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Comparative Reactivity Method – A new tool to measure total OH Reactivity

V. Sinha , J.Williams, J. Crowley, J. Lelieveld

Air Chemistry Department, Max-Planck Institute for Chemistry, J.J. Becher Weg 27, D-55020 Mainz, Germany

(vsinha@mpch-mainz.mpg.de/Phone:+49-6131-305417)

OH radicals play a vital role in maintaining the oxidizing capacity of the atmosphere. To understand variations in OH radicals both source and sink terms must be understood. Currently the overall sink term, or the total atmospheric reactivity to OH, is poorly constrained. This term is often estimated by summing available VOC measurements, although it is by no means certain that all relevant ambient VOCs have been quantified.

Here, we present a new on-line method to directly measure the total OH reactivity (i.e loss rate of OH radicals in the atmosphere). In this method a reactive molecule (X), not normally present in air, is passed through a flow tube reactor and its concentration is monitored with a suitable detector. Next, a constant amount of OH radicals are introduced in the flow tube to react with X, first in the absence of ambient air and then in the presence of ambient air containing VOCs and other OH reactive species. Comparing the amount of X exiting the reactor with and without the ambient air allows the air reactivity to be inferred. In our existing set up, X is pyrrole and the detector is a PTR-MS. The present dynamic range of the method is from 3 per second to 200 per second of reactivity. The system has been tested and calibrated with different single and mixed hydrocarbon standards. Field tests in the tropical rainforest of Suriname and the urban atmosphere of Mainz, Germany show the promise of the new method. Potential interferences from NO and relative humidity changes are also discussed. Preliminary results indicate that this new method can measure ambient reactivity and should be compared with the existing, but less mobile / more expensive, laser induced fluorescence (LIF) based reactivity measurement technique.