Supplement: A small-footprint Cavity Ring-Down Spectroscopy instrument for direct measurements of NO_3 and N_2O_5

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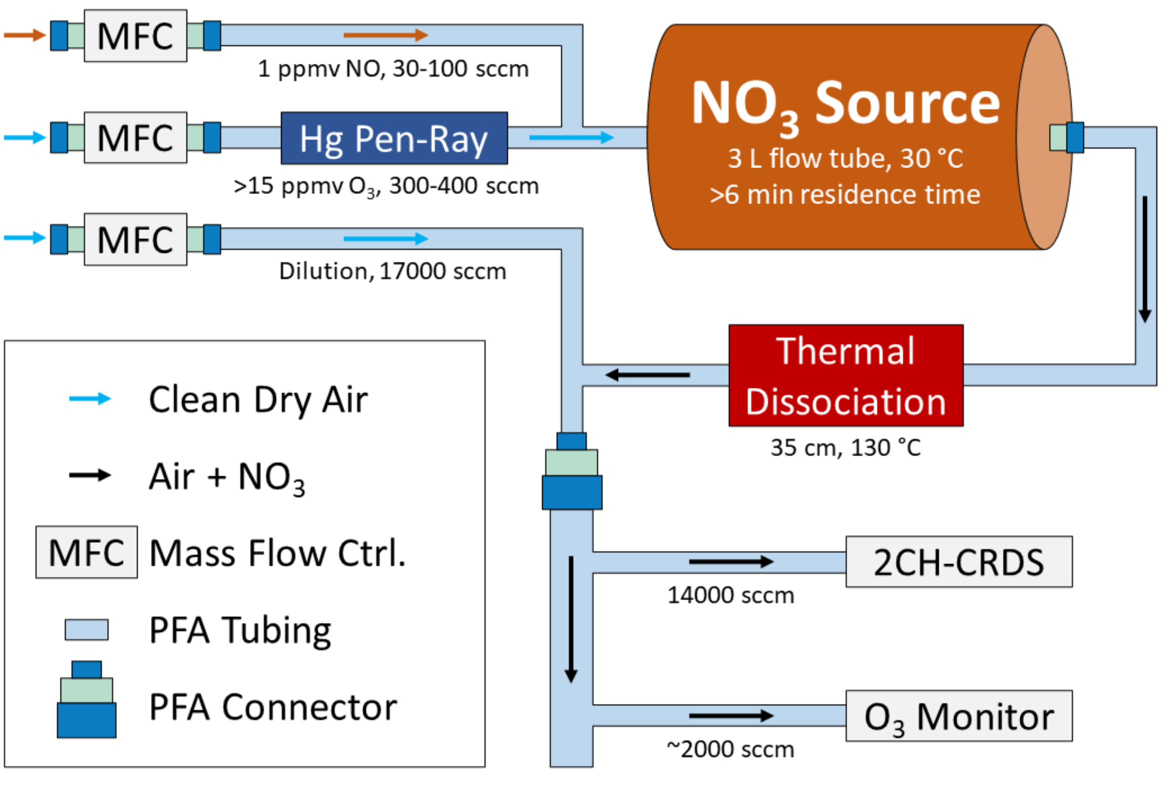

Figure S1: Schematics of the flow tube NO3 source. The inflow of NO, O3 and clean air for dilution is controlled with MFCs (Alicat). A mercury Pen-Ray lamp is used to produce ozone. Due to the high O3 concentration and large rate coefficient, we estimate the mixing ratio of NO to be significantly less than 1 pptv less than 5 seconds after entering the NO3 source. The source and thermal dissociation element are temperature controlled by PT1000 sensors at center-length. An O3 monitor is used to estimate corrections (titration NO, see Section 3.3).

Table S1: Overview of estimated maximum transmission factors for new PTFE filters of different brands.

Label	**Manufacturer ID**	$\boldsymbol{T_{max}}$ **in %**
Pall #1	AW15675	97.5 ± 0.8
Merck #1	W20309094	97.1 ± 0.7
Merck #2	W20309097	98.3 ± 0.6
Merck #3	W20309095	96.0 ± 0.6
Merck #4	W20309096	98.8 ± 0.5
Pall #2	AW15680	98.5 ± 0.7
Pall #3	AW15679	101.0 ± 0.5
Cytiva #1	C1898521	95.4 ± 0.6
Cytiva #2	C1898520	98.7 ± 0.7
Cytiva #3	C1898519	98.3 ± 0.5
Cytiva #4	C1898518	100.5 ± 0.9

Notes: The uncertainties of T_{max} were calculated by the square root of the covariances of the fit and do not reflect small NO_3 source fluctuations.

S1 Additional Information to PTFE Filter Transmission Measurements

In Section 3.5, we discussed our method to derive the maximum NO_3 transmission T_{max} and showed a comparison of PTFE filters from Pall and Merck. Similarly, the comparison between new filters from Pall and Cytiva is presented in Figure S1 and shows that all filter brands are very similar regarding their NO_3 transmission. Therefore, all tested filters show similar behaviour, have high maximum NO_3 transmission (see Table 1) and can be used for $[NO_3]$ measurements. The procedure to clean used filters with high concentrations of O_3 is described in this section.

We first note that not all used filters can be cleaned and reused. Mechanical damage, such as punctures and tears in the PTFE membrane, renders a filter unusable, and it is discarded immediately after use. Dust and other visibly deposited particles can be removed by washing with deionized water. Subsequently, filters are placed in a 3D-printed (PLA) cubic housing for drying with zero air, whereby the filters are loosely lined up vertically while the air flows diagonally through the cube, but does not directly pass through the filters. In the same setup, we apply ozone: We use the maximum output of an ozone generator (COM-CD-HF4, Anseros) supplied with about 100 sccm of oxygen 5.0, which results in more than 5 % of O_3. The filter surfaces are exposed to O_3 for about 10 minutes before switching off the generator and flushing the cube for another 5 minutes.
We tested the transmission of previously used Pall filters directly after this procedure and present the results from different cleaning methods in Figure S2. The first filter (#1) was measured for about 20 seconds before cleaning and initially showed a transmission of < 0.2. After our procedure, the initial transmission exceeded 0.9. The results were confirmed by filter #2, which was cleaned in the same way. Similar results were achieved for filter #3, which was separately flushed by about 3000 sccm (zero air with 15 ppmv of O_3) for 100 minutes before measuring the transmission. For comparison, filter #4 was not cleaned beforehand and did not reach its maximum within our measurement time. These experiments show that, with sufficient O_3 exposure, PTFE filters can regain their original (high) NO_3 transmission, but the required combination of exposure time and concentration will vary on the degree of contamination. We have not tried to clean filters with major discolouration.

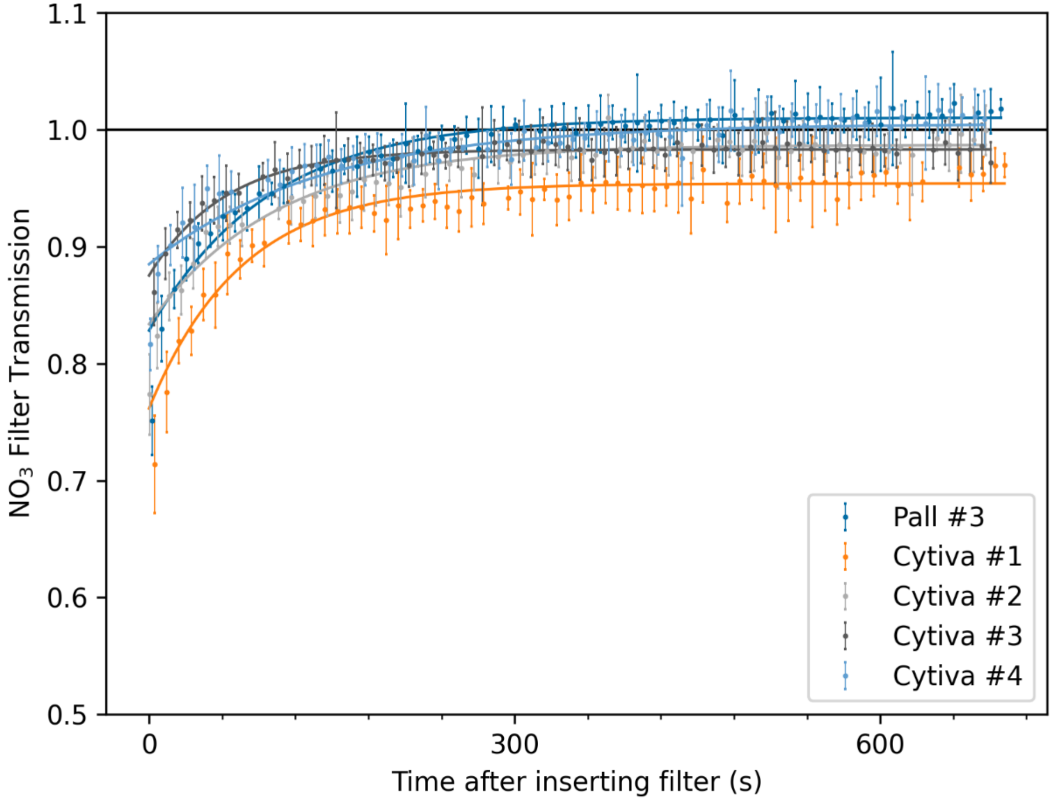

Figure S2: PTFE filter transmission of NO_3 using new filters from Pall and Cytiva. The error bars only represent the statistical uncertainty (2σ) based on averaging 10-second data. Equation (3) was used to derive the maximum transmission. The measurement "Pall #4" was excluded due to major source instabilities. The overview of all $\boldsymbol{T_{max}}$ can be seen in Table 1, and a comparison between filters from Pall and Merck is shown in Figure 5 of the main manuscript.

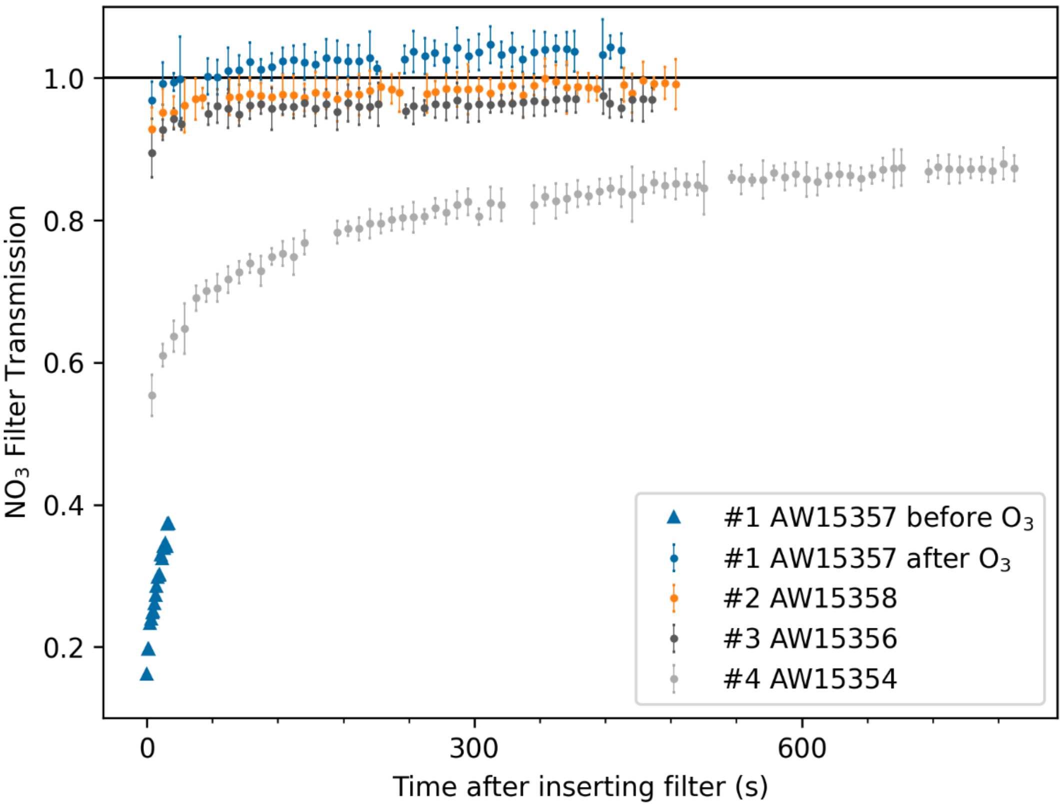

Figure S3: NO_3-Transmission measurements for filters that had been used during a field campaign in Hyytiälä, Finland. AW15357 (blue) was measured before (triangles) and after (circles with error bars) the exposure to high amounts of ozone, while AW15358 (orange) was measured only afterwards. AW15356 (dark grey) was inserted into a sealed filter holder and flushed by about 3000 sccm (zero air with 15 ppmv of O_3) for 100 minutes while AW15354 (light grey) was not exposed to ozone prior to measuring its transmission.

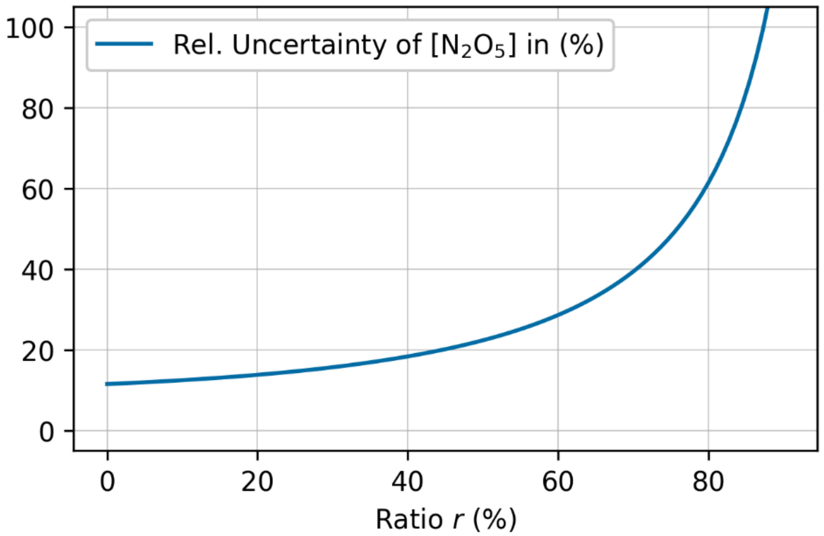

Figure S4: The dependence of the relative uncertainty of our true, ambient [N_2O_5] measurements on ***r*** which describes the ratio of NO_3 over the sum of NO_3 and N_2O_5 in the heated cavity and can be approximated by the equilibrium constant with an additional ambient NO_2 measurement (see main text). The values are calculated using the relative uncertainties in Table 2 and the equations presented in Section 3.6.

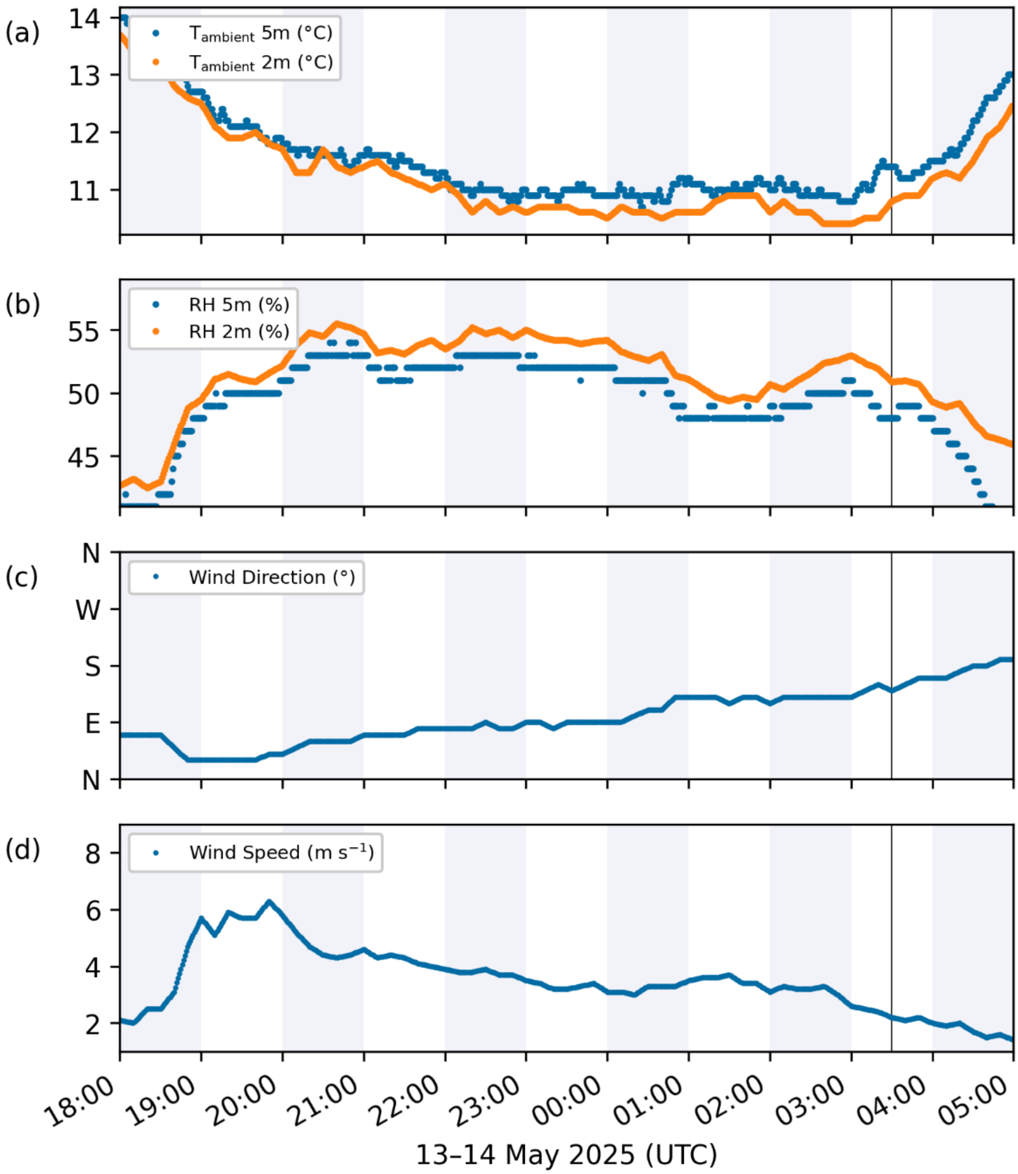

Figure S5: Meteorological data from a field campaign in May 2025 at the Kleiner Feldberg, Germany. Measurements of (a) ambient temperature and (b) relative humidity close to our sampling inlet (5m) and from a DWD station (2m) about 15 m to the east. (c) Wind direction and (d) wind speed provided by DWD.

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