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Experience with novel technologies for direct measurement of atmospheric NO_2

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Nitrogen dioxide (NO_2) is an air pollutant that has a large impact on human health and ecosystems, and it plays a key role in the formation of ozone and secondary particulate matter. Consequently, legal limit values for NO_2 are set in the EU and elsewhere, and atmospheric observation networks typically include NO_2 in their measurement programmes. Atmospheric NO_2 is principally measured by chemiluminescence detection, an indirect measurement technique that requires conversion of NO_2 into nitrogen monoxide (NO) and finally calculation of NO_2 from the difference between total nitrogen oxides (NO_x) and NO. Consequently, NO_2 measurements with the chemiluminescence method have a relatively high measurement uncertainty and can be biased depending on the selectivity of the applied NO_2 conversion method.
In the past years, technologies for direct and selective measurement of NO_2 have become available, e.g. cavity attenuated phase shift spectroscopy (CAPS), cavity enhanced laser absorption spectroscopy and quantum cascade laser absorption spectrometry (QCLAS). These technologies offer clear advantages over the indirect chemiluminescence method. We tested the above mentioned direct measurement techniques for NO_2 over extended time periods at atmospheric measurement stations and report on our experience including comparisons with co-located chemiluminescence instruments equipped with molybdenum as well as photolytic NO_2 converters. A still open issue related to the direct measurement of NO_2 is instrument calibration. Accurate and traceable reference standards and NO_2 calibration gases are needed. We present results from the application of different calibration strategies based on the use of static NO_2 calibration gases as well as dynamic NO_2 calibration gases produced by permeation and by gas-phase titration (GPT).