

Supporting Information

Estimated Timescales for Wet Deposition of Organic Compounds as a Function of Henry's Law Constants

Chenyang Bi, Gabriel Isaacman-VanWertz*

Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, Virginia, 24060, USA

Correspondence to: Gabriel Isaacman-VanWertz (ivw@vt.edu)

Influence of air diffusivity

We note that the air diffusivity (D_g), assumed to be $0.06 \text{ cm}^2 \text{ s}^{-1}$ in Equation 2, is in fact a compound-dependent parameter. To examine the uncertainty caused by this assumption, here, we estimate the variability of air diffusivity for oxygenated semivolatile atmospheric compounds produced in α -pinene oxidation reactions from the Master Chemical Mechanism (MCM).¹ Air diffusivity is calculated based on the molecular weight of those compounds using $D_g = 1.55/\text{MW}^{0.65}$,² where MW is the molecular weight. The air diffusivity is found to have a minimum of $0.04 \text{ cm}^2 \text{ s}^{-1}$ and a maximum of $0.08 \text{ cm}^2 \text{ s}^{-1}$ for target compounds. As shown in Figure S1, median wet deposition timescales during a rain is plotted using the minimum, assumed, and maximum air diffusivity using data from SGP. The uncertainty of varying air diffusivity is no more than 25%.

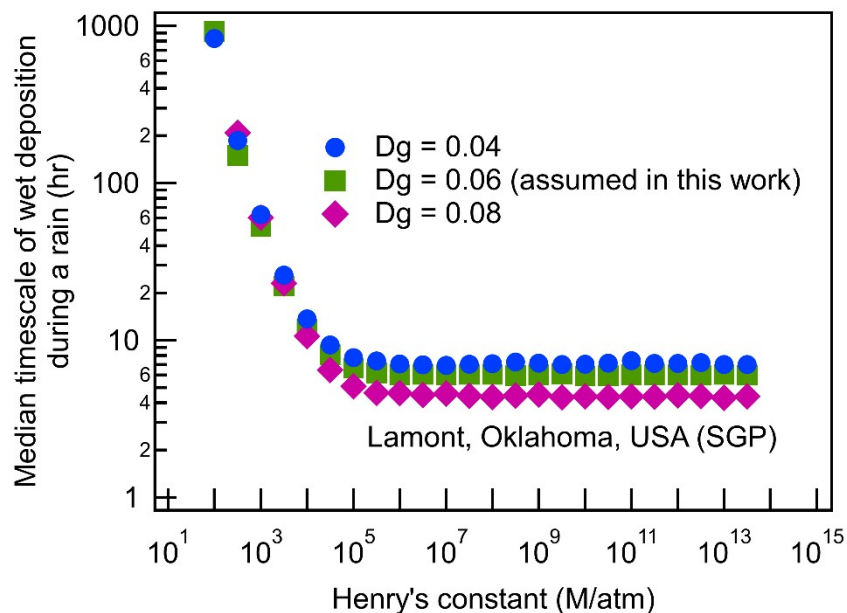


Figure S1. The uncertainty of wet deposition timescale in rain estimated for varying air diffusivity using data collected from Lamont, Oklahoma, US (SGP).

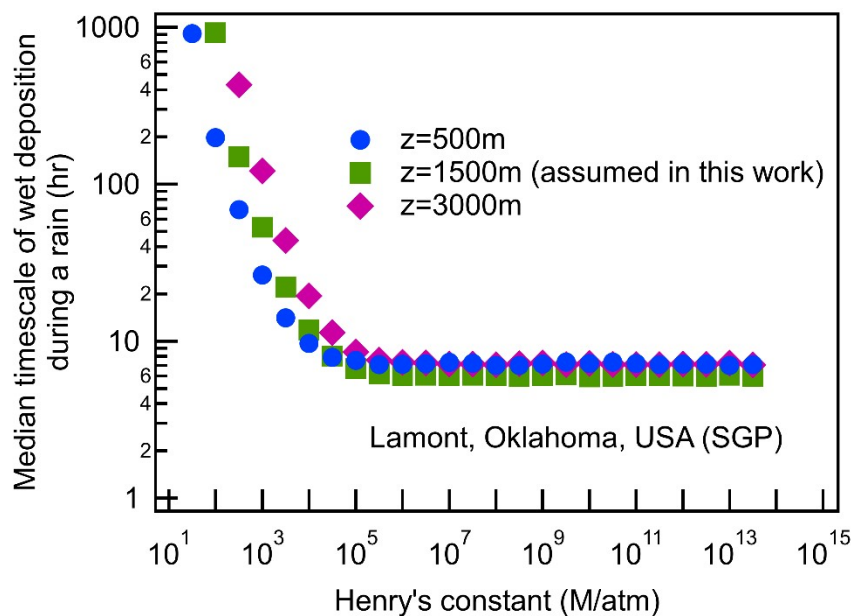


Figure S2. The uncertainty of wet deposition timescale in rain estimated for varying precipitation height using data collected from Lamont, Oklahoma, US (SGP).

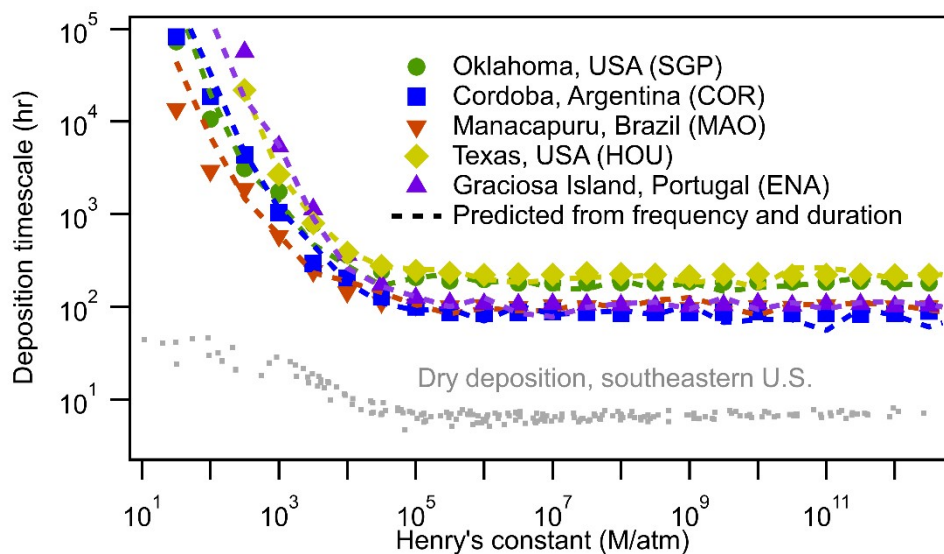


Figure S3. Overall timescale for wet deposition as a function of Henry's law constants using rain characteristics collected from five sites: SGP, COR, MAO, HOU, and ENA. Dashed lines are predicted median timescale in this study based on rain frequency and duration, and site-specific timescale during rainy period.

Estimation of timescales for less soluble species

Because the relationship between wet deposition timescales and Henry's law constants are generally similar between sites (Figure 5), timescales for compounds with $H < 10^5 \text{ M atm}^{-1}$ can be estimated as a function of wet deposition timescales for more soluble species. It is consequently only necessary to calculate the time taken to reach cumulative 5 hours of rain at a given location as an estimate for compounds with $H > 10^5 \text{ M atm}^{-1}$, reducing the computational load. The equation describing the average wet deposition timescale during a precipitation event is approximated as an exponential decay. Because timescales below $H = 10^3 \text{ M atm}^{-1}$ are poorly constrained due to long computational times, the equation is presented here referenced to this lower bound for solubility.

$$\log(t_H) = \log(t_{min}) + \log\left(\frac{t_{H=10^3}}{t_{min}}\right) e^{-\tau \log\left(\frac{H}{10^3}\right)} \quad (\text{S1})$$

Where t_H is the wet deposition timescale (hr) for a given Henry's law constants, H (M atm^{-1}), and t_{min} is the estimated wet deposition timescale for compounds with $H > 10^5 \text{ M atm}^{-1}$ (hr), beyond which timescales plateau at their minimum. The decay constant, τ , is estimated as 1.0, and the ratio of average timescales at

$H = 10^3 \text{ M atm}^{-1}$ and $H > 10^5 \text{ M atm}^{-1}$, $\frac{t_{H=10^3}}{t_{min}}$, is equal to 8.7. With these two estimated constants, which are constrained by the averaged data (dashed lines shown in Figure 5), timescales can be calculated for any compound using only an observationally constrained t_{min} , as shown in Figure S4. Uncertainty increases substantially for solubilities of $H < 10^3 \text{ M atm}^{-1}$, but wet deposition timescales for such compounds are likely significantly longer than timescales for other removal processes

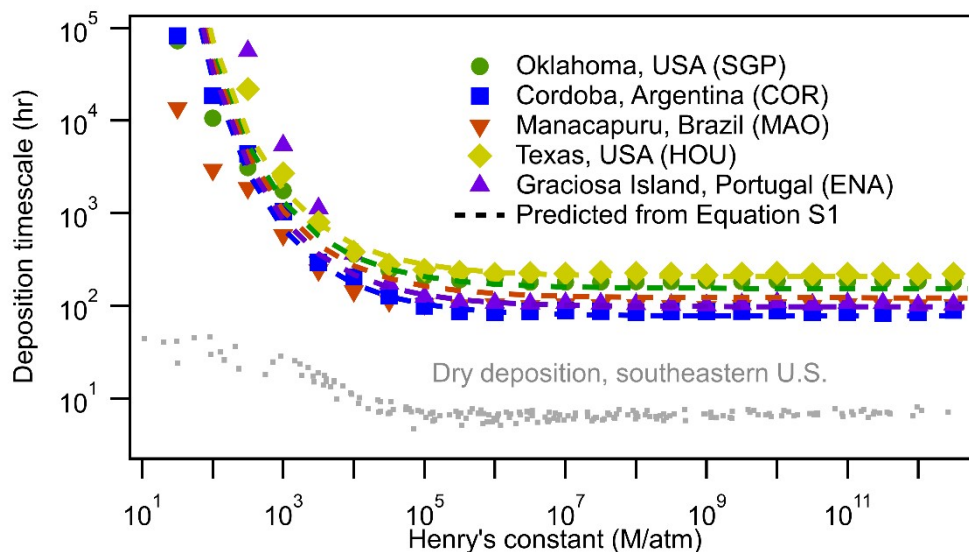


Figure S4. Figure S4. Predicted wet deposition timescales (dashed lines) using Equation S1 for five sites: SGP, COR, MAO, HOU, and ENA, and their comparisons to the estimations using rain characteristics (i.e., identical markers as in Figure 5). t_{min} for each site is set to be the timescale for compounds with $H > 10^5 \text{ M atm}^{-1}$ predicted using precipitation frequency and duration (i.e., plateaus of dashed lines in Figure 5).

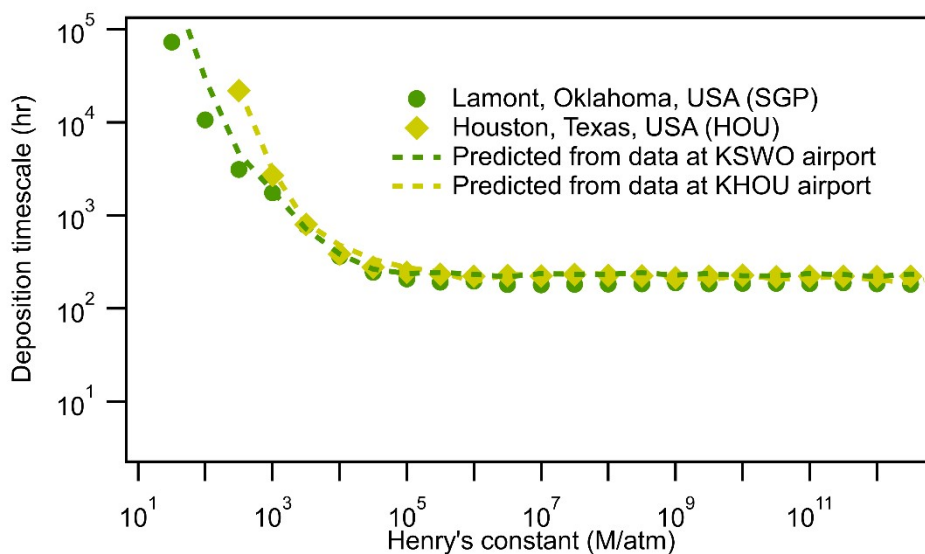


Figure S5. Comparisons of estimated overall timescale for wet deposition based on rain frequency and duration from DOE-ARM sites (i.e., SGP and HOU) vs from nearby airport (KSWO and KHOU) using the same site-specific timescale during rainy period (i.e., comparison between HOU and SGP in Figure S3 and two nearby airports).

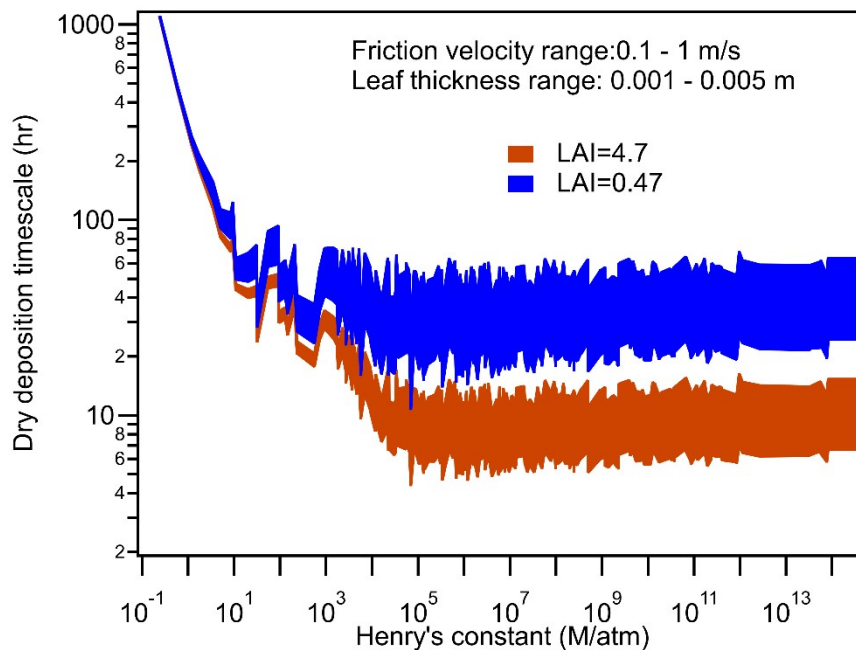


Figure S6. The uncertainty of dry deposition timescale estimated for a range of friction velocity and characteristic leaf thickness using Monte-Carlo style simulations with leaf area index (LAI) = 0.47 and 4.7.

References:

- (1) Saunders, S. M.; Jenkin, M. E.; Derwent, R. G.; Pilling, M. J. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds. *Atmospheric Chemistry and Physics* **2003**, 3 (1), 161-180. DOI: 10.5194/acp-3-161-2003.
- (2) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 3rd Edition; 2016.