

## Diagnostics of model-data mismatches

We introduce here diagnostics of model-data mismatch across the site network by analysing the Root Mean Square Error (RMSE) of simulated concentrations calculated using prior and posterior fluxes with the regional transport models STILT and FLEXPART - i.e., CS3 and CF3 inversion set-ups, relative to the measured concentrations. RMSE is an indicative metric to assess the model-data mismatch uncertainty assigned to the inversion for constructing the covariance matrices of measurements. Model-data mismatches typically reflect inaccuracies in the transport, prior fluxes, and measurements. However, the flux uncertainty is explicitly prescribed in the inversion according to the prior flux model allowing for more flexibility to correct the prior fluxes. Figure 1S illustrates the misfits to observations at hourly, weekly, and yearly time steps computed across the observing sites (sorted according to the mean of hourly RMSE, averaged over the STILT and FLEXPART simulations). The results exhibit a reduction of the error in the a-posteriori simulations compared to their respective prior simulations indicating the convergence of inversions towards observations.

Generally, hourly simulations demonstrate larger RMSE than weekly and yearly simulations do. This can be deduced from the mean values of RMSE calculated with STILT and FLEXPART (Table 1S). STILT and FLEXPART agree quite well with the biases calculated using posterior fluxes, demonstrating smaller biases in comparison with those that resulting from using prior fluxes. However, the concentrations of CO<sub>2</sub> simulated with the two models using the optimised fluxes are expected to not vary between the transport models as the transport error is interpreted as flux adjustments in the inversions.

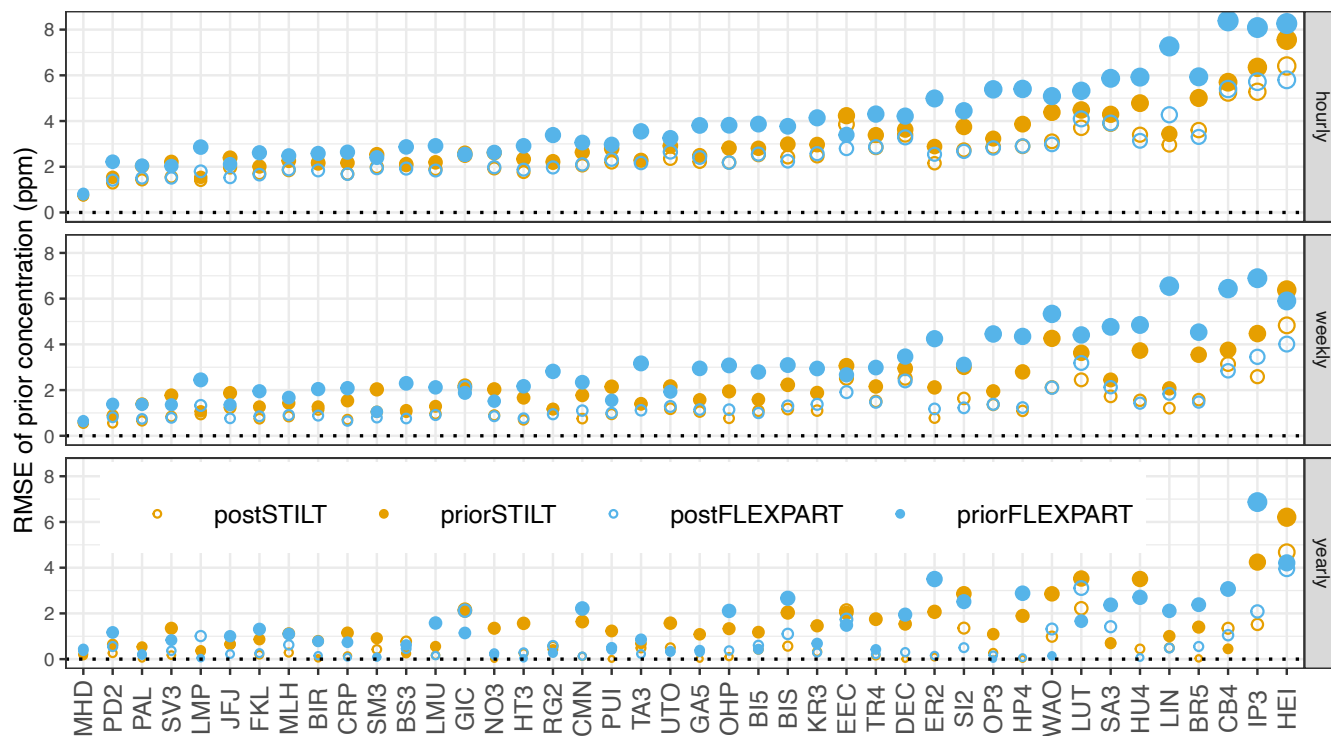
**Table 1S: Summary of RMSE calculated with STILT and FLEXPART using prior and posterior fluxes at hourly, weekly, and yearly time steps. Units are in ppm.**

Model	Flux type used	Hourly		Weekly		Yearly	
		Range	Mean	Range	Mean	Range	Mean
STILT	Prior	0.75-7.56	3.13	0.58-6.38	2.23	0.04-6.21	1.51
FLEXPART		0.83-8.39	3.97	0.66-6.89	3.07	0.00-6.87	1.43
STILT	Posterior	0.72-6.41	2.60	0.54-4.83	1.39	0.00-4.68	0.63
FLEXPART		0.78-5.80	2.60	0.61-4.01	1.41	0.06-3.95	0.68

Despite the variable performances of transport models over stations, STILT exhibits less hourly and weekly mean biases computed using prior fluxes than does FLEXPART, whereas yearly mean biases appear to be more consistent in both models, albeit slightly smaller with FLEXPART. At the same time, weekly mismatches are in good agreement with the weekly uncertainty assumed to the observational sites (1.5 (ppm) for towers, ocean, and mountains, 2.5 (ppm) for surface stations, and 4 (ppm) for polluted sites as listed in Table 1). This ensures that the values of model-data mismatch errors used

to construct the measurement covariance matrix were realistic. Note that some stations such as HEI and IP3 are prone to large influences from the anthropogenic emissions that lead to increasing RMSE regardless of the transport model used.

30



**Figure S1: RMSE of model-data mismatches calculated at hourly, weekly and yearly timesteps using prior and posterior fluxes with STILT and FLEXPART models (sorted by the mean of hourly values of STILT and FLEXPART).**