

Electrochemical sensors onboard a Zeppelin NT: In-flight evaluation of low-cost trace gas measurements

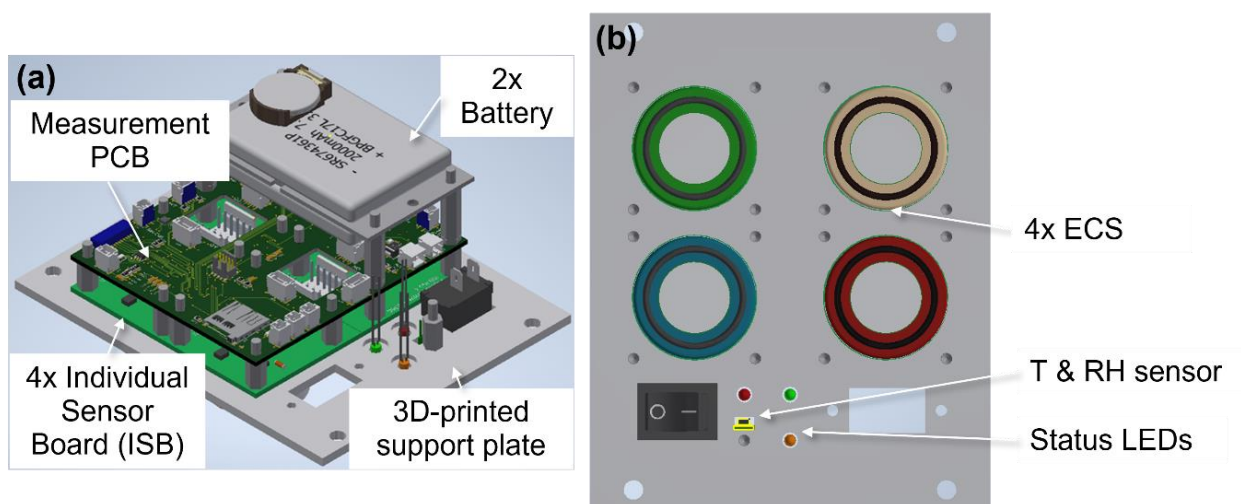
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Supplement



10 **Figure S1: (a) Electrical and mechanical components of the sensor setup we currently use. It is slightly modified, mainly for weight and space reasons, compared to what was used for this study, but the functionality is the same. (b) Bottom view of the setup. PCB: printed circuit board; ECS: electrochemical sensor; T & RH: temperature and relative humidity.**

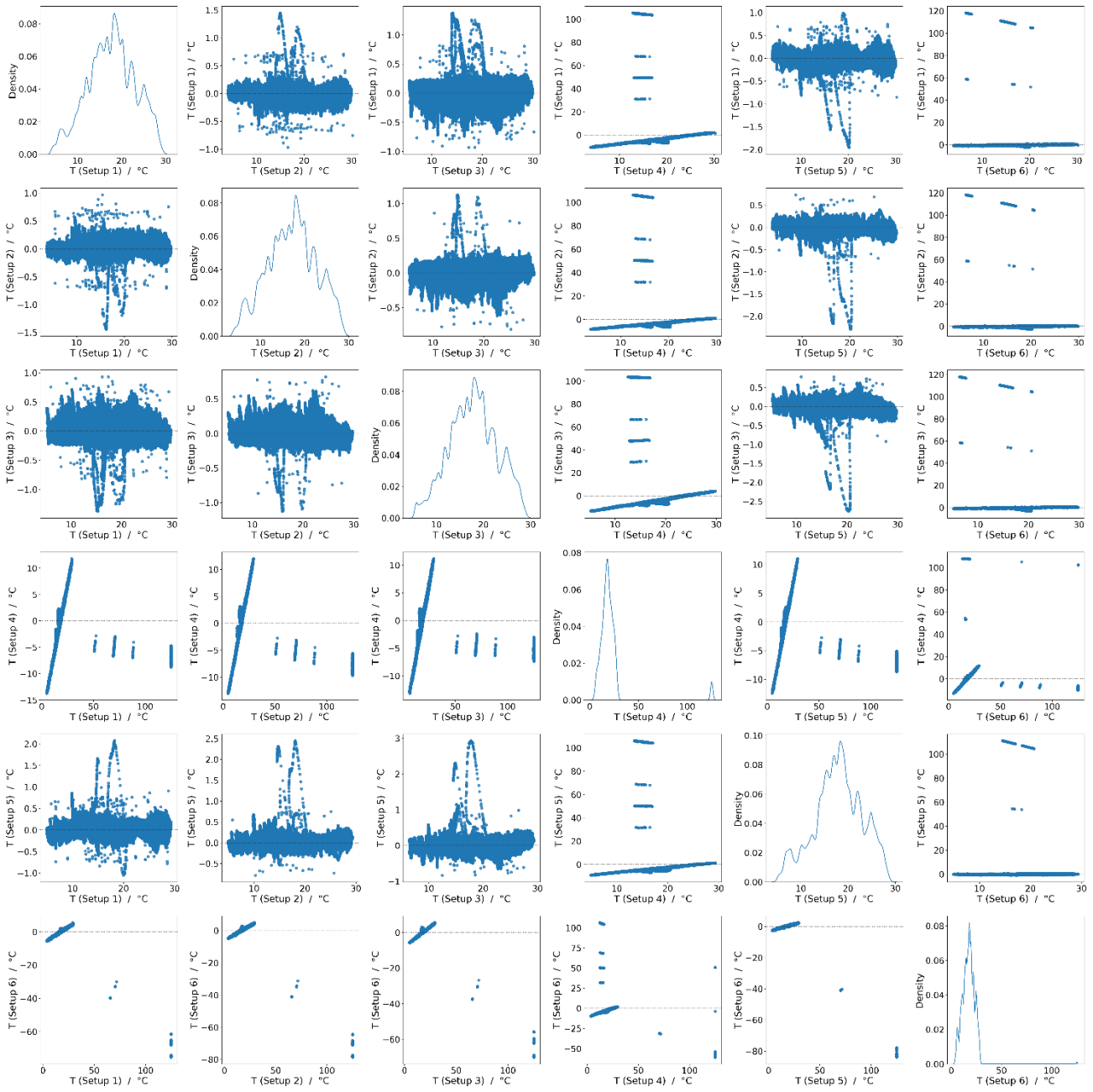
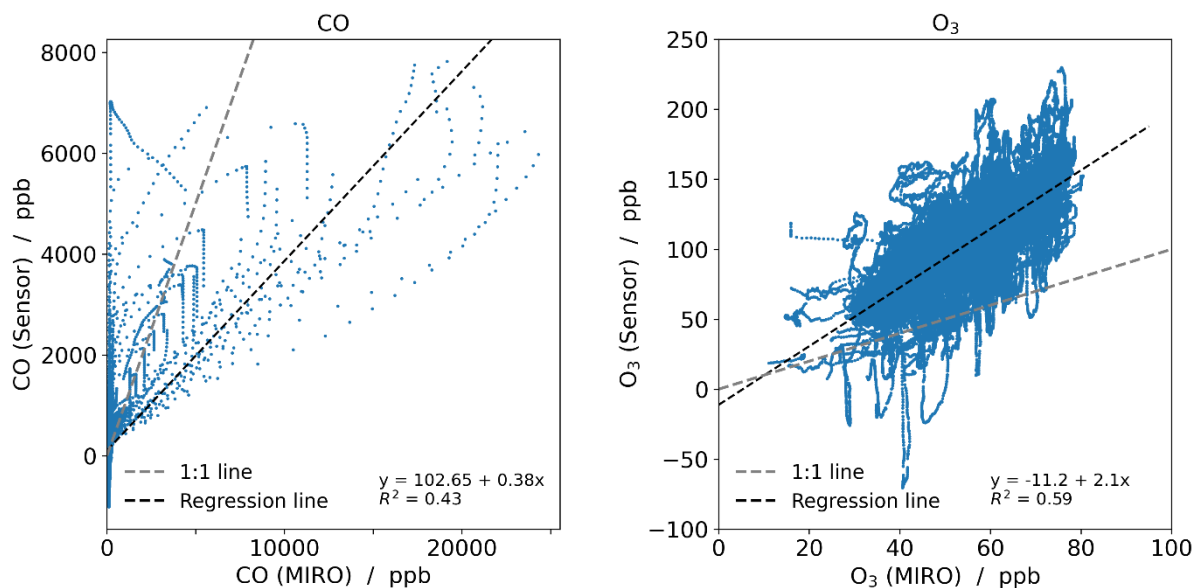


Figure S2: Residual matrix of all temperature sensors. In the diagonal, the density distributions of the measured values for each setup are shown.



20 **Figure S3: Corrected sensor data with the suggested algorithms from the manufacturer compared to MIRO data for CO and O₃.** To use the algorithm, the voltage output for O₃, WE_{O_3} , is needed. It is obtained via subtraction of the NO₂ signal from the total Ox sensor output, WE_{Ox} . The NO₂ concentration is determined with the NO₂ sensor on the setup. Equation to obtain the O₃ voltage output: $WE_{O_3} = WE_{Ox} - S_{Ox} \times x_{NO_2}$ with the sensitivity of the Ox sensor, S_{Ox} , and the NO₂ amount fraction, x_{NO_2} .

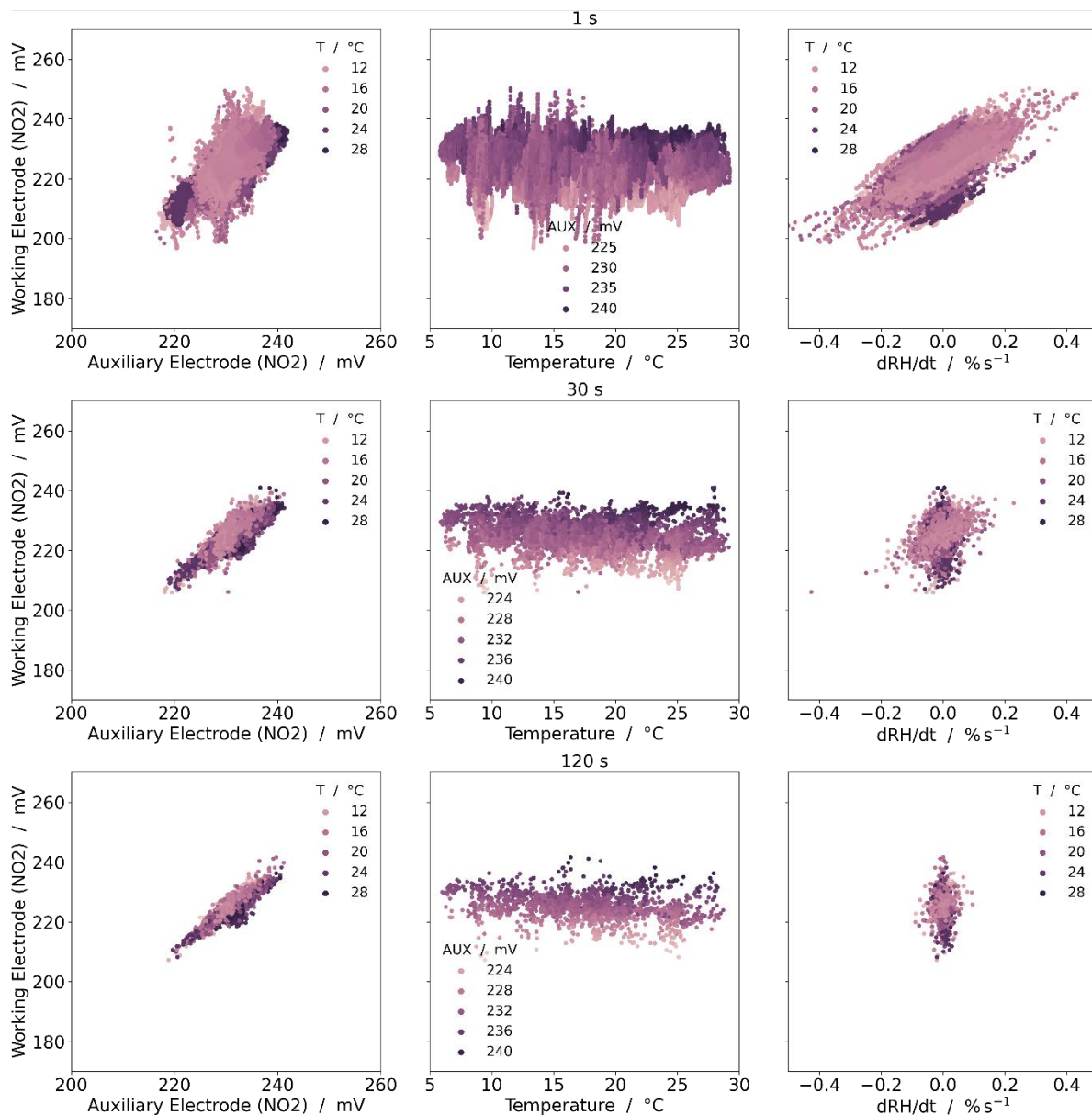


Figure S4: Scatterplots of NO₂ sensor: WE vs. AUX, T and dRH/dt with different time resolutions. The colors are used to show collinearity between AUX and T, and that the shift of WE voltages in the dRH/dt plot is a temperature interference.

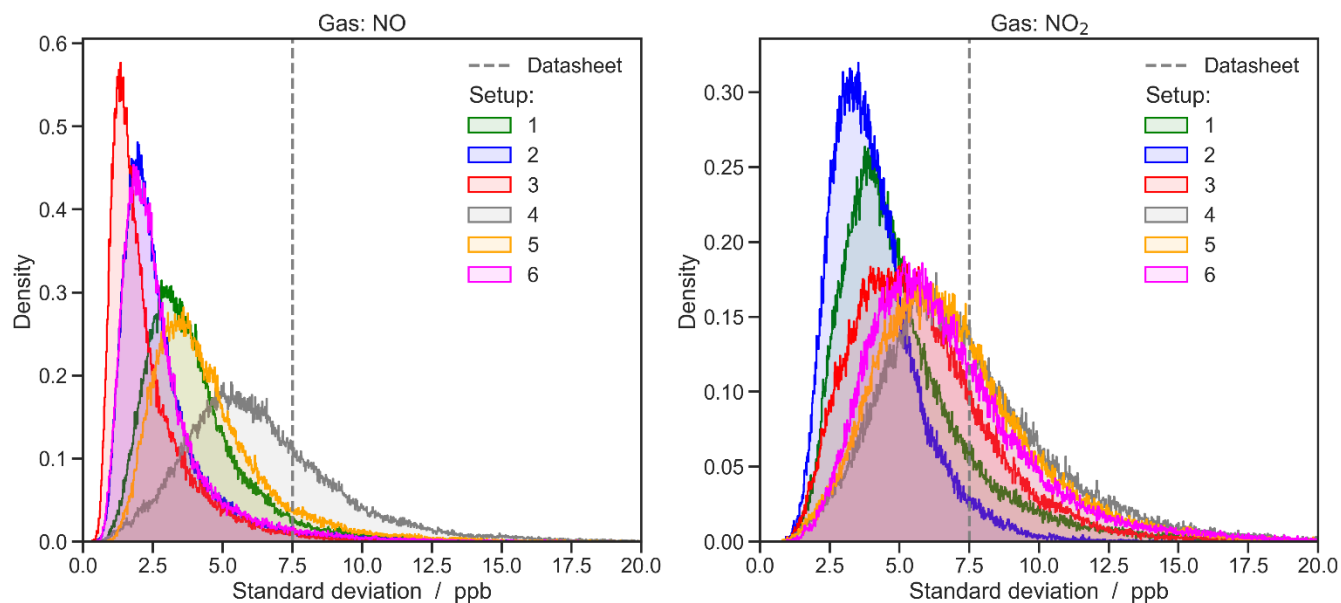


Figure S5: Density distributions of the rolling standard deviations in 31 s windows. This represents the noise of the sensors. The colors correspond to the different sensor setups and the dashed line highlights the data sheet specification of 7.5 ppb (1 σ).

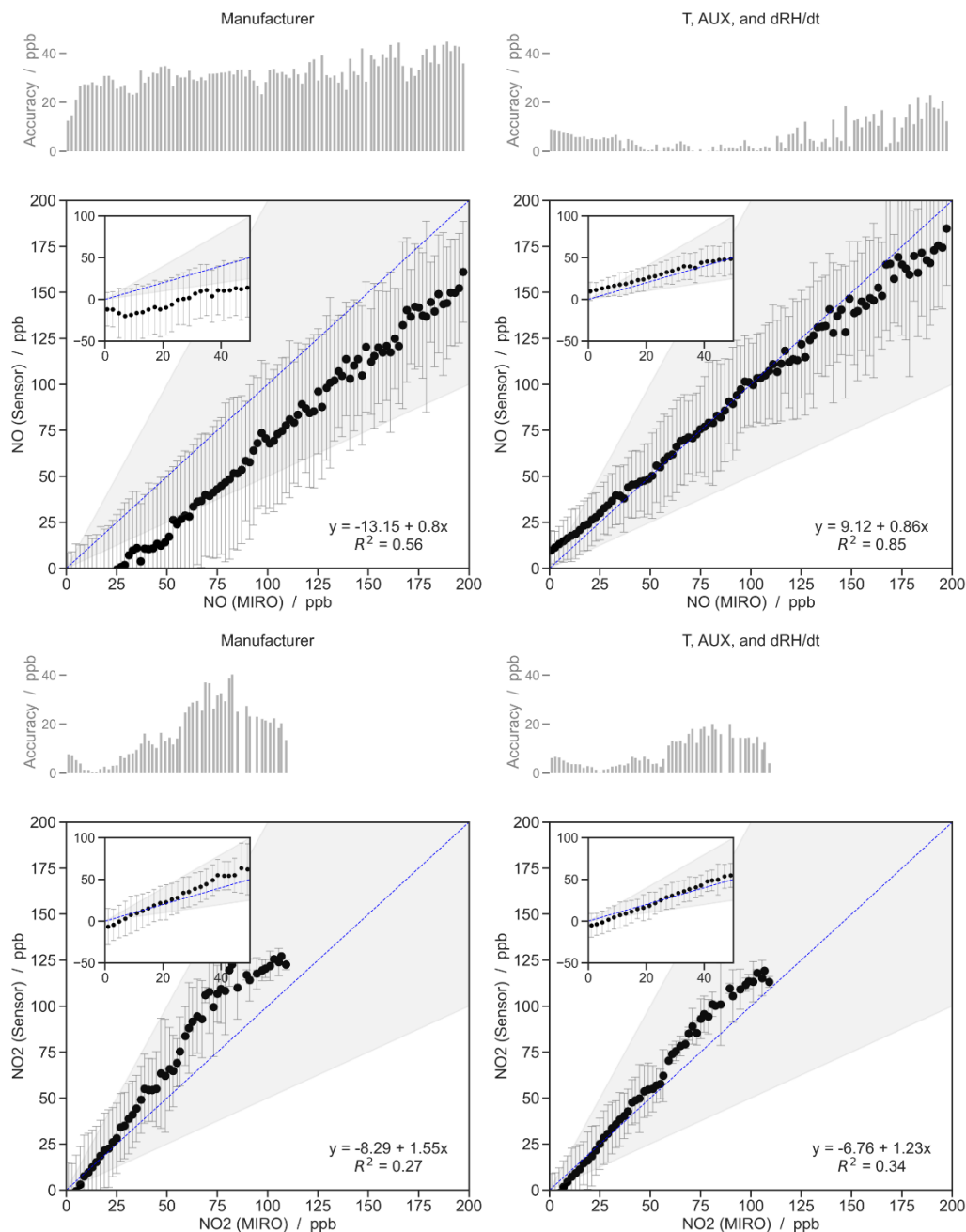


Figure S6: Scatterplots of the corrected sensor data of setup #2 (top: NO, bottom: NO₂) vs. MIRO MGA (reference) data classified in 2 ppb bins and two times the standard deviations ($\pm 2\sigma$). On top of the scatterplots the accuracies for each bin are shown. Manufacturers correction on the left, our correction method on the right. The dashed blue line marks the 1:1 line and the range of 2:1 and 1:2 is shaded in grey. The inlet plots show the data in a higher resolution from 0 to 50 ppb of the reference instrument. In addition, the linear regression results are shown on the bottom right.

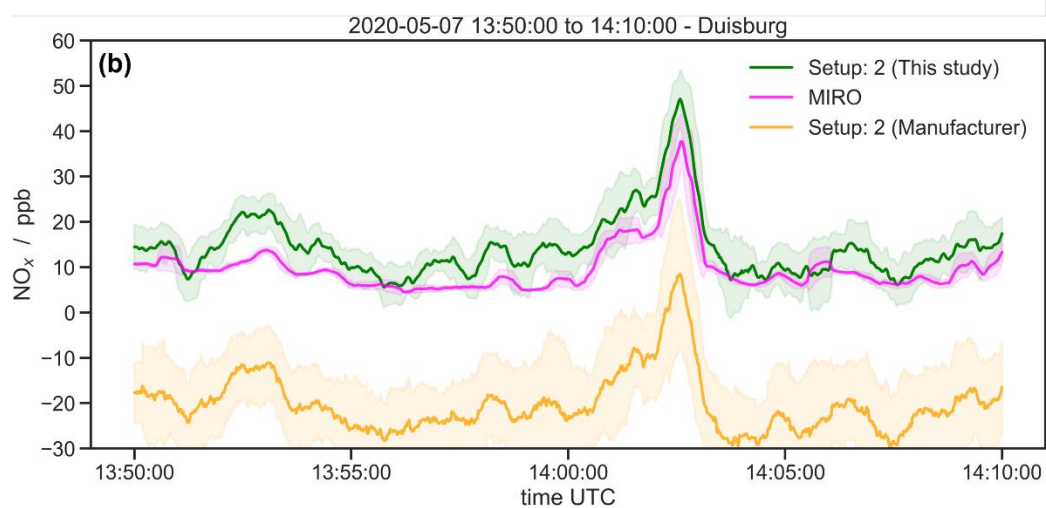
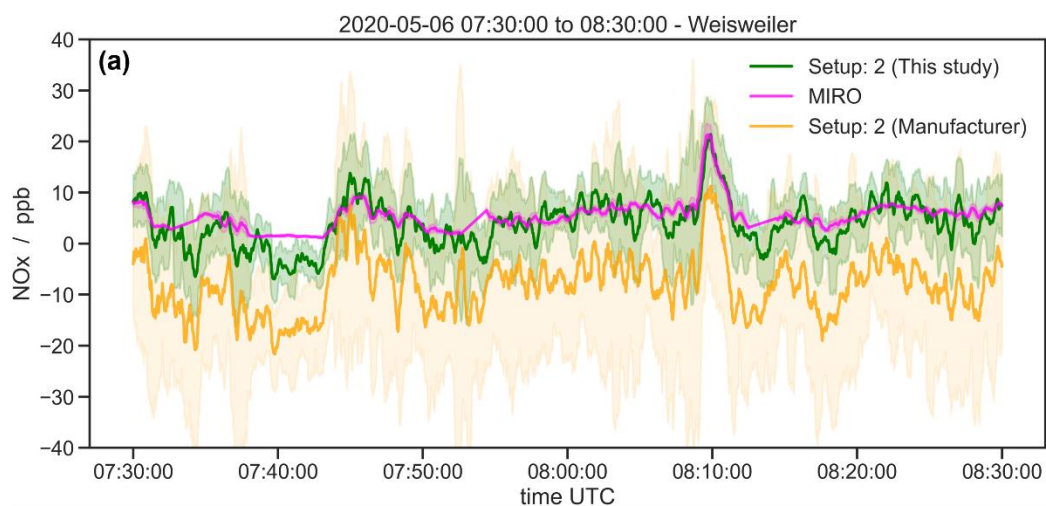


Figure S7: NO_x time series of the flight around Weisweiler (a) and Duisburg (b). Corrected with the algorithms of the manufacturer (orange) and with those developed in this study (green).

Table S1: Specifications of all sensors provided by the manufacturer. Subscripts of the working electrode (WE) and auxiliary electrode (AUX) represent zero values (0) and electronic offsets (e).

Analyte	Setup	Sensitivity / mV ppb ⁻¹	WE ₀ / mV	AUX ₀ / mV	WE _e / mV	AUX _e / mV
CO	1	0.440	411	314	361	322
	2	0.500	429	353	333	341
	3	0.449	441	359	354	344
	4	0.475	430	348	341	346
	5	0.446	422	344	353	348
	6	0.468	400	351	332	355
NO	1	0.580	342	369	276	297
	2	0.573	345	360	279	288
	3	0.540	343	341	286	278
	4	0.580	336	358	275	285
	5	0.526	348	325	282	285
	6	0.560	345	360	285	291
NO ₂	1	0.254	202	231	213	231
	2	0.269	229	226	228	233
	3	0.247	220	227	221	223
	4	0.268	226	232	231	233
	5	0.266	237	232	239	233
	6	0.239	233	222	239	234
Ox	1	0.252	226	230	232	235
	2	0.253	228	232	231	234
	3	0.281	223	220	226	223
	4	0.271	213	228	221	223
	5	0.274	218	229	223	232
	6	0.231	221	230	222	235

Table S2: Regression parameters to correct for T , AUX and dRH/dt .

Analyte	Setup #	dRH/dt correction		T, AUX correction		
		β_0 / mV % ⁻¹ s	α / mV (intercept)	β_1 / mV (T)	β_2 / °C ⁻¹ (T)	β_3 / - (AUX)
NO	1	-83.53	108.99	2.03	0.09	0.55
	2	-80.25	135.61	1.88	0.09	0.48
	3	-58.44	141.09	1.76	0.08	0.50
	4	-81.15	130.32	0.47	0.13	0.50
	5	-82.50	≈ 0.00	0.31	0.14	0.98
	6	-77.99	139.59	1.39	0.09	0.49
NO ₂		β_0 / mV % ⁻¹ s	α / mV (intercept)	β_1 / °C ⁻¹ (T)	β_2 / - (AUX)	-
	1	78.17	-97.06	-0.28	1.36	-
	2	54.48	-64.66	-0.14	1.27	-
	3	47.90	-94.21	-0.13	1.43	-
	4	55.63	-24.17	-0.19	1.10	-

5	50.10	-4.80	-0.19	1.06	-
6	74.76	-21.49	-0.17	1.12	-

Correction procedure

Eq. (3) and (4) describe the correction procedure developed in this work that accounts for the *AUX*, temperature and dRH/dt dependencies of the NO and NO₂ sensors. To numerically correct the *WE* measurements each of these dependencies is separately accounted for by following the above steps.

First, the 1 s time resolution *WE* raw data are plotted vs. dRH/dt for periods of low analyte concentrations and within changes of ± 0.25 %/s to ± 0.6 %/s, as shown in Fig. S8. A linear correlation is observed and is used to account for the dRH/dt dependence using the following equation:

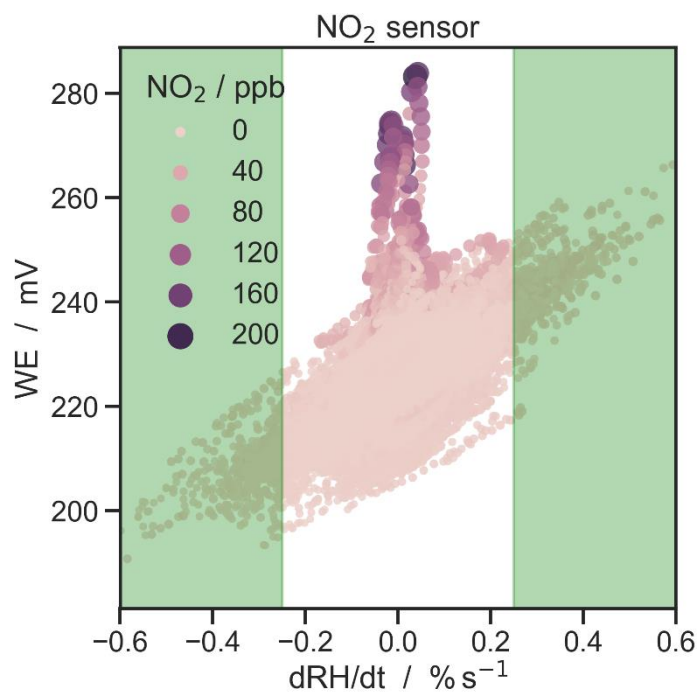
$$WE_{dRH/dt}(t) = WE_{raw}(t) - \beta_0 \times \frac{dRH}{dt}(t) \quad (S1)$$

In the next step, a modified version of the method developed by Mead et al. (2013) is used to correct the $WE_{dRH/dt}$ for the interference of temperature and possible other influencing factors covered by the auxiliary electrode measurements. Mead et al. (2013) show that a high time resolution (1 s) linear regression analysis of *WE* vs. temperature is challenging due to the longer response times of the ECS which is also evident in this work. Therefore, we use a time window ranging from 60 s up to 600 s gradually shifted over the entire data set. In each window, the minimum of $WE_{dRH/dt}$ and the arithmetic mean values of *T* and *AUX* are determined, respectively. Then the minima $WE_{dRH/dt,min}$ are plotted over the mean *T* and *AUX* and a corresponding function is fitted. The time window that results the highest coefficient of determination is the chosen to describe the fit functions as follows:

$$WE_{NO,T,AUX,dRH/dt}(t) = WE_{NO,dRH/dt}(t) - (\alpha + \beta_1 \times \exp(\beta_2 \times T(t)) + \beta_3 \times AUX(t)), \quad (S2)$$

$$WE_{NO_2,T,AUX,dRH/dt}(t) = WE_{NO_2,dRH/dt}(t) - (\alpha + \beta_1 \times T(t) + \beta_2 \times AUX(t)), \quad (S3)$$

The $WE_{dRH/dt}$ minima are used here to describe periods of low concentrations below the limit of detection of the sensors. This way the observed correlations will reflect the interferences of the sensors rather than their response to increases of the analyte concentrations. This is a valid approximation for NO and NO₂, since the amount fractions during flights are usually close to 0 ppb and emission peaks tend to be short. However, this method cannot be applied to other gases that have high background concentrations in the troposphere, e.g., ozone and carbon monoxide, given that this background would be subtracted (Popoola et al., 2016).



80 **Figure S8: WE (NO₂) vs. dRH/dt, green shaded areas used for regression to mitigate analyte concentration influences on the sensor signal which are mainly found in periods with low values for dRH/dt.**