

Response to the comments of Anonymous Referee #1

Referee General Comment:

The authors have developed a new parameterization that predicts volatility of organic compounds containing oxygen, nitrogen and sulfur from the elemental composition that can be measured by soft-ionization high-resolution mass spectrometry. The parameterization is based on data from over 30,000 compounds taken from the National Cancer Institute (NCI) open database whose volatility was estimated by the US EPA's Estimation Programs Interface (EPI) Suite software. The newly developed parameterization is then used to predict volatility of 9053 organic compounds that were observed in various laboratory and field studies. The manuscript is well written and suitable for publication in ACP after addressing the following comments.

Responses:

We thank Anonymous Referee #1 for the review and the positive evaluation of our manuscript. Based on your constructive suggestions for improvement, we will expand discussions in the revised manuscript as detailed below.

Referee Comment 1:

1) There is some confusion in the way the term “volatility” is used in this manuscript. Both EPI suite software and EVAPORATION model predict saturation vapor pressure, which depends only on the given chemical compound and temperature. On the other hand, the term “volatility” is now routinely defined in atmospheric organic aerosol literature as effective saturation vapor pressure, which is saturation vapor pressure multiplied by activity coefficient. The activity coefficient is often not known, but it depends on temperature and which other compounds (and their relative amounts) are mixed with the compound of interest.

While the authors have actually developed the parameterization for predicting saturation vapor pressures, the confusion arises by referring to it as volatility and discussing the term in the context of literature on various volatility basis set (VBS)

frameworks that have been developed in the recent years (text on page 27879). The authors also state on line 26 on page 27879: “Volatility is a consequence of molecular characteristics of molar mass and chemical composition and structure,” which refers to “effective saturation vapor pressure” not “saturation vapor pressure.”

I suggest the authors replace “volatility” with “saturation vapor pressure” throughout the manuscript (including the title), except where the term “volatility” actually refers to “effective saturation vapor pressure.” The authors should also clearly define these two terms early in the manuscript to avoid any confusion.

Response: Thanks for this helpful comment. Following your suggestion, the terms “saturation vapor pressure”, “saturation mass concentration”, and “effective saturation mass concentration (volatility)” have been clarified in the section of Introduction. In the title we would like to keep “volatility”, which is a more common notation. We will include the below description in the revised manuscript.

“Saturation vapor pressure or the pure compound saturation mass concentration (C_0) is one of the key thermodynamic properties describing the equilibrium gas to particle partitioning of organic compounds (Pankow, 1994; Odum et al., 1996; Donahue et al., 2006; Krieger et al., 2012; Bilde et al., 2015). Effective saturation mass concentration (C^*) or volatility includes the effect of non-ideal thermodynamic mixing with an activity coefficient (γ): $C^* = \gamma C_0$ (Donahue et al., 2011, 2014; Zuend and Seinfeld, 2012). The terms volatility and saturation mass concentration can be used interchangeably with an ideal thermodynamic mixing assumption. The extent of importance of non-ideal mixing depends strongly on contents of hydrophobic and hydrophilic organic compounds, electrolytes and water (Zuend and Seinfeld, 2012; Shiraiwa et al., 2013b).”

2) Since the saturation vapor pressure for a given compound depends on temperature, please state the temperature at which the parameterization was developed. And so that it can be of practical use, please comment on how the parameterization might change with temperature.

Response: Thanks for this helpful comment. Following your suggestion, we will

expand discussions in the revised manuscript as detailed below.

“The temperature dependence of C_0 can be approximated by an Arrhenius type equation resembling the Clausius Clapeyron equation (Donahue et al., 2006; Cappa and Jimenez, 2010):

$$C_0(T) = C_0(T_{\text{ref}}) \left(\frac{T_{\text{ref}}}{T}\right) \exp\left[-\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right] \quad (3)$$

where T_{ref} is the temperature at a reference state (298 K in this study). The enthalpy of vaporization ΔH_{vap} (kJ mol⁻¹) could be estimated by C_0 , as there is a nearly linear relationship between $\log_{10}C_0$ (300K) and ΔH_{vap} (Epstein et al., 2010).”

Editorial comments:

Figure 1(c) legend: Please change to “tertiary amine” to “tertiary amine”.

Response: It has been corrected following your suggestion.

Figure 1(d) legend: Please change the first letter of the chemicals to small case.

Response: They have been corrected following your suggestion.

In Figure 1, X-axis is volatility and Y-axis is molar mass. In Figures 5-9 the X and Y axes are reversed. Please revise so that all figures have the same X and Y axes.

Response: Thanks for your suggestion. We would like to keep the axes in Fig. 1 to keep in accordance to the original representation of “molecular corridors” (Shiraiwa et al., 2014). We displayed saturation mass concentration as a function of molar mass in Figs. 5-9, which appears more straightforward for direct comparisons to mass spectra.

Figure 3 X-axis label: Please change “EPI suit” to “EPI suite”.

Response: It has been corrected following your suggestion.