Supplement to: The ICAD (Iterative Cavity Enhanced DOAS) Method

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S1 Comparison of Mobile Measurements to Air Quality Stations

The temporal variation of the NO_2 levels during the measurement cruise (from section 5.2) is further compared to the hourly NO_2 levels measured by the air quality stations operated by the State Office for the Environment, Measurements and Nature Conservation of the Federal State of Baden-Württemberg (LUBW) [1] (fig. S2). The hourly averages of the ICAD NO_2 measure-
5 ments are similar to the LUBW stations. This indicates that the large scale average of the NO_2 mixing ratio is well represented by the air quality network. However, on the local scale the ICAD time series shows a strong variability with peak values being almost four times higher than the hourly average. The peak levels of NO_2 regularly exceed 105 ppb, the hourly EU limit value. Such peak values are especially found in street canyons where ventilation is limited and at intersections of big roads where cars frequently accelerate from a standstill position. This hints, that there are areas where we have NO_2 levels are strongly
10 underestimated by the average values from the monitoring stations, and therefore require a reassessment of the air quality. However, to make a certain statement on the air quality measurement drove from this pilot study would need to be repeated over a longer time period and also would need to revisit the same points at different times of day to reduce systematic errors induced by traffic pattern and meteorology.

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[1]Data taken from the data and map service (UDO) of the LUBW. https://udo.lubw.baden-wuerttemberg.de Accessed 04-15-2018

S2 Figures
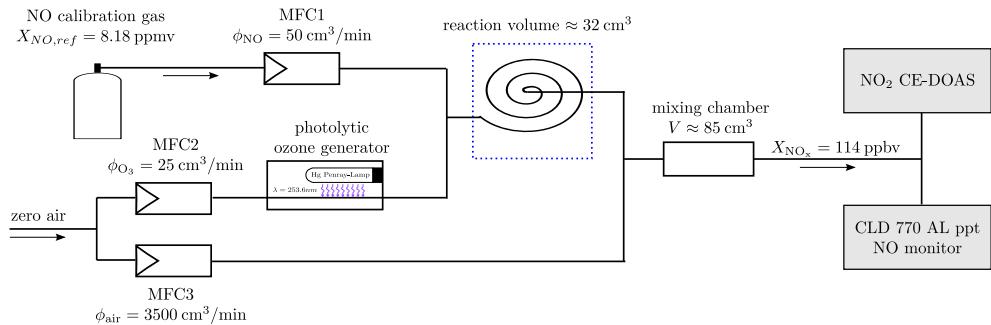
Figure S1. Measurement setup for the laboratory measurements. To produce NO_2, NO from a calibration gas cylinder is titrated with O_3, generated photolytically from zero air from a gas bottle. Two calibrated mass flow controllers (MFC1, MFC2) provide a constant gas flow. They are adjusted to ensure that the gas phase titration is completed to at least 99% after one third of the residence time in the reaction volume. After the titration the gas mixture is further diluted with zero air to achieve a NO_x mixing ratio of 114 ppbv. During the measurement all gas flows are kept constant. To produce different NO_2 mixing ratios the O_3 concentration is adjusted through the electrical current of the UV-light source. Simultaneously to the NO_2 ICAD measurements, the NO mixing ratio in the sample gas is measured by a calibrated NO Chemiluminescence Detector (Eco Systems, CLD 770 Al ppt). This allows to calculate the exact NO_2 mixing ratio from the comparison with a measurement at deactivated ozone generator as the total NO_x mixing ratio is constant ($X_{NO_2} = X_{NO_x} - X_{NO}$).
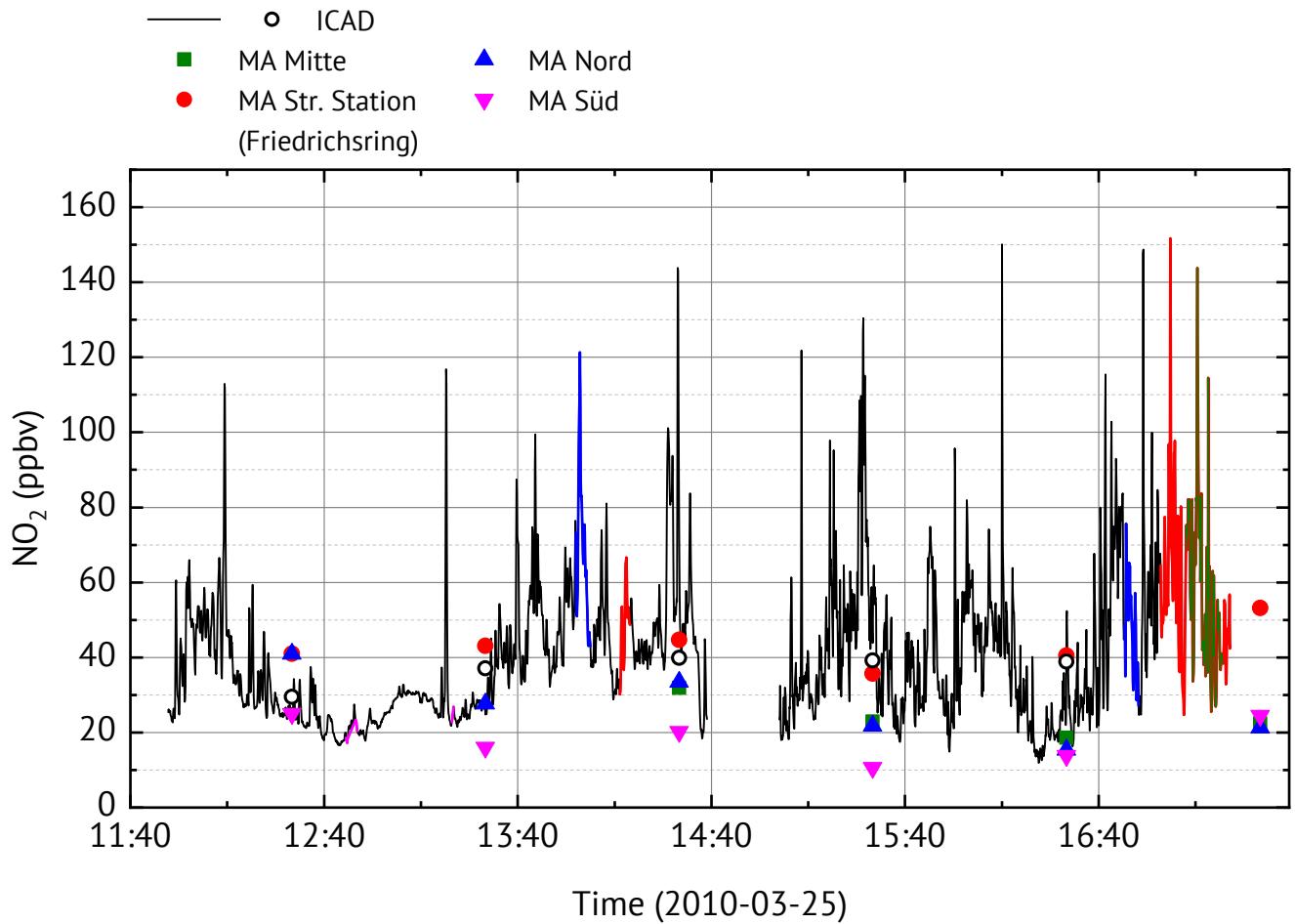
Figure S2. NO_2 time series for the automobile measurements (instrument configuration 1). The line graph shows the ICAD measurements at full time resolution. Additionally the hourly averages from the ICAD and four air quality stations are shown for comparison. The line graph has the colour of an air quality station at time intervals where the car is closer than 1.5 km to the station.