Supplemental information for:

Effects of Gas-Wall Partitioning in Teflon Tubing and Instrumentation on Time-Resolved Measurements of Gas-Phase Organic Compounds

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Supplemental Information

Error introduced by approximating laminar flow as perfectly mixed flow

The error introduced by modeling flow through the bins as perfectly mixed rather than laminar is shown in Fig. S1. The concentration profile for laminar flow was produced using the residence time distribution *E(t)* shown in Eq. (S1).

$$E(t) = \frac{{t_m}^2}{2\,t^3} \tag{S1}$$

where t_m is the mean residence time and t is the time elapsed (Fogler, 2006). The error introduced by modeling the flow as perfectly mixed is small, and this effect will only need to be accounted for when the tubing delays due to partitioning are very short (of the order of a few seconds), if more accurate results are desired.

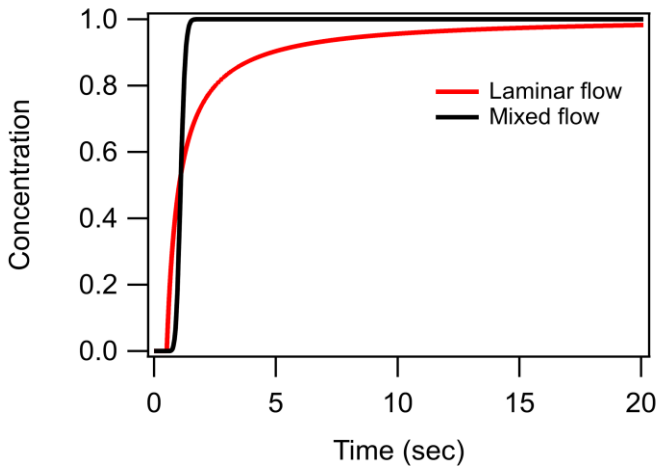

Figure S1. Simulated time profiles of compound concentrations at the tubing exit assuming flow in bins is perfectly mixed rather than laminar. The mixed flow profile was generated by running the model with gas-wall partitioning turned off. The profiles are for 1 m of tubing with 3/16 in. ID at a flow rate of 1 L min^{-1}.

References

Fogler, S. H.: Elements of chemical reaction engineering, 4th ed., Prentice Hall, Upper Saddle River, NJ., 2006.

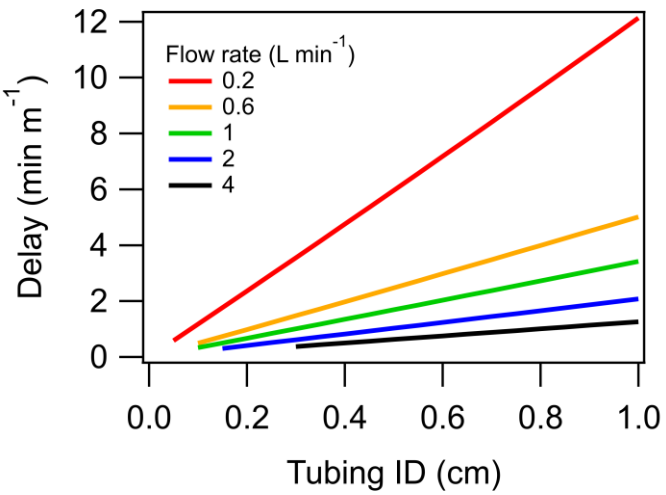

Figure S2. Simulated tubing delays presented as a function of tubing ID at various flow rates for a compound with $c^* = 10^5$ μg m^{-3} sampled through PFA tubing.

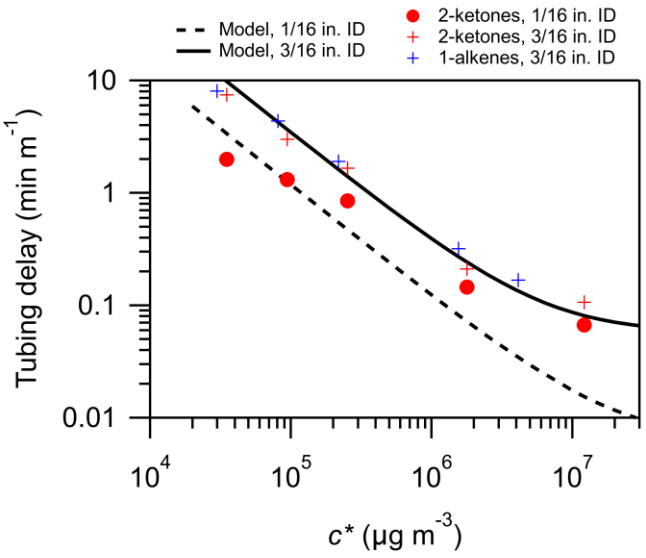

Figure S3. Comparison of measured and modeled tubing delays for 1/16 in. ID and 3/16 ID PFA Teflon tubing sampling at 0.36 L min^{-1}. Values of c^* were calculated using SIMPOL.1 (Pankow and Asher, 2007).

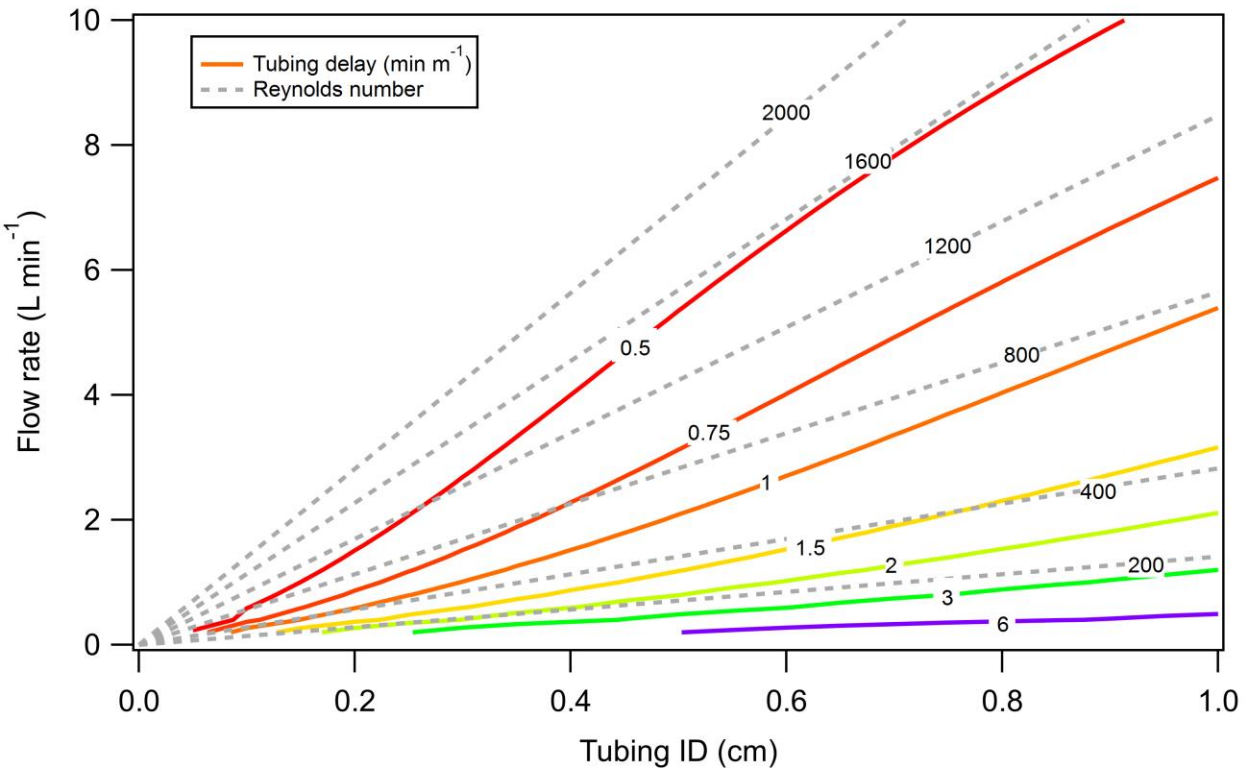

Figure S4. Simulated tubing delays presented as a function of tubing ID and flow rate for a compound with $c^* = 10^5$ μg m^{-3} sampled through PFA tubing. Reynolds numbers are overlaid to illustrate the nonlinear relationship between tubing delay, flow rate and tubing diameter.

Convolving model output with instrument response time scale

When measuring gas-phase organic compounds one must account for delays arising from tubing and from instrument surfaces. The chromatography model developed here allows one to simulate the delays from tubing, and the procedure described in the text allows one to measure delays from the instrument. The instrument response *R(t)* is then the convolution of the tubing model output *F(t)* with the instrument response function *I(t)*, as in Eq. (S1).

$$R(t) = F(t) * I(t) = \int_0^\infty [F(t-\tau) \times I(\tau)]\, d\tau \quad \text{(S1)}$$

This approach was evaluated by sampling a set of 2-ketones from an equilibrated environmental chamber into the PTR-MS in a 60 s pulse, with the PTR-MS sampling clean air before and after the pulse. The experiment was conducted with 1 m of 3/16 in. ID PFA tubing sampling at 0.36 L min^{-1}. As seen in Fig. S5, the convolution of the model output with the instrument response function for each 2-ketone gives excellent agreement with the experimental data. For example, a 60 s pulse of 1-tridecanone is convoluted to a response lasting more than 20 min, underscoring the importance of accounting for both tubing and instrument delays.

After the experiments described in this work were completed we removed all extraneous tubing from the inlet of the PTR-MS in an attempt to minimize the instrument response time for future work. This was a success, and we decreased the instrument response time by a factor of 5 by reconfiguring the inlet. This result again shows the importance of minimizing the total amount of tubing in a sampling configuration when fast instrument response is needed.

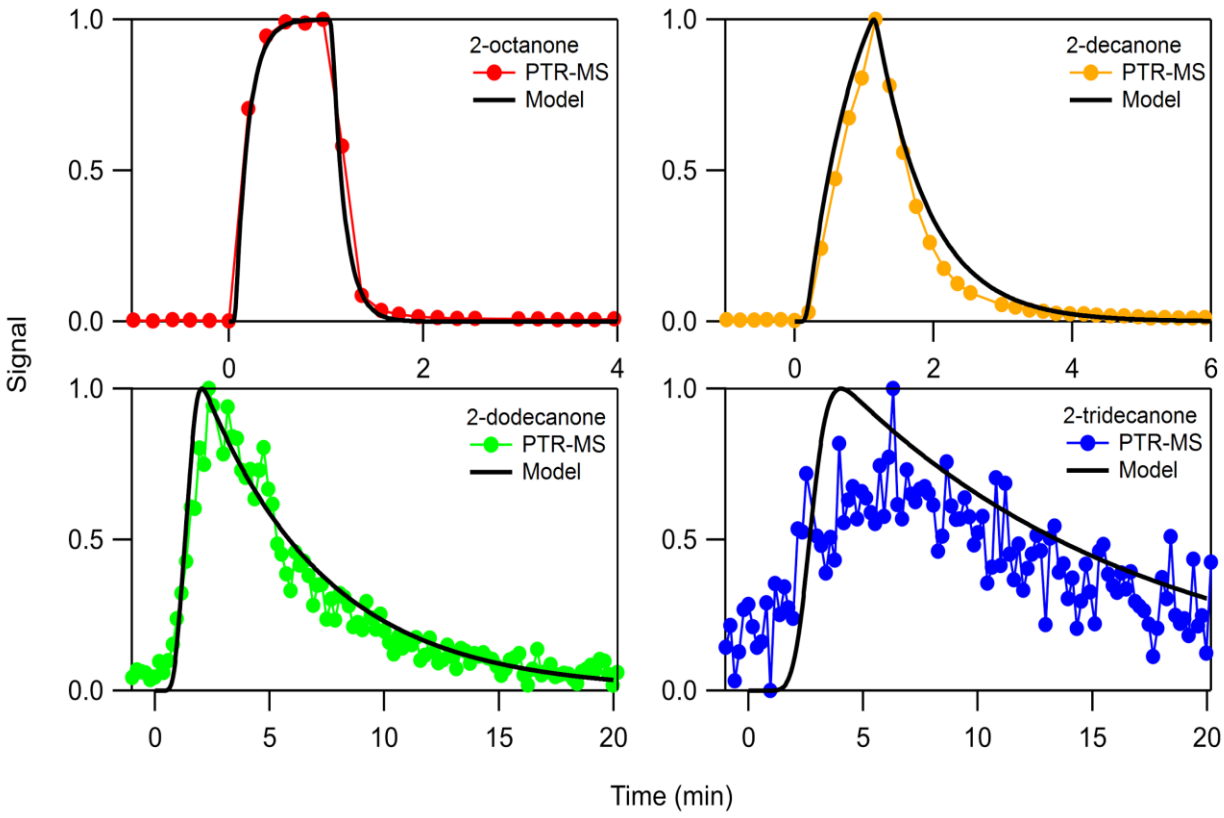

Figure S5. Measured and modeled time profiles for a 60-second pulse of 2-ketones measured by the PTR-MS through 1 m of 3/16 in. ID PFA Teflon tubing at 0.36 L min^{-1}. The tubing model output was convolved with the instrument response function for each 2-ketone to generate the profiles.