> )	1.64/1.54		0.98/0.96		2.14/2.07		1.72/1.70	1.67/1.61
MAE (µg m <sup>-3</sup> )	0.95/0.87		0.68/0.70		1.72/1.63		0.88/0.88	1.06/1.02
Slope	0.62/0.64		0.90/0.94		0.81/0.83		0.95/0.95	0.91/0.92
Delta Slope	0.38/0.36		0.10/0.06		0.19/0.17		0.05/0.05	0.09/0.08
Intercept	1.93/1.93		0.60/0.50		0.08/0.03		0.12/0.19	0.05/0.15
Intercept	1.93/1.93		0.60/0.50		0.08/0.03		0.12/0.19	0.05/0.15
AELCM009								
Rs		0.97/0.96		0.98/0.98		0.95/0.96		0.97/0.97
R <sup>2</sup>		0.96/0.96		0.96/0.96		0.95/0.95		0.96/0.96
RMSE (µg m <sup>-3</sup> )		0.97/0.64		0.85/0.81		1.63/1.31		1.20/0.96
MAE (µg m <sup>-3</sup> )		0.81/0.53		0.63/0.58		1.27/0.99		0.90/0.70
Slope		0.83/1.01		0.87/1.02		0.88/1.04		0.86/1.02
Delta Slope		0.17/0.01		0.13/0.02		0.12/0.04		0.14/0.02
Intercept		0.65/0.05		0.34/0.21		0.15/-0.14		0.36/0.06
Intercept		0.65/0.05		0.34/0.21		0.15/0.14		0.36/0.06

**Table S43.** Performance metrics of the single PM<sub>2.5</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on ridge regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from daily mean values.

1 month ridge regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.92/0.92		0.88/0.88		0.89/0.89		0.98/0.98	0.92/0.93
R <sup>2</sup>	0.77/0.79		0.81/0.82		0.88/0.88		0.99/0.99	0.94/0.94
RMSE (µg m <sup>-3</sup> )	2.09/2.06		1.27/1.20		2.24/2.08		1.01/1.02	1.73/1.66
MAE (µg m <sup>-3</sup> )	1.43/1.44		0.85/0.82		1.77/1.59		0.70/0.76	1.19/1.15
Slope	0.46/0.45		0.72/0.72		0.84/0.82		0.99/0.97	0.94/0.92
Delta Slope	0.54/0.55		0.28/0.28		0.16/0.18		0.01/0.03	0.06/0.08
Intercept	3.12/3.28		1.80/1.91		-0.22/0.11		0.41/0.67	-0.05/0.22
Intercept	3.12/3.28		1.80/1.91		0.22/0.11		0.41/0.67	0.05/0.22
AELCM009								
Rs		0.92/0.96		0.94/0.96		0.95/0.95		0.95/0.97
R <sup>2</sup>		0.93/0.96		0.94/0.95		0.95/0.95		0.93/0.94
RMSE (µg m <sup>-3</sup> )		1.46/1.29		1.31/1.04		1.53/1.19		1.44/1.18
MAE (µg m <sup>-3</sup> )		1.14/1.06		0.96/0.97		1.19/0.95		1.10/0.99
Slope		0.59/0.61		0.79/0.80		0.93/0.93		0.85/0.85
Delta Slope		0.41/0.39		0.21/0.20		0.07/0.07		0.15/0.15
Intercept		2.57/3.02		0.30/1.69		-0.34/1.06		0.38/1.48
Intercept		2.57/3.02		0.30/1.69		0.34/1.06		0.38/1.48

**Table S44.** Performance metrics of the single PM<sub>2.5</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on multiple linear regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the one-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from daily mean values.

1 month multiple linear regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.95/0.95		0.93/0.93		0.90/0.90		0.98/0.98	0.96/0.96
R <sup>2</sup>	0.89/0.90		0.87/0.87		0.88/0.88		0.99/0.99	0.96/0.96
RMSE (µg m <sup>-3</sup> )	1.67/1.53		1.03/0.98		2.11/2.02		2.02/2.19	1.76/1.75
MAE (µg m <sup>-3</sup> )	0.96/0.88		0.69/0.65		1.67/1.59		1.28/1.40	1.15/1.13
Slope	0.63/0.65		0.90/0.92		0.83/0.84		0.87/0.85	0.86/0.84
Delta Slope	0.37/0.35		0.10/0.08		0.17/0.16		0.13/0.15	0.14/0.16
Intercept	1.67/1.70		0.46/0.47		-0.02/0.00		0.66/0.76	0.35/0.58
Intercept	1.67/1.70		0.46/0.47		0.02/0.00		0.66/0.76	0.35/0.58
AELCM009								
Rs		0.97/0.96		0.97/0.97		0.95/0.95		0.98/0.97
R <sup>2</sup>		0.98/0.96		0.96/0.96		0.95/0.95		0.96/0.96
RMSE (µg m <sup>-3</sup> )		0.89/0.71		1.01/0.69		1.76/1.16		1.28/0.88
MAE (µg m <sup>-3</sup> )		0.75/0.58		0.74/0.51		1.36/0.94		0.95/0.68
Slope		0.94/1.08		0.87/1.03		0.85/0.96		0.88/1.00
Delta Slope		0.06/0.08		0.13/0.03		0.15/0.04		0.12/0.00
Intercept		-0.30/-0.56		0.00/-0.08		0.28/0.33		0.06/0.05
Intercept		0.30/0.56		0.00/0.08		0.28/0.33		0.06/0.05

**Table S45.** Performance metrics of the single PM<sub>2.5</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on extreme gradient boosting, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from daily mean values.

2 month xgboost (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.94/0.94	0.94/0.94			0.90/0.89	0.96/0.97		0.95/0.95
R <sup>2</sup>	0.86/0.86	0.95/0.95			0.89/0.89	0.97/0.97		0.90/0.90
RMSE (µg m <sup>-3</sup> )	2.12/2.01	1.38/1.28			2.53/2.44	1.26/1.14		1.90/1.80
MAE (µg m <sup>-3</sup> )	1.28/1.18	1.11/1.02			2.07/1.98	1.02/0.94		1.37/1.28
Slope	0.52/0.54	0.78/0.79			0.76/0.78	0.91/0.93		0.80/0.82
Delta Slope	0.48/0.46	0.22/0.21			0.24/0.22	0.09/0.07		0.20/0.18
Intercept	2.01/1.99	0.57/0.60			0.07/0.04	0.16/0.04		0.37/0.33
Intercept	2.01/1.99	0.57/0.60			0.07/0.04	0.16/0.04		0.37/0.33
AELCM009								
Rs			0.92/0.92	0.96/0.97			0.96/0.96	0.97/0.97
R <sup>2</sup>			0.80/0.80	0.95/0.96			0.96/0.95	0.95/0.95
RMSE (µg m <sup>-3</sup> )			1.48/1.27	0.79/0.90			3.04/2.96	2.01/1.93
MAE (µg m <sup>-3</sup> )			1.10/0.96	0.68/0.80			1.82/1.86	1.20/1.20
Slope			0.77/0.76	0.87/0.86			0.79/0.78	0.81/0.80
Delta Slope			0.23/0.24	0.13/0.14			0.21/0.22	0.19/0.20
Intercept			0.92/1.51	0.72/1.29			1.40/1.89	0.97/1.52
Intercept			0.92/1.51	0.72/1.29			1.40/1.89	0.97/1.52

**Table S46.** Performance metrics of the single PM<sub>2.5</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on random forest, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from daily mean values.

2 month random forest (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.95/0.95	0.96/0.95			0.89/0.89	0.97/0.96		0.95/0.95
R <sup>2</sup>	0.88/0.88	0.96/0.95			0.89/0.89	0.97/0.97		0.91/0.91
RMSE (µg m <sup>-3</sup> )	1.64/1.57	0.81/0.73			2.14/2.09	0.96/0.95		1.49/1.44
MAE (µg m <sup>-3</sup> )	0.95/0.91	0.65/0.58			1.72/1.66	0.77/0.75		1.02/0.97
Slope	0.62/0.63	0.89/0.93			0.81/0.82	0.97/0.99		0.86/0.88
Delta Slope	0.38/0.37	0.11/0.07			0.19/0.18	0.03/0.01		0.14/0.12
Intercept	1.93/1.91	0.42/0.29			0.08/0.02	-0.03/-0.08		0.39/0.35
Intercept	1.93/1.91	0.42/0.29			0.08/0.02	0.03/0.08		0.39/0.35
AELCM009								
Rs			0.93/0.93	0.98/0.97			0.97/0.97	0.98/0.98
R <sup>2</sup>			0.85/0.84	0.96/0.96			0.96/0.95	0.96/0.95
RMSE (µg m <sup>-3</sup> )			1.18/1.19	0.85/0.84			2.98/2.64	1.92/1.74
MAE (µg m <sup>-3</sup> )			0.86/0.87	0.63/0.61			1.77/1.50	1.09/0.99
Slope			0.84/0.98	0.87/1.01			0.84/0.85	0.84/0.86
Delta Slope			0.16/0.02	0.13/0.01			0.16/0.15	0.16/0.14
Intercept			0.65/0.54	0.34/0.34			0.44/0.87	0.55/1.18
Intercept			0.65/0.54	0.34/0.34			0.44/0.87	0.55/1.18

**Table S47.** Performance metrics of the single PM<sub>2.5</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on ridge regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from daily mean values.

2 month ridge regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.92/0.92	0.92/0.94			0.89/0.89	0.96/0.96		0.92/0.93
R <sup>2</sup>	0.77/0.79	0.95/0.95			0.88/0.88	0.96/0.96		0.85/0.85
RMSE (µg m <sup>-3</sup> )	2.09/2.06	1.20/1.19			2.24/2.06	1.12/1.14		1.74/1.67
MAE (µg m <sup>-3</sup> )	1.43/1.46	0.93/0.95			1.77/1.55	0.83/0.83		1.24/1.20
Slope	0.46/0.45	0.66/0.65			0.84/0.82	1.01/0.99		0.84/0.82
Delta Slope	0.54/0.55	0.34/0.35			0.16/0.18	0.01/0.01		0.16/0.18
Intercept	3.12/3.34	2.36/2.50			-0.22/0.19	0.16/0.51		0.84/1.11
Intercept	3.12/3.34	2.36/2.50			0.22/0.19	0.16/0.51		0.84/1.11
AELCM009								
Rs			0.84/0.90	0.94/0.96			0.98/0.98	0.96/0.97
R <sup>2</sup>			0.76/0.81	0.94/0.95			0.98/0.98	0.97/0.97
RMSE (µg m <sup>-3</sup> )			1.78/1.26	1.31/1.09			1.86/1.65	1.67/1.35
MAE (µg m <sup>-3</sup> )			1.26/0.93	0.96/1.01			1.25/1.27	1.16/1.07
Slope			0.62/0.66	0.79/0.79			0.92/0.88	0.90/0.87
Delta Slope			0.38/0.34	0.21/0.21			0.08/0.12	0.10/0.13
Intercept			1.80/2.60	0.30/1.82			-0.02/1.51	-0.20/1.28
Intercept			1.80/2.60	0.30/1.82			0.02/1.51	0.20/1.28

**Table S48.** Performance metrics of the single PM<sub>2.5</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on multiple linear regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the two-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from daily mean values.

2 month multiple linear regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.95/0.95	0.96/0.96			0.90/0.90	0.96/0.96		0.95/0.95
R <sup>2</sup>	0.89/0.90	0.97/0.97			0.88/0.88	0.95/0.95		0.90/0.91
RMSE (µg m <sup>-3</sup> )	1.67/1.56	0.73/0.63			2.11/2.00	1.10/1.10		1.50/1.42
MAE (µg m <sup>-3</sup> )	0.96/0.89	0.59/0.50			1.67/1.56	0.90/0.89		1.03/0.96
Slope	0.63/0.65	0.94/0.97			0.83/0.85	0.95/0.97		0.88/0.90
Delta Slope	0.37/0.35	0.06/0.03			0.17/0.15	0.05/0.03		0.12/0.10
Intercept	1.67/1.67	-0.00/-0.08			-0.02/-0.07	0.45/0.43		0.26/0.25
Intercept	1.67/1.67	0.00/0.08			0.02/0.07	0.45/0.43		0.26/0.25
AELCM009								
Rs			0.93/0.93	0.97/0.97			0.98/0.98	0.98/0.98
R <sup>2</sup>			0.86/0.84	0.96/0.96			0.98/0.98	0.97/0.96
RMSE (µg m <sup>-3</sup> )			1.34/1.18	1.01/0.67			3.61/2.76	2.30/1.78
MAE (µg m <sup>-3</sup> )			1.02/0.84	0.74/0.50			2.53/1.84	1.43/1.06
Slope			0.85/1.02	0.87/1.01			0.77/0.81	0.77/0.82
Delta Slope			0.15/0.02	0.13/0.01			0.23/0.19	0.23/0.18
Intercept			0.28/0.00	0.00/0.01			0.61/0.92	0.64/1.13
Intercept			0.28/0.00	0.00/0.01			0.61/0.92	0.64/1.13

**Table S49.** Performance metrics of the single PM<sub>2.5</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on extreme gradient boosting, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from daily mean values.

3 month xgboost (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.94/0.94	0.94/0.93	0.92/0.93				0.97/0.97	0.97/0.96
R <sup>2</sup>	0.86/0.84	0.95/0.93	0.86/0.85				0.95/0.95	0.94/0.94
RMSE (µg m <sup>-3</sup> )	2.12/2.02	1.38/1.27	1.30/1.16				3.28/3.19	2.17/2.07
MAE (µg m <sup>-3</sup> )	1.28/1.19	1.11/1.03	0.92/0.82				1.88/1.76	1.29/1.20
Slope	0.52/0.52	0.78/0.78	0.80/0.80				0.81/0.81	0.80/0.79
Delta Slope	0.48/0.48	0.22/0.22	0.20/0.20				0.19/0.19	0.20/0.21
Intercept	2.01/2.31	0.57/0.82	0.76/1.08				0.69/0.86	0.56/0.83
Intercept	2.01/2.31	0.57/0.82	0.76/1.08				0.69/0.86	0.56/0.83
AELCM009								
Rs			0.96/0.97	0.87/0.87	0.95/0.95			0.95/0.95
R <sup>2</sup>			0.95/0.96	0.85/0.86	0.93/0.94			0.90/0.90
RMSE (µg m <sup>-3</sup> )			0.79/0.78	2.34/1.99	1.34/1.31			1.62/1.44
MAE (µg m <sup>-3</sup> )			0.68/0.69	1.82/1.49	1.06/1.03			1.18/1.07
Slope			0.87/0.90	0.75/0.78	0.89/0.93			0.85/0.88
Delta Slope			0.13/0.10	0.25/0.22	0.11/0.07			0.15/0.12
Intercept			0.72/0.90	0.60/0.80	0.98/1.08			0.66/0.81
Intercept			0.72/0.90	0.60/0.80	0.98/1.08			0.66/0.81

**Table S50.** Performance metrics of the single PM<sub>2.5</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on random forest, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from daily mean values.

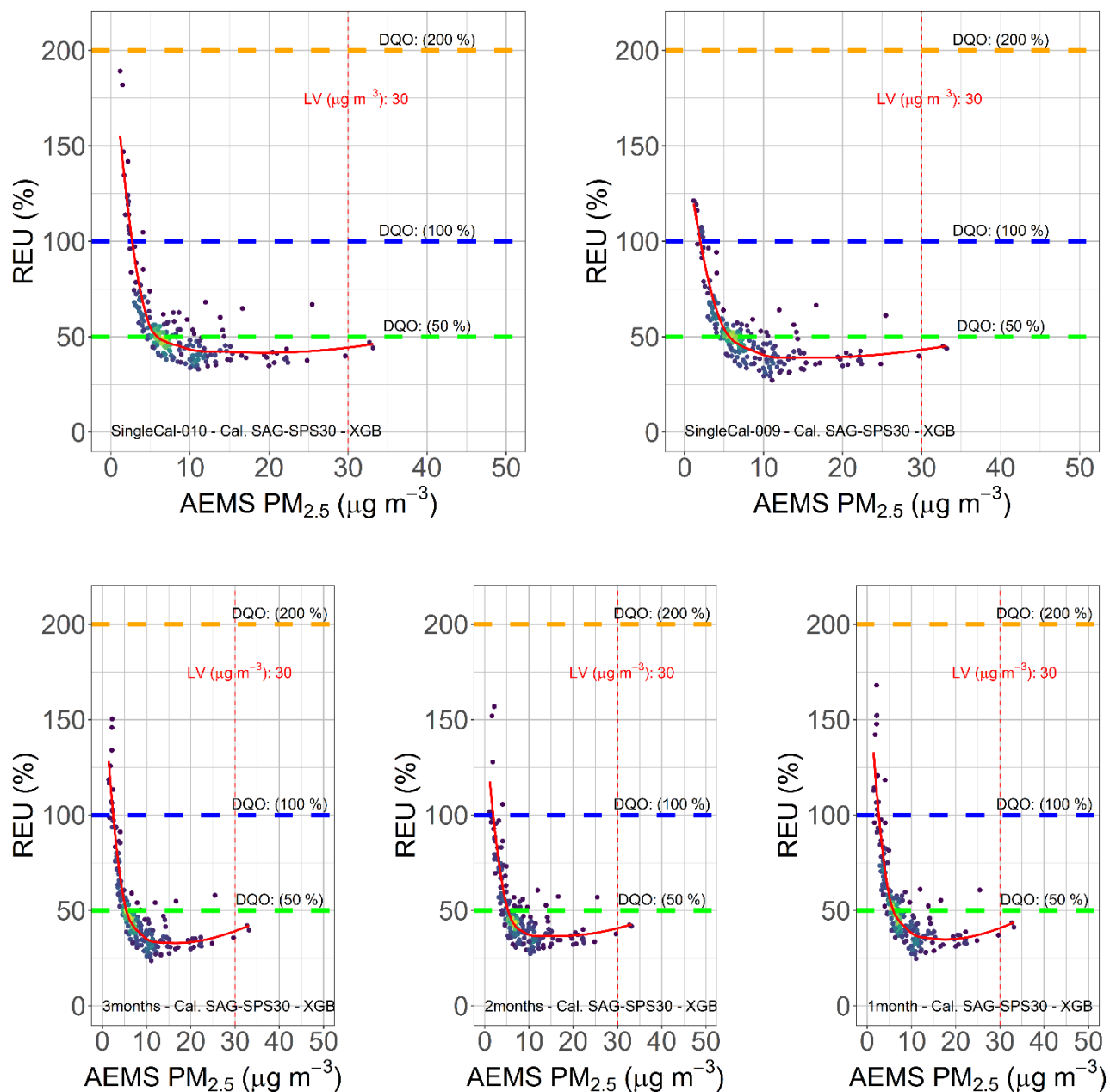
3 month random forest (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.95/0.95	0.96/0.93	0.93/0.93				0.97/0.97	0.97/0.97
R <sup>2</sup>	0.88/0.85	0.96/0.93	0.87/0.85				0.98/0.97	0.96/0.96
RMSE (µg m <sup>-3</sup> )	1.64/1.61	0.81/0.83	0.98/1.12				1.72/1.70	1.35/1.36
MAE (µg m <sup>-3</sup> )	0.95/1.01	0.65/0.67	0.68/0.86				0.88/0.91	0.79/0.86
Slope	0.62/0.61	0.89/0.90	0.90/0.94				0.95/0.94	0.92/0.92
Delta Slope	0.38/0.39	0.11/0.10	0.10/0.06				0.05/0.06	0.08/0.08
Intercept	1.93/2.34	0.42/0.66	0.60/0.80				0.12/0.30	0.24/0.63
Intercept	1.93/2.34	0.42/0.66	0.60/0.80				0.12/0.30	0.24/0.63
AELCM009								
Rs				0.98/0.97	0.90/0.90	0.95/0.95		0.96/0.96
R <sup>2</sup>				0.96/0.96	0.88/0.88	0.95/0.95		0.92/0.91
RMSE (µg m <sup>-3</sup> )				0.85/0.66	2.60/2.23	1.63/1.27		1.84/1.53
MAE (µg m <sup>-3</sup> )				0.63/0.54	2.08/1.76	1.27/1.01		1.33/1.11
Slope				0.87/0.95	0.73/0.81	0.88/1.04		0.82/0.95
Delta Slope				0.13/0.05	0.27/0.19	0.12/0.04		0.18/0.05
Intercept				0.34/0.10	0.32/0.01	0.15/-0.41		0.29/-0.17
Intercept				0.34/0.10	0.32/0.01	0.15/0.41		0.29/0.17

**Table S51.** Performance metrics of the single PM<sub>2.5</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on ridge regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from daily mean values.

3 month ridge regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.92/0.92	0.92/0.95	0.88/0.89				0.98/0.99	0.95/0.96
R <sup>2</sup>	0.77/0.80	0.95/0.96	0.81/0.83				0.99/0.99	0.95/0.95
RMSE (µg m <sup>-3</sup> )	2.09/2.01	1.20/1.19	1.27/1.16				1.01/1.06	1.45/1.41
MAE (µg m <sup>-3</sup> )	1.43/1.52	0.93/1.03	0.85/0.88				0.70/0.86	0.98/1.07
Slope	0.46/0.45	0.66/0.66	0.72/0.72				0.99/0.95	0.93/0.90
Delta Slope	0.54/0.55	0.34/0.34	0.28/0.28				0.01/0.05	0.07/0.10
Intercept	3.12/3.64	2.36/2.81	1.80/2.27				0.41/0.93	0.38/1.05
Intercept	3.12/3.64	2.36/2.81	1.80/2.27				0.41/0.93	0.38/1.05
AELCM009								
Rs				0.94/0.96	0.89/0.89	0.95/0.95		0.94/0.95
R <sup>2</sup>				0.94/0.95	0.87/0.87	0.95/0.95		0.89/0.90
RMSE (µg m <sup>-3</sup> )				1.31/0.93	3.18/2.16	1.53/1.16		2.17/1.51
MAE (µg m <sup>-3</sup> )				0.96/0.85	2.75/1.62	1.19/0.93		1.63/1.13
Slope				0.79/0.80	0.75/0.75	0.93/0.93		0.85/0.85
Delta Slope				0.21/0.20	0.25/0.25	0.07/0.07		0.15/0.15
Intercept				0.30/1.41	-0.51/0.75	-0.34/0.80		-0.30/0.88
Intercept				0.30/1.41	0.51/0.75	0.34/0.80		0.30/0.88

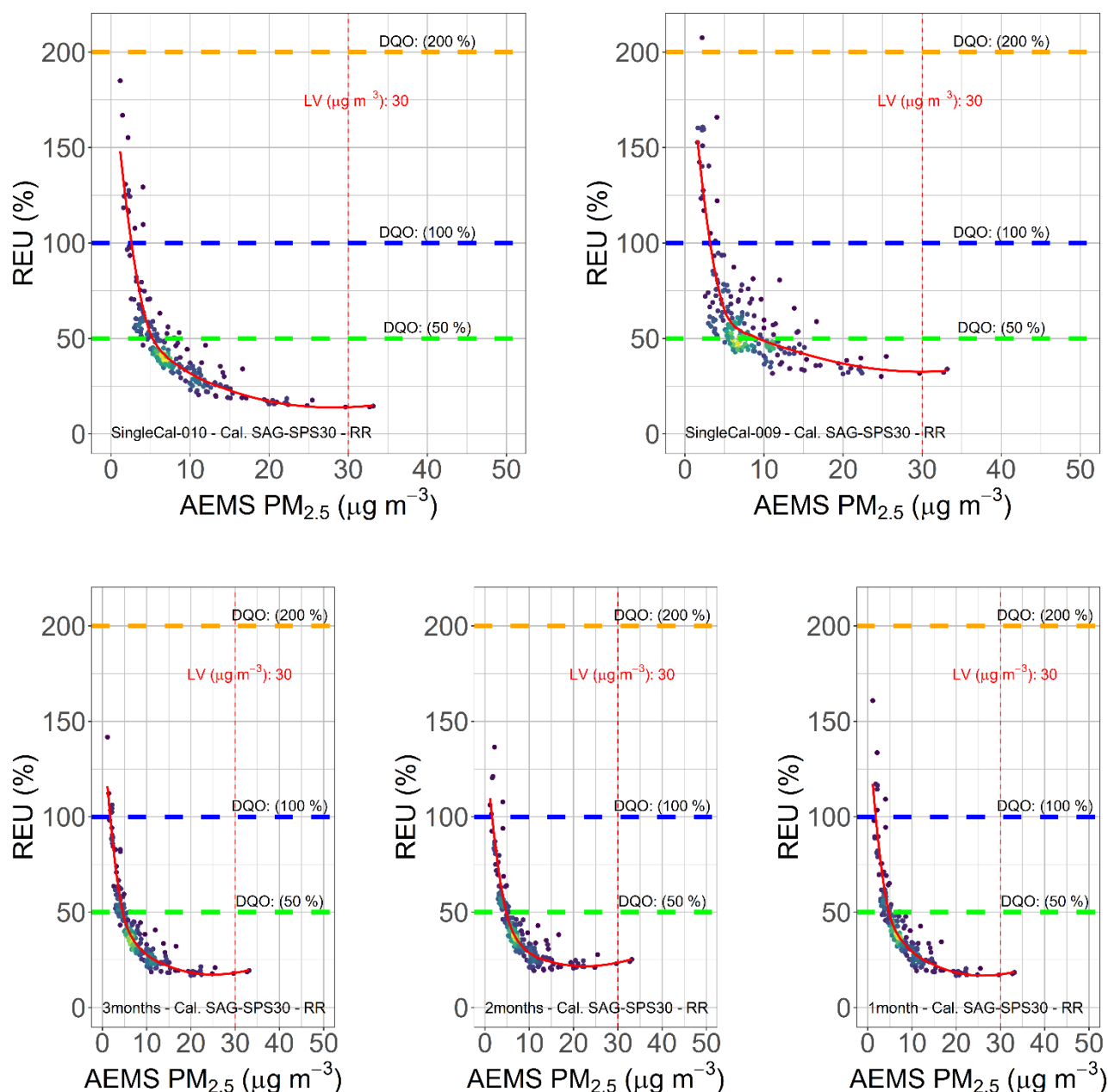
**Table S52.** Performance metrics of the single PM<sub>2.5</sub> LCS in each AELCM box (AELCM010 and AELCM009) across different test periods (TP) following calibration. The calibration models are based on multiple linear regression, using both single (ST) and extended training (ET) variants. The extended training is characterized by the three-month variant for each AELCM box. The ‘All’ column shows performance metrics calculated from data aggregated across all test periods. Performance metrics are calculated from daily mean values.

3 month multiple linear regression (AELCM010, AELCM009)								
Metric	TP 1 (ST / ET)	TP 2 (ST / ET)	TP 3 (ST / ET)	TP 4 (ST / ET)	TP 5 (ST / ET)	TP 6 (ST / ET)	TP 7 (ST / ET)	All (ST / ET)
AELCM010								
Rs	0.95/0.95	0.96/0.97	0.93/0.93				0.98/0.98	0.97/0.97
R <sup>2</sup>	0.89/0.90	0.97/0.97	0.87/0.87				0.99/0.99	0.97/0.97
RMSE (µg m <sup>-3</sup> )	1.67/1.33	0.73/0.60	1.03/1.06				2.02/2.25	1.45/1.44
MAE (µg m <sup>-3</sup> )	0.96/0.82	0.59/0.48	0.69/0.78				1.28/1.47	0.88/0.89
Slope	0.63/0.69	0.94/1.03	0.90/0.99				0.87/0.84	0.87/0.84
Delta Slope	0.37/0.31	0.06/0.03	0.10/0.01				0.13/0.16	0.13/0.16
Intercept	1.67/1.76	-0.00/-0.11	0.46/0.40				0.66/0.92	0.50/1.11
Intercept	1.67/1.76	0.00/0.11	0.46/0.40				0.66/0.92	0.50/1.11
AELCM009								
Rs				0.97/0.97	0.90/0.90	0.95/0.95		0.96/0.96
R <sup>2</sup>				0.96/0.96	0.88/0.88	0.95/0.95		0.92/0.92
RMSE (µg m <sup>-3</sup> )				1.01/0.69	2.79/2.15	1.76/1.24		1.99/1.49
MAE (µg m <sup>-3</sup> )				0.74/0.57	2.31/1.71	1.36/1.00		1.47/1.09
Slope				0.87/0.98	0.76/0.86	0.85/0.94		0.82/0.91
Delta Slope				0.13/0.02	0.24/0.14	0.15/0.06		0.18/0.09
Intercept				0.00/-0.09	-0.14/-0.30	0.28/0.24		0.04/-0.01
Intercept				0.00/0.09	0.14/0.30	0.28/0.24		0.04/0.01



**Figure S21.** Calculated REU values for XGB calibrated  $PM_{2.5}$  LCS daily data belonging to the test periods (TP1–TP7, 11 June 2022–6 January 2023) of AELCM009 and AELCM010. The calibration variants are single training (ST) (top row) and extended training (ET) (bottom row). The extended training is characterized by ET variants of 1, 2 and 3 months for each AELCM box. Horizontal dashed lines describe the data quality objectives ( $PM_{2.5}$  Class 1 DQO = 50 %, Class 2 DQO = 100 % and Class 3 DQO = 200 %). The vertical dashed line describes the limit value for  $PM_{2.5}$  (LV =  $30 \mu g m^{-3}$ ). The fitted smooth curve (red) is based on locally estimated scatterplot smoothing (LOESS). Data density is shown through colour, where darker colours express lower data density and brighter colours express higher data density.





**Figure S22.** Calculated REU values for RR calibrated  $PM_{2.5}$  LCS daily data belonging to the test periods (TP1–TP7, 11 June 2022–6 January 2023) of AELCM009 and AELCM010. The calibration variants are single training (ST) (top row) and extended training (ET) (bottom row). The extended training is characterized by ET variants of 1, 2 and 3 months for each AELCM box. Horizontal dashed lines describe the data quality objectives ( $PM_{2.5}$  Class 1 DQO = 50 %, Class 2 DQO = 100 % and Class 3 DQO = 200 %). The vertical dashed line describes the limit value for  $PM_{2.5}$  (LV =  $30 \mu g m^{-3}$ ). The fitted smooth curve (red) is based on locally estimated scatterplot smoothing (LOESS). Data density is shown through colour, where darker colours express lower data density and brighter colours express higher data density.