Title:	Total OH reactivity measurements using a new fast gas chromatographic photo-ionization detector (GC-PID)
Authors:	Sinha, V. (/jspui/browse?type=author&value=Sinha%2C+V.)
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Abstract:	The primary and most important oxidant in the atmosphere is the hydroxyl radical (OH). Currently OH sinks, particularly gas phase reactions, are poorly constrained. One way to characterize the overall sink of OH is to measure directly the ambient loss rate of OH, the total OH reactivity. To date, direct measurements of total OH reactivity have been either performed using a Laser-Induced Fluorescence (LIF) system ("pump-and-probe" or "flow reactor") or the Comparative Reactivity Method (CRM) with a Proton-Transfer-Reaction Mass Spectrometer (PTR-MS). Both techniques require large, complex and expensive detection systems. This study presents a feasibility assessment for CRM total OH reactivity measurements using a new detector, a Gas Chromatographic Photoionization Detector (GC-PID). Such a system is smaller, more portable, less power consuming and less expensive than other total OH reactivity measurement techniques. Total OH reactivity is measured by the CRM using a competitive reaction between a reagent (here pyrrole) with OH alone and in the presence of atmospheric reactive molecules. The new CRM method for total OH reactivity has been tested with parallel measurements of the GC-PID and the previously validated PTR-MS as detector for the reagent pyrrole during laboratory experiments, plant chamber and boreal field studies. Excellent agreement of both detectors was found when the GC-PID was operated under optimum conditions. Time resolution (60-70 s), sensitivity (LOD 3-6 sg-1) and overall uncertainty (25% in optimum conditions) for total OH reactivity were similar to PTR-MS based total OH reactivity measurements. One drawback of the GC-PID system was the steady loss of sensitivity and accuracy during intensive measurements lasting several weeks, and a possible toluene interference. Generally, the GC-PID system has been shown to produce closely comparable results to the PTR-MS and thus in suitable environments (e.g. forests) it presents a viably economical alternative for groups interested in total OH reactivity observations.
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