Supplementary Materials

Ozone Reactivity Measurement of Biogenic Volatile Organic Compound Emissions

Detlev Helmig[1,2,*], Alex Guenther[2], Jacques Hueber[1], Ryan Daly[1], Wei Wang[1], Jeong-Hoo Park[1], Anssi Liikanen[3], Arnaud P. Praplan[3]

[1]Institute of Arctic and Alpine Research, University of Colorado, Boulder, CO 80309, USA
[2] now at: Boulder Atmosphere Innovation Research LLC, Boulder, CO 80305, USA
[3] University of California Irvine, CA, USA
[1]Atmospheric Research Composition, Finnish Meteorological Institute, 0011 Helsinki, Finland
***corresponding author: dh.bouldair@gmail.com**

For manuscript submitted to

Atmospheric Measurement Techniques

October 25, 2021

Supplement A - Ozone Reactivity Calculation

The rate equation for a reaction of BVOCs with ozone is

$$-\frac{d[O3]}{dt} = k_1[BVOC_1][O_3] + k_2[BVOC_2][O_3] + \cdots + k_i[BVOC_i][O_3] = \sum_i k_i[BVOC_i][O_3] \quad \text{(S1)}$$

Here k_i is the reaction rate constant for $BVOC_i$ and ozone (O_3). $[BVOC_i]$ is the concentration of the i*th* BVOC in the gas sample, and *t* is the reaction elapse time. The ozone reactivity is defined as:

$$RO_3 = \sum_i k_i[BVOC_i] \quad \text{(S2)}$$

with a unit of s^{-1}. It is also defined as the inverse of ozone lifetime.

Combining (S1) and (S2) leads to:

$$RO_3 = -\frac{d[O_3]}{dt}\frac{1}{[O_3]} \quad \text{(S3)}$$

Then, integrating (S3) yields:

$$RO_3 \int_0^t dt = -\int_{[O_3]_0}^{[O_3]_t} \frac{1}{[O_3]} d[O_3] \quad \text{(S4)}$$

$$RO_3\Delta t = -(\ln([O_3]_t) - \ln([O_3]_0)) = -\ln\left(\frac{[O_3]_t}{[O_3]_0}\right) = -\ln\left(\frac{[O_3]_0 - \Delta[O_3]}{[O_3]_0}\right)$$

$$= -\ln\left(1 - \frac{\Delta[O_3]}{[O_3]_0}\right) \quad \text{(S5)}$$

If $\frac{\Delta[O_3]}{[O_3]_0}$ is small, (S5) can be simplified using the Taylor approximation $\ln(1+x) \approx -x$ (if $x \approx 0$), so that:

$$RO_3 \approx -\left(-\frac{\Delta[O_3]}{[O_3]_0}\right)\frac{1}{\Delta t} = \frac{\Delta[O_3]}{[O_3]_0\Delta t} \quad \text{(S6)}$$

This assumes that RO_3 is constant, i.e. $[BVOC_i]$ remain constant. This assumption holds when $[BVOC_i]$ is much larger than $[O_3]$ or when k_i is slow. Under certain circumstances, therefore, RO_3 cannot be calculated with this equation.

$\Delta[O_3]$, Δt, and $[O_3]_0$ are all experimental parameters, so that total RO_3 can be measured. With TORM, $\Delta[O_3]$ is measured directly, and $[O_3]_0$ is monitored/kept at a constant value. Δt is the residence time in the reactor, constrained by its volume and the flow through it.

Supplement B – Modelled Decay of BVOCs in the Ozone Reactivity Reactor

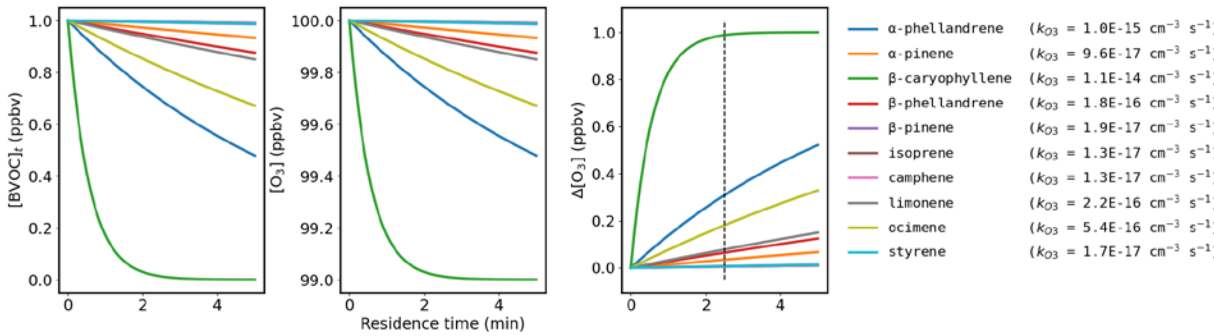

Figure S1

$[BVOC]_t$, $[O_3]$, and $\Delta[O_3]$ for some typically measured BVOC plotted against the elapsed reaction time t. The typical residence time of the ozone reactivity apparatus used in the study presented here is 2.5 min (dotted line). The compounds with relatively fast reaction rates with ozone, such as β-caryophyllene with a $k > 9 \times 10^{-15}$ cm^3 s^{-1}, would have reacted completely within the 2.5 min residence time. The compounds with reaction rates ranging from 9×10^{-15} to 4×10^{-16} cm^3 s^{-1} would be reduced to 10-90% of the starting concentration. Only the ones with $k < 4 \times 10^{-16}$ cm^3 s^{-1} would have more than 90% of the BVOC remaining after 2.5 min.

Supplement C – Ozone Reactivity System Setup for Testing

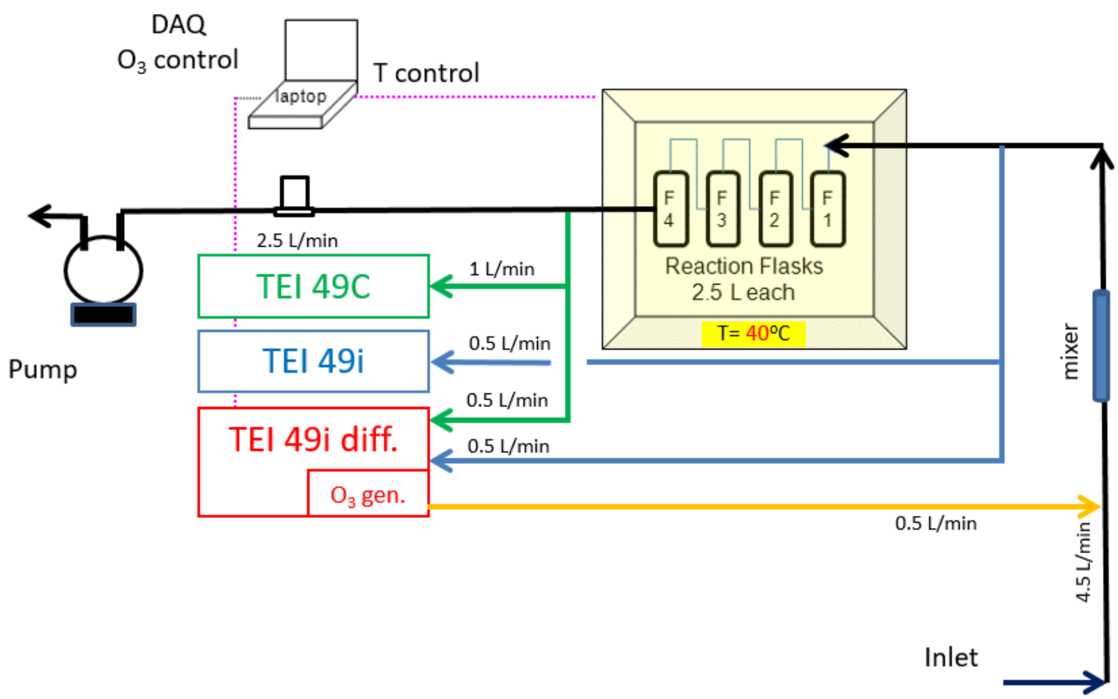

Figure S2
Configuration of the TORM during the testing phase with the directly measured ozone differential in comparison of the difference in ozone determined from two individual ozone monitor measurements.

Supplement D – Chamber Blank Experiment

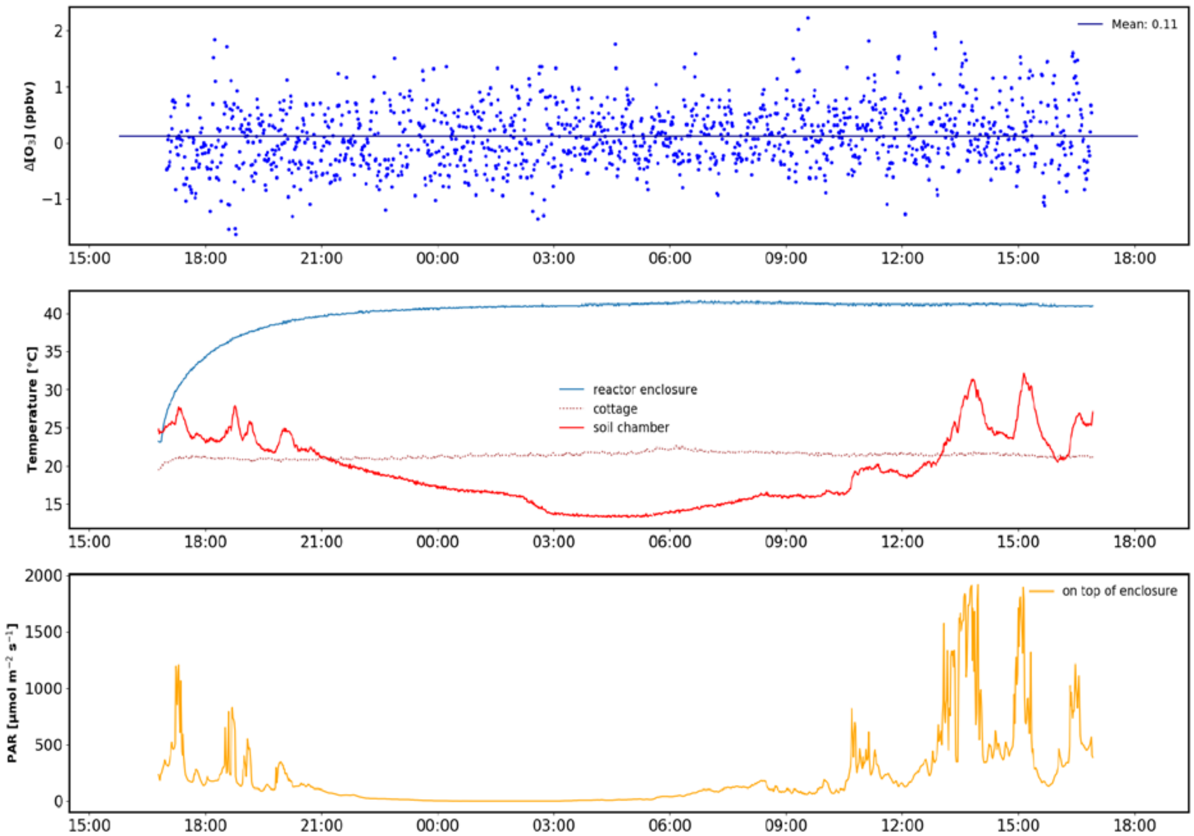

Figure S3

24-Hour experiment with an empty soil chamber enclosure. The chamber was placed outside of a measurement hut on an inert surface (FEP film) with the instrument being inside the building. Plotted data are the ozone reactivity signal (top panel), the soil chamber inside temperature, the reactor temperature, the building temperature (middle panel) and photosynthetically active radiation measured on top of the chamber (bottom panel). For this experiment, the O_3 level before the reactor was kept at 150 ppbv.

Supplement E – Dependency of Pressure Differential on Reactor Flow Rate

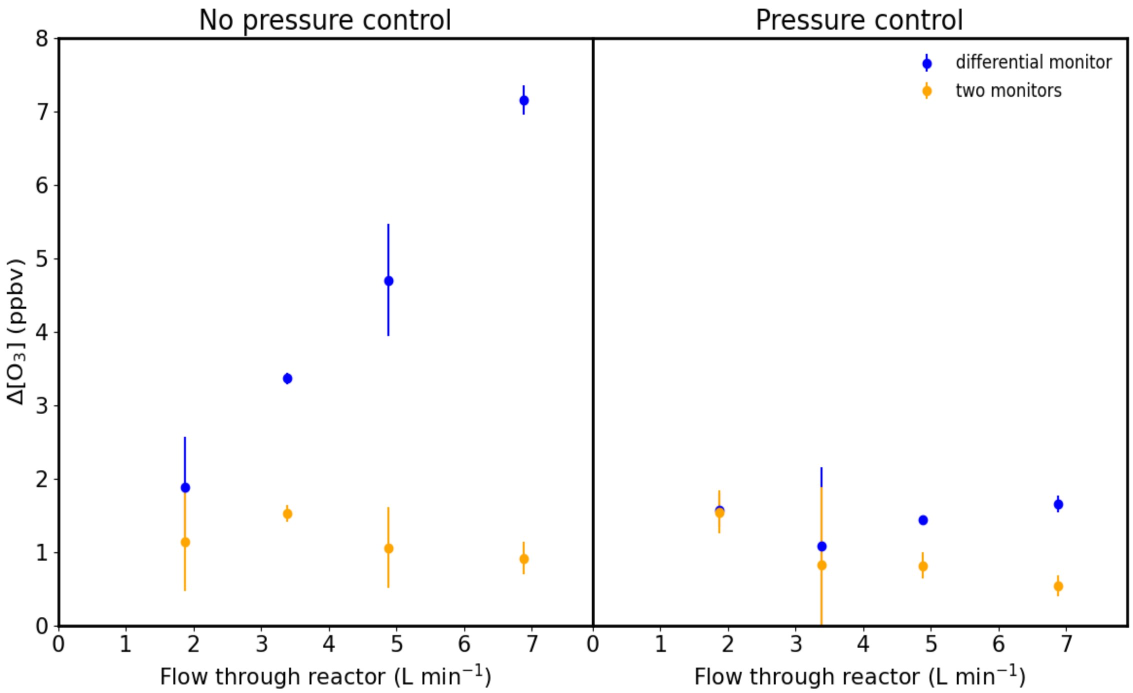

Figure S4

Recordings of the differential 49i ozone monitor (blue) and the difference between two monitors placed before and after the reactor (orange) in the configuration shown in Fig. 2 at increasing flow rate through the reactor without and with the balancing of the pressures using the flow restrictor valve (left and right panels, respectively).

Supplement F – Residence Time inside the Reactor

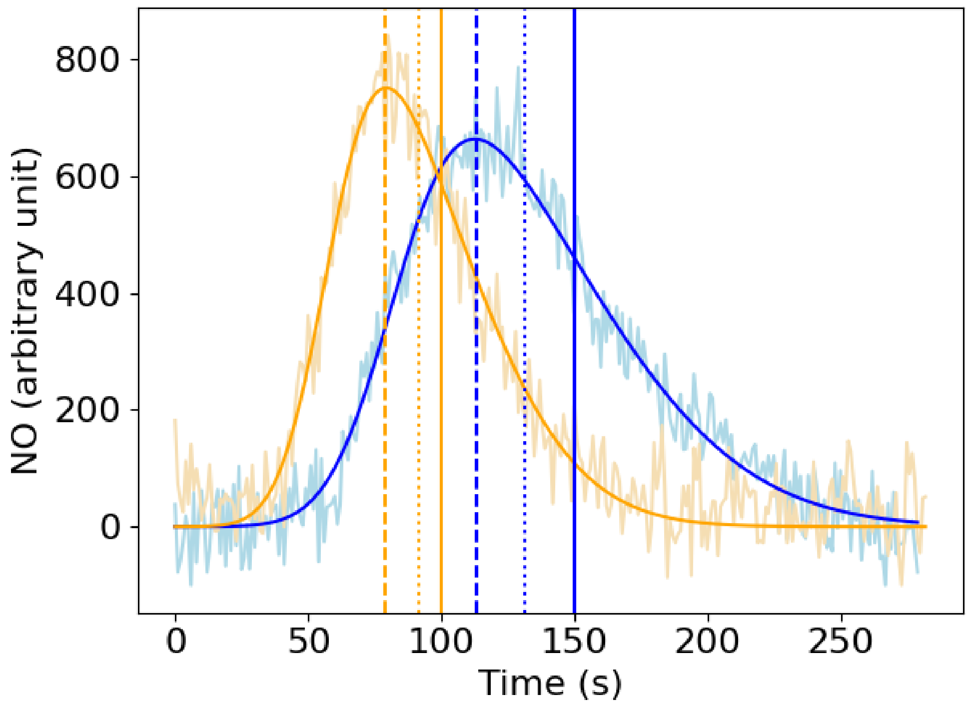

Figure S5
NO measured after the reactor for injections of 2 ml of NO at the reactor inlet at time 0 s for two different flows through the reactor: 4 L min^{-1} (blue) and 6 L min^{-1} (orange), with skewed Gaussian fit lines. The solid vertical lines correspond to the theoretical residence times for a 10 L reactor volume for each flow rate with matching colors (150 and 100 s, respectively). The dashed vertical lines represent the median value (113 and 79, respectively) and the dotted vertical lines represent the mean residence time in the reactor for each distribution (131 and 91 s).

Supplement G – Nafion Dryer Tests

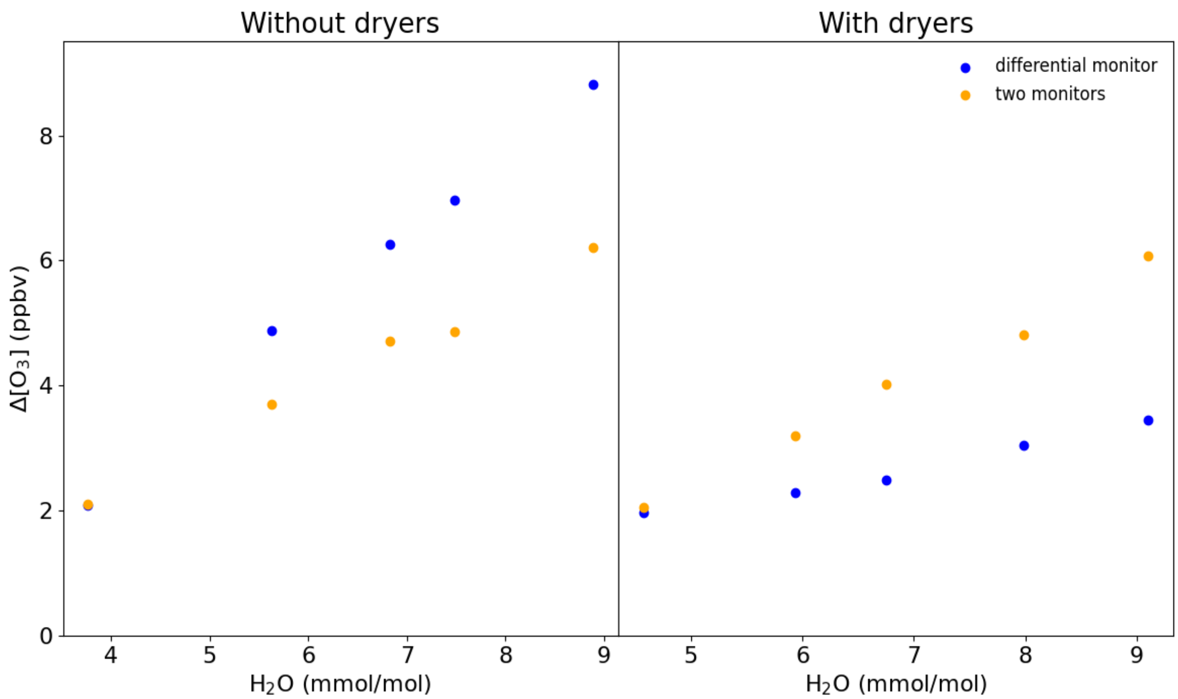

Figure S6
Maximum values of $\Delta[O_3]$ for signal changes observed by the differential analyzer and the two-monitor system (blue and orange, respectively) from injection of various amount of liquid water (20 to 100 µl) through a septum port upstream of the reactor without and with Nafion dryers (left and right panels, respectively).