Measurement of ambient NO_3 reactivity: Design, characterization and first deployment of a new instrument

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Abstract. We describe the first instrument for measurement of the rate constant (s^{-1}) for reactive loss (i.e. the total reactivity) of NO_3 in ambient air. Cavity-ring-down spectroscopy is used to monitor the mixing ratio of synthetically generated NO_3 (≈ 30-50 pptv) after passing through a flow-tube reactor with variable residence time (generally 10.5 s). The change in concentration of NO_3 upon modulation of the bath gas between zero-air and ambient air is used to derive its loss rate constant, which is then corrected for formation and decomposition of N_2O_5 via numerical simulation. The instrument is calibrated and characterized using known amounts of NO and NO_2 and tested in the laboratory with an isoprene standard. The lowest reactivity that can be detected (defined by the stability of the NO_3 source, instrumental parameters and NO_2 mixing ratios) is 0.005 s^{-1}. An automated dilution procedure enables measurement of NO_3 reactivities up to 45 s^{-1}, this upper limit being defined mainly by the dilution accuracy. The typical total uncertainty associated with the reactivity measurement at the centre of its dynamic range is 16 %, though this is dependent on ambient NO_2 levels. Results from the first successful deployment of the instrument at a forested mountain site with urban influence are shown and future developments outlined.