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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Molecular corridors and parameterizations of volatility in the evolution of organic aerosols" *by* Y. Li et al.

Anonymous Referee #2

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Summary:

This paper furthers previous efforts to model the volatility of organic compounds based on their elemental composition. This is of great interest to members of the atmospheric community coupling soft ionization and high-resolution mass spectrometry techniques, which allows for precise molecular formula determination, but does not provide insight into molecular structure. To accomplish this, the authors utilized the Estimation Programs Interface (EPI) Suite to estimate the vapor pressure of more than 31,000 organic molecules contained in the National Cancer Institute open database. Each compound was grouped into one of six categories (CH, CHO, CHN, CHON, CHOS, CHONS) based upon its molecular formula. Multi-linear least squares analysis for each category was used to determine the proper coefficients to estimate saturation concentrations

based on Eq.1 in the text. This is an extension of saturation concentration estimates presented by Donahue et al. (2011), which now includes contributions from nitrogen- and sulfur-containing functional groups. Reasonable agreement is demonstrated for the volatilities predicted by Eq. 1 compared to both the EPI and EVAPORATION models. With the new volatility estimates, over 9,000 compounds observed in chamber or field measurements are presented within the molecular corridor framework outlined by Shiraiwa et al. (2014). This provides further evidence that molecular weight and volatility are key parameters that can effectively constrain reaction pathways for organic compounds in a variety of locations and oxidation regimes. This study is worthy of publication in ACP once the following comments have been addressed.

General Comments:

1) The EPI suite reports vapor pressures calculated in multiple ways (Antoine method, modified Grain method, Mackay method, mean of Antoine and Grain methods) with the MPBPWIN model. Which of these calculated values were used for the compounds in the NCI database? Additionally, it should be explicitly shown how these vapor pressures are converted to the saturation concentrations used for comparison with Eq. 1.

2) While the new parameters derived for use with Eq. 1 are very useful in the extension to nitrogen- and sulfur-containing organic compounds, this model still does not capture differences in volatility due to the number of hydrogens in the molecule. For example, an aldehyde with the molecular formula CxH2xO and a primary alcohol (CxH2x+2O) would erroneously be predicted to have the same saturation concentration. Even though this was also true for the equation reported by Donahue et al., 2011, it may be worth noting if efforts have been made to account for the number of hydrogen atoms in a given molecule.

3) While a thorough statistical analysis is presented for the comparison of volatilities from the EPI suite and Eq. 1, a similar analysis is lacking for the comparison of the EVAPORATION model with volatilities from Eq.1 and Donahue et al. (Figure 4). It is

reported “our newly developed parameterization also agrees well with EVAPORATION predictions and shows better agreement than Donahue et al. (2011).” This claim should be demonstrated from a statistical perspective. Additionally, from a visual perspective the new parameters appear to result in saturation concentrations biased high relative to the EVAPORATION estimates. Potential reasons for this discrepancy should be discussed.

4) For the figures showing multiple molecular corridor plots (Figures 5,6,7, and especially Figure 1), the larger symbols (representing the average properties for a given subclass of compounds) are indistinguishable unless the figure is magnified by a factor of 4-5. This muddles many of the discussion points focused on these reported averages (e.g. lines 10-12, page 27882 discussing trends in the CHN molecular weight, volatility relationship). Either these larger symbols need to be more pronounced over the smaller, individual compound symbols, or they should be plotted separately. Either way, Figure 1 especially needs to be increased in size. Also, figure 1 axes are switched from the remaining plots, why not just start with the axes plotted the way you will display throughout the remainder of the paper?

5) In Figure 8, there exists a homologous series of organosulfates with molecular weights between 400 – 600 g mol-1 and log10(C0) < -10, which appear to have distinct, lower dlogC0/dM values. Any characteristics of these compounds that differentiate them from the organosulfate and organonitrate compounds contained in the orange oval should be mentioned.

6) In Table S1, the log10(C0) values are being reported with units of μg m-3 when they should be dimensionless. The same issue exists with the reported mean bias and mean absolute gross error values. These statistics were either calculated with the dimensionless saturation concentrations, and should be reported as dimensionless, or should be recalculated as such.

Specific Comments:

1) Page 27879, Lines 26-27: Reword to read “Volatility is a consequence of the molecular characteristics of molar mass, chemical composition, and structure.”

2) Page 27880, Line 15: These references are not all soft ionization techniques. Please check these references, or be more generic to how these studies determined elemental composition. This is an important point though. Methods not using soft ionization will contain fragments and not necessarily original molecules. Please describe the measurement methods used to obtain atmospheric data (section 4).

3) Page 27882, Lines 6-9: The sentence concerning the oxidation state of nitrogen- and sulfur-containing compounds should be moved to the end of the paragraph after the introduction of Figures 1d-f.

4) Page 27882, Lines 10-12: At this point in the text it has not been mentioned that the large symbols in these molecular corridor plots correspond to averages for the different compound sub-classes. Doing so would help drive home the point for the trends with the CHN compounds (along with addressing general comment #4).

5) Page 27884, Lines 11-13: Are the reported statistics (R, MAGE, MB) for each major class (CH, CHO, etc...) limited to compounds with molecular weights below 500 g mol-1? If so, why restrict this analysis to the lower molecular weight compounds when this was not apparently done in Figure 3? Please clarify what statistics are being reported here. Additionally, see general comment #6 concerning the use of units for these statistics.

6) Page 27886, Line 1: Change “events” to “event”.

7) Figure 1: Number of compounds in each class only shown in panels (a) and (b). Please add this information to panels c-f.

8) Figure 3: Change x-axes label from “EPI suit” to “EPI suite”.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 27877, 2015.