Supplement of

Vapor wall deposition in Teflon chambers

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1. Time-scale for gas-wall equilibrium partitioning

Eqs (S1) and (S2) describe the dynamic behavior of compound $i$ in the gas phase ($C_{v,i}$) and on chamber walls ($C_{w,i}$), respectively.

$$\frac{dC_{v,i}}{dt} = -k_{w,\text{depo},i}C_{v,i} + k_{w,\text{evap},i}C_{w,i} \quad (S1)$$

$$\frac{dC_{w,i}}{dt} = -k_{w,\text{evap},i}C_{w,i} + k_{w,\text{depo},i}C_{v,i} \quad (S2)$$

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

$$k_{w,\text{evap},i} = \frac{k_{w,\text{depo},i}}{K_{w,i}C_w} \quad (S3)$$

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

$$K_{w,i} = \frac{RT}{p^0_{L,i} \gamma_i \bar{M}_w} \quad (S4)$$

where $p^0_{L,i}$ is the vapor pressure of compound $i$ as a liquid, $\gamma_i$ is its activity coefficient on a mole fraction basis, $R$ is the gas constant, $T$ is temperature, and $\bar{M}_w$ 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 ($k_{w,\text{depo},i}$) for each organic vapor is unknown, upper and lower limits can be obtained. Note that CIMS measured overall decay rate of organic vapor $i$ ($k_{w,i}$) is a function of $k_{w,\text{depo},i}$ and $k_{w,\text{evap},i}$. The upper limit ($k_{w,\text{depo},i} = 6 \times 10^{-4}$ s$^{-1}$) is governed by the mixing status in the chamber,

$$k_{w,\text{depo}} = \frac{\pi}{2} \left( \frac{A}{V} \right) (D_vK_e)^{1/2} \quad (S5)$$
The lower limit \((k_{w,\text{depo},i} = 1 \times 10^{-6} \text{ s}^{-1})\) is chosen as the lowest dark decay rate among 25 organic vapors measured by CIMS. The middle value \((k_{w,\text{depo},i} = 3 \times 10^{-5} \text{ s}^{-1})\) is the average of upper and lower limits. The evaporation rates \((k_{w,\text{evap},i})\) can be obtained via Eq (S3) using the \(C_w\) values calculated from Section 4.2 in the main text. Predicted temporal profiles of \(\bar{C}_{v,i}\) and \(\bar{C}_{w,i}\) 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 \(k_{w,\text{depo},i} = 6 \times 10^{-4} \text{ s}^{-1}\) vs. lower limit \(k_{w,\text{depo},i} = 1 \times 10^{-6} \text{ s}^{-1}\)). 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 \((k_{w,\text{depo},i} = 3 \times 10^{-5} \text{ s}^{-1})\) 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.
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 $k_{w,\text{depo},i}$ are incorporated in the simulation here, representing the upper limit ($k_{w,\text{depo},i} = 6 \times 10^{-4} \text{ s}^{-1}$), average ($k_{w,\text{depo},i} = 3 \times 10^{-5} \text{ s}^{-1}$), and lower limit ($k_{w,\text{depo},i} = 1 \times 10^{-6} \text{ s}^{-1}$) of vapor deposition rate on chamber walls, respectively. The evaporation rates from chamber walls ($k_{w,\text{evap},i}$) 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.