S1 Analytical solution to evaporation differential equation and curve-fitting procedure

To make the fitting procedure less computationally expensive, rather than repeatedly numerically integrating the differential equation we developed an analytical expression that approximates a closed-form solution to Maxwellian flux under certain simplifying assumptions. In particular, we assumed three quantities were time-invariant:

First, the droplet radius did not vary with time because the butenedial reflects only a fraction of the total droplet composition. For our experiments, the full numerical integration calculation showed particle radius decreased by less than 10% with complete butenedial evaporation and has a negligible effect on the vapor pressure calculation compared to overall uncertainty in our experiments.

Second, the mole fraction of water in the droplet did not vary with time. This approximation is true to the extent that the RH in the EDB remains constant and the change in composition over the droplet's residence of the EDB does not lead to a change in the activity coefficient of water.

Third, all components in the droplet that are not butenedial or water (i.e., PEG-6, NaCl and Na_2SO_4) did not evaporate over the timescale of the experiment.

Using these assumptions, it can be shown that the Maxwell flux expression can be simplified to

$$\frac{dN_i}{dt} = -a\frac{N_i}{b + cN_i} \qquad \text{(S1)}$$

where

$$a = 4\pi \frac{P_{\mathrm{vap,eff}_i} D_{\mathrm{g}_i} r}{kT} \qquad \text{(S2)}$$

$$b = \frac{1}{1 - X_{\mathrm{H_2O}}}\left(N_{\mathrm{PEG-6}} + N_{\mathrm{inorg}}\right) \qquad \text{(S3)}$$

$$c = \frac{1}{1 - X_{\mathrm{H_2O}}} \qquad \text{(S4)}$$

and N_i is the time-dependent number of molecules of compound i.

This form of differential equation has an analytical solution in the form:

$$N_i(t) = \frac{b}{c} W\left(\frac{c}{b} e^{-\frac{a}{b}t + \frac{C_0}{b}}\right) \qquad \text{(S5)}$$

where W is the Lambert W function and C_0 is an integration constant. From this solution it further can be shown that

$$C_0 = b\ln\left(N_{\mathrm{BD,(t=0)}}\right) + cN_{\mathrm{BD,(t=0)}} \qquad \text{(S6)}$$

The data was fit to Eq. S5 with the values of b, c, and C_0 constrained as input parameters and a as the free parameter whose value was determined via non-linear curve fitting. The fitting procedure used the Trust Region Reflective algorithm, which allows for fitting to an arbitrary function with parameters constrained to only take on physically meaningful positive values (Branch et al., 1999), as implemented in the SciPy scientific computing package (Jones et al., 2001–).

S2 Validation of analytical solution

The agreement between Eq. S5 and numerical integration was verified for our experimental conditions using the dry experiment because that is the experiment for which the largest change in droplet radius is expected to have taken place.

To confirm that the assumptions made in deriving the closed form solution to the Maxwell flux differential equation do not substantially affect the shape of the evaporation curve or the extracted vapor pressure, the closed form solution was compared to the best fit forward run of the Maxwell flux equation. Minimizing the root mean squared deviation (RMSD) of the forward model run from the observed butenedial evaporation was used as the metric to determine the forward run of best fit. As shown in Fig. S1 and Fig. S2, the best fit forward run was compared to the closed form solution for both the dry and humid measurements without inorganics present. In both cases, the vapor pressures converged to the same value within the uncertainty range, verifying that assuming constant radius, mole fraction of water, and nonvolatility of hexaethylene glycol does not alter the vapor pressure estimate significantly for the instrumental setup.

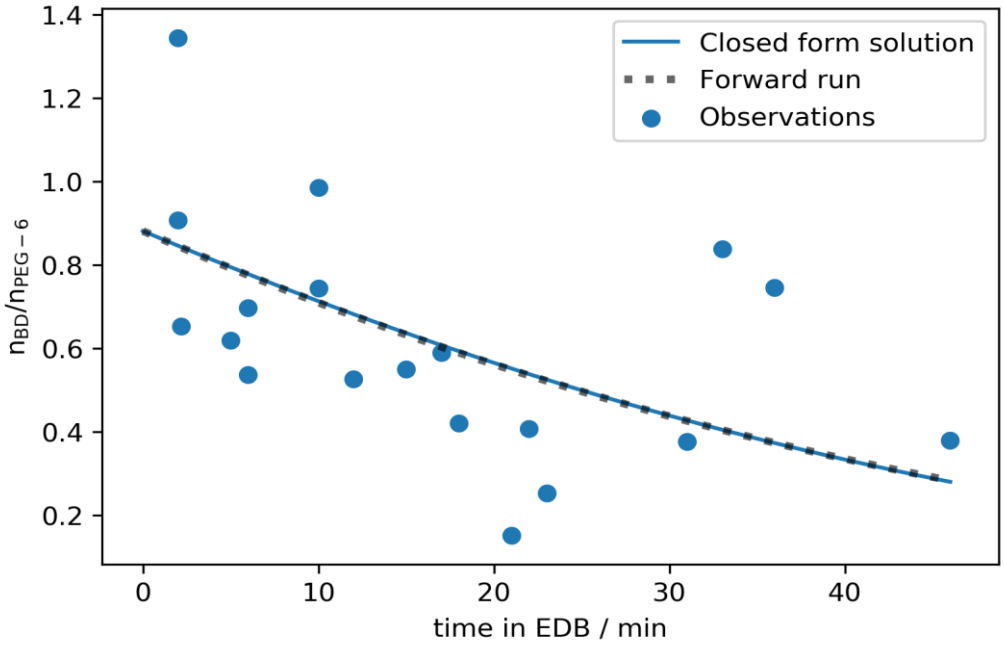

Figure S1: Validation of closed-form approximation, dry BD + PEG-6 experiment.

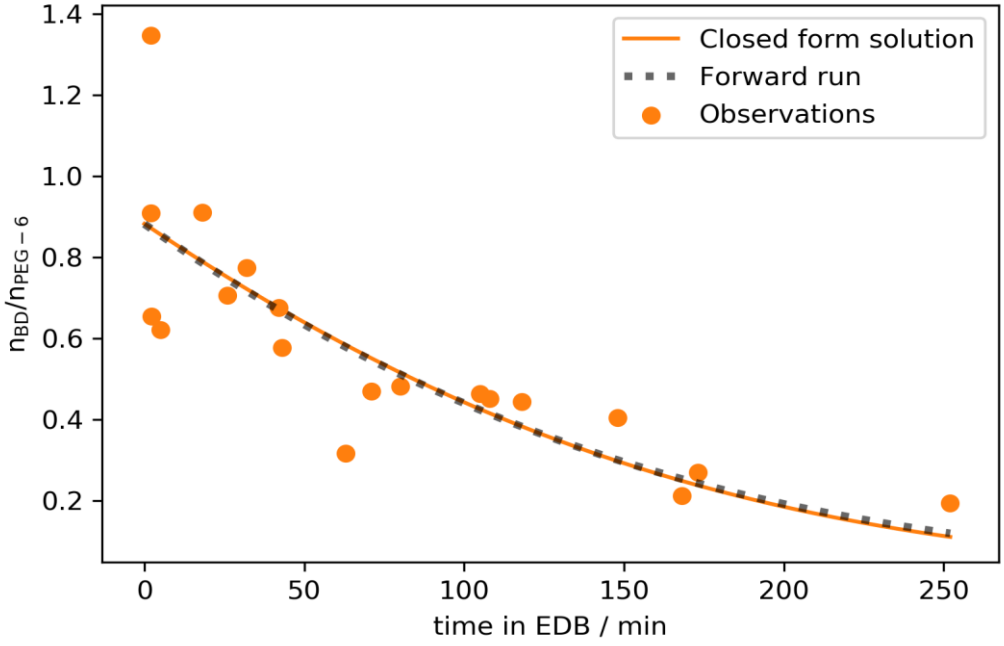

Figure S2: Validation of closed-form approximation, humid BD + PEG-6 experiment.

S3 Monte Carlo uncertainty analysis

The overall strategy of the Monte Carlo uncertainty analysis was to obtain a distribution of extracted butenedial vapor pressures was obtained by repeating the fitting procedure in Sect. S1 10000 times, each time using a set of parameter values sampled at random from the set of distributions describing their uncertainties. The mean of the extracted butenedial vapor pressures provides a central value for the butenedial effective vapor pressure. The standard deviation describes the uncertainty due to uncertainties in the other model input parameters as well as the standard error in the model fit coefficient.

The source of the uncertainty in diameter arises from a combination of inherent uncertainty in the measurement and droplet-to-droplet variability, though the characteristics of each droplet were kept as consistent as possible. The uncertainties in gas-phase diffusivity and scaling factor reflect uncertainties in the underlying parameters, rather than reflecting any variability in the values from particle to particle. The uncertainty in temperature does reflect the extent to which the EDB temperature drifted with time, though it should be noted the effect of temperature on the evaporation model over this range is limited. Each input parameter was represented by a Gaussian distribution centered at the mean value and with standard deviation based upon the variability or uncertainty in its measurements. The Monte Carlo approach assumes independence between each of the model input parameters, which is a reasonable assumption for this set of parameters. The distribution of each input parameter was treated separately for each experiment type (i.e., dry, humid, NaCl #1, NaCl #2, Na_2SO_4).

To calculate $P_{\mathrm{vap,eff}}$ for each iteration of the Monte Carlo technique, a value of a was used that accounted for the standard error in the value of a extracted from the curve-fitting procedure. A single value of a was sampled from a standard distribution centered at the optimal estimate of a, arising from the current iteration of curve-fitting procedure, and with standard deviation equal to the square root of the variance of the a estimate, again from the current iteration of the curve-fitting procedure. Using this sampled value of a in Eq. S2, the value of P_{vap} was calculated for a single iteration of the Monte Carlo technique.

References

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Jones, E., Oliphant, T., Peterson, P. and others: SciPy: Open source scientific tools for Python, [online] Available from: http://www.scipy.org/ (Accessed 23 February 2019), 2001–.