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Vapor wall deposition in Teflon chambers

X. Zhang et al.

Correspondence to: J. H. Seinfeld (seinfeld@caltech.edu)

1. Time-scale for gas-wall equilibrium partitioning

Eqs (S1) and (S2) describe the dynamic behavior of compound *i* in the gas phase ($\overline{C}_{\mathrm{v,i}}$) and on chamber walls ($\overline{C}_{\mathrm{w,i}}$), respectively.

$$\frac{d\overline{C}_{\mathrm{v,i}}}{dt} = -\,k_{\mathrm{w,depo,i}}\overline{C}_{\mathrm{v,i}} + k_{\mathrm{w,evap,i}}\overline{C}_{\mathrm{w,i}} \tag{S1}$$

$$\frac{d\overline{C}_{\mathrm{w,i}}}{dt} = -\,k_{\mathrm{w,evap,i}}\overline{C}_{\mathrm{w,i}} + k_{\mathrm{w,depo,i}}\overline{C}_{\mathrm{v,i}} \tag{S2}$$

where $k_{\mathrm{w,depo,i}}$ (s^{-1}) is the deposition rate coefficient to the wall and $k_{\mathrm{w,evap,i}}$ (s^{-1}) is the evaporation rate coefficient from the wall. The relationship between these two parameters is

$$k_{\mathrm{w,evap,i}} = \frac{k_{\mathrm{w,depo,i}}}{K_{\mathrm{w,i}}C_{\mathrm{w}}} \tag{S3}$$

where C_{w} is the total mass of equivalent absorbing organic material on the chamber walls, and $K_{\mathrm{w,i}}$ is the gas-wall partition coefficient, which depends on the vapor pressure of compound *i*,

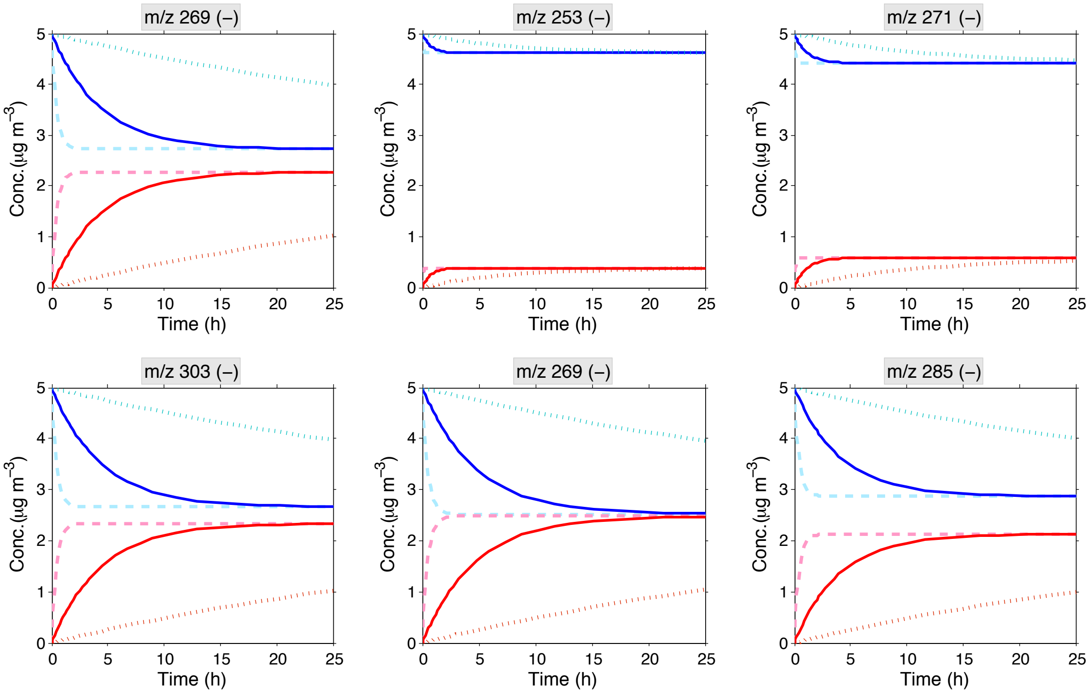
$$K_{\mathrm{w,i}} = \frac{RT}{p^{0}_{\mathrm{L,i}}\gamma_{\mathrm{i}}\overline{M_{\mathrm{w}}}} \tag{S4}$$

where $p^{0}_{\mathrm{L,i}}$ is the vapor pressure of compound *i* as a liquid, γ_{i} is its activity coefficient on a mole fraction basis, R is the gas constant, T is temperature, and $\overline{M_{\mathrm{w}}}$ is the average molecular weight of the absorbing organic material on the wall.

Simulations were performed to estimate timescales associated with gas-wall equilibrium partitioning for the 25 intermediate/semi-volatile organic vapors investigated. Although the deposition rate coefficient ($k_{\mathrm{w,depo,i}}$) for each organic vapor is unknown, upper and lower limits can be obtained. Note that CIMS measured overall decay rate of organic vapor *i* ($k_{\mathrm{w,i}}$) is a function of $k_{\mathrm{w,depo,i}}$ and $k_{\mathrm{w,evap,i}}$. The upper limit ($k_{\mathrm{w,depo,i}} = 6 \times 10^{-4}\ s^{-1}$) is governed by the mixing status in the chamber,

$$k_{\mathrm{w,depo}} = \frac{\pi}{2}\left(\frac{\mathrm{A}}{\mathrm{V}}\right)(\mathcal{D}_{\mathrm{v}}K_{\mathrm{e}})^{1/2} \tag{S5}$$

The lower limit ($k_{\mathrm{w,depo,i}} = 1 \times 10^{-6}\ \mathrm{s}^{-1}$) is chosen as the lowest dark decay rate among 25 organic vapors measured by CIMS. The middle value ($k_{\mathrm{w,depo,i}} = 3 \times 10^{-5}\ \mathrm{s}^{-1}$) is the average of upper and lower limits. The evaporation rates ($k_{\mathrm{w,evap,i}}$) can be obtained via Eq (S3) using the C_{w} values calculated from Section 4.2 in the main text. Predicted temporal profiles of $\overline{C}_{\mathrm{v,i}}$ and $\overline{C}_{\mathrm{w,i}}$ are shown in Figure S1. In general, vapors with lower volatilities tend to require a longer time to establish gas-wall equilibrium. For a specific compound, the equilibrium timescale is estimated to vary from a few minutes to over a day, depending on the deposition rate coefficients applied (upper limit $k_{\mathrm{w,depo,i}} = 6 \times 10^{-4}\ \mathrm{s}^{-1}$ vs. lower limit $k_{\mathrm{w,depo,i}} = 1 \times 10^{-6}\ \mathrm{s}^{-1}$). For the 25 vapors studied, gas-wall equilibrium partitioning is estimated to require > 20 min to < 25 h when the average deposition rate coefficient is employed ($k_{\mathrm{w,depo,i}} = 3 \times 10^{-5}\ \mathrm{s}^{-1}$) in the simulation. These results suggest that it is generally reasonable to estimate C_{w} assuming equilibrium partitioning after ~ 18 h of wall-induced vapor decay.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m/z 253 (–)
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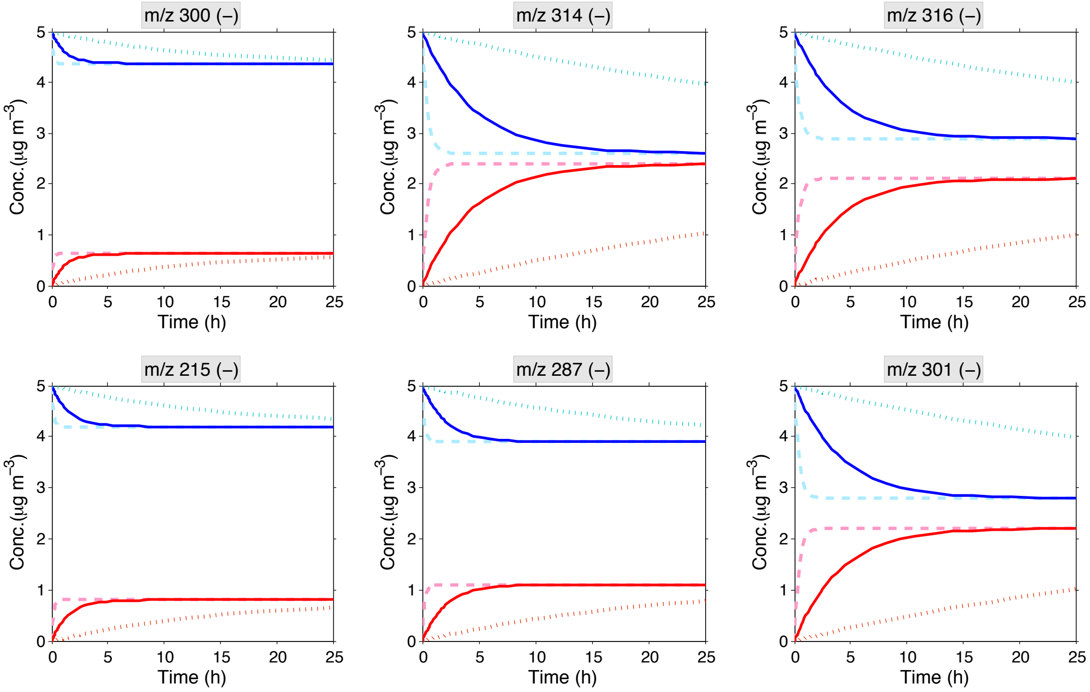
m/z 269 (–)
m/z 285 (–)
Conc.(μg m−3)
Time (h)
0
1
2
3
4
5
0
5
10
15
20
25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Conc.(μg m−3)
Time (h)
0
1
2
3
4
5
0
5
10
15
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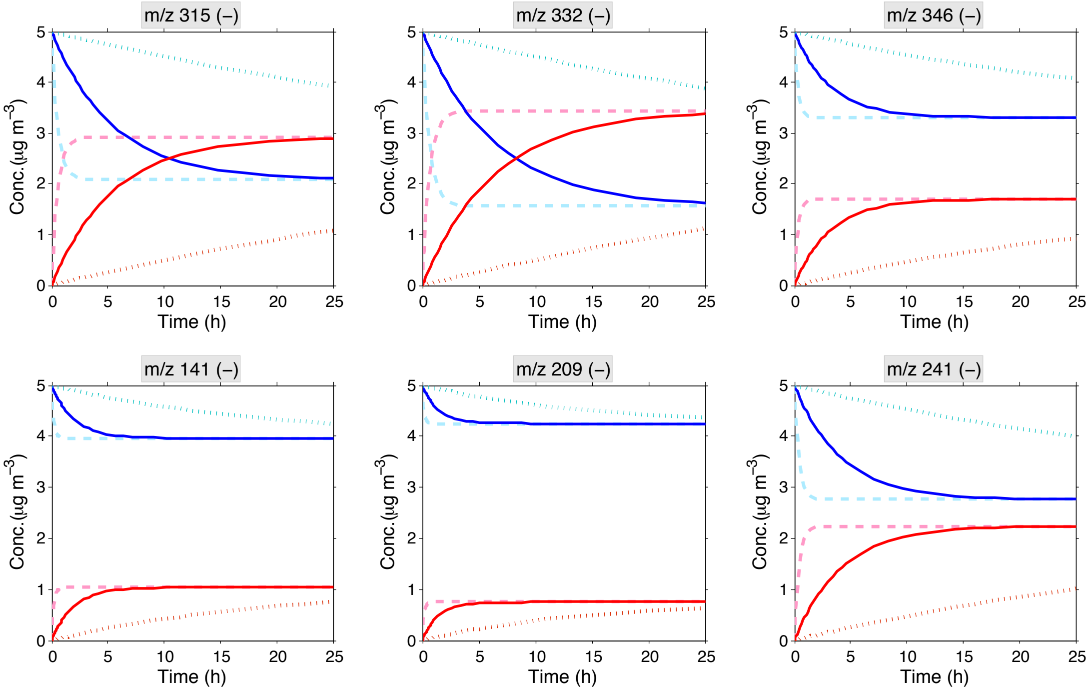
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Time (h)
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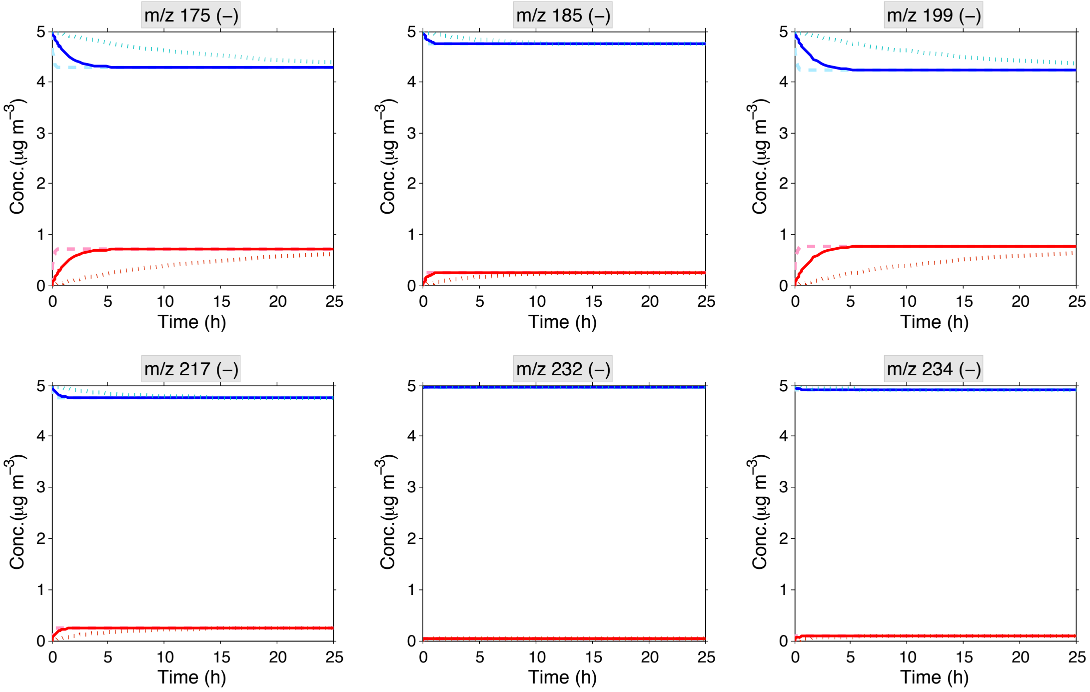
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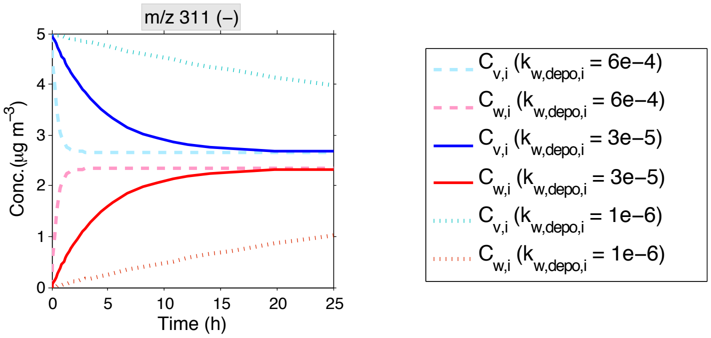

Figure S1. Timescales for gas-wall equilibrium partitioning of intermediate/semi-volatile organic vapors generated from photooxidation of isoprene, toluene, α-pinene, and dodecane. Three values of $k_{w,depo,i}$ are incorporated in the simulation here, representing the upper limit ($k_{w,depo,i} = 6 \times 10^{-4}$ s^{-1}), average ($k_{w,depo,i} = 3 \times 10^{-5}$ s^{-1}), and lower limit ($k_{w,depo,i} = 1 \times 10^{-6}$ s^{-1}) of vapor deposition rate on chamber walls, respectively. The evaporation rates from chamber walls ($k_{w,evap,i}$) are calculated using C_w derived from Eqs (12) and (13) in the main text (See Section 4 for more details). Initial concentrations of vapor *i* in the gas phase and on chamber walls are assumed to be 5 and 0 μg m^{-3}, respectively.