Supplementary Information

Both the EPA Estimation Program Interface (EPI) Suite and the SIMPOL group contribution method show an error on the order of half an order of magnitude in calculated vapor pressures in the volatility range of the compounds used in this work (Pankow and Asher 2008; U.S. EPA 2008). Therefore, the decision to use one over the other is a question of empirical fit to the data. Figure S1 shows the precision of the planar fit in the case of the EPI method and the SIMPOL method (Figures S1a and b respectively), where the calculated values are used to create a planar fit and then the known compounds are mapped back on to this fit. The values calculated and those estimated from the fit fall along the 1:1 line in both cases, but fall much closer to the line in the case of the EPI method. Furthermore, and perhaps more importantly, the error in the SIMPOL fit is strongly functional group dependent, suggesting a systematic error that is likely to adversely affect the \( v_p \)-fit. In addition, SIMPOL does not include a group contribution for a nitrile group, so alkynitriles are excluded from this fit though they are known to be present in the atmosphere. The error of these fits is shown in Figure S2 as the residual of the planar fit (that is, how far off of the 1:1 line a compound falls). The standard deviation for the error of the EPI method is 0.5 orders of magnitude, which is approximately the error expected from a group contribution method. The error for the SIMPOL method is twice that. The EPI method is therefore selected because it has a better fit, less systematic error, and a method that allows a fit to be drawn based on a more inclusive suite of compounds. It must be noted that this is not necessarily a universal decision and does not speak to the accuracy of one method over another. Instead, this simply suggests that the properties that affect retention times for the particular columns used in this work are more closely mirrored by the parameterization of the EPI method. Future applications of this method should perform a similar sensitivity analysis.

Table S1. List of 25 known and 10 confidently identified aliphatic compounds used in parameter fits. Forward Match (FM) and Reverse Match (RM) are measures of the certainty of the NIST library search match; in general, higher numbers indicate greater
certainty. All of the compounds in this table have been identified with high certainty. For a more in depth discussion, see Worton et al. (in review). "FM and RM are shown only for compounds identified in ambient samples. All other compounds used are from known standards."
<table>
<thead>
<tr>
<th>Compound</th>
<th>$t_R^1$</th>
<th>$t_R^2$</th>
<th>Compound class</th>
<th>O/C</th>
<th>$FM^a$</th>
<th>$RM^a$</th>
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<td>n-Tetradecane</td>
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<td>5-Hexyldihydro-2(3H)-furanone</td>
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<td>acid</td>
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<td>ester</td>
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<td>alkane</td>
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<td>3.1</td>
<td>ester</td>
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<td>740</td>
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<td>800</td>
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<td>n-Tetradecanoic acid</td>
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<td>0.9</td>
<td>acid</td>
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<td>6,10,14-Trimethyl-2-pentadecanone</td>
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<td>ketone</td>
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<td>617</td>
<td>684</td>
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<td>3.2</td>
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<td>617</td>
<td>684</td>
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<td>1.7</td>
<td>nitrile</td>
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<td>927</td>
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<td>ester</td>
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<tr>
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<td>1.7</td>
<td>nitrile</td>
<td>-</td>
<td>794</td>
<td>824</td>
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<td>0.3</td>
<td>alkane</td>
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<td>1.0</td>
<td>acid</td>
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<td>(Z)-9-Octadecenoic acid</td>
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<td>0.9</td>
<td>acid</td>
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<td>n-Octadecanoic acid</td>
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<td>0.9</td>
<td>acid</td>
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<td>alkane</td>
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<td>2.6</td>
<td>ester</td>
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<td>724</td>
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<td>1.4</td>
<td>ester</td>
<td>0.18</td>
<td>859</td>
<td>874</td>
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</table>
Figure S1. Vapor pressures as calculated by the (a) EPI method and (b) SIMPOL method compared to the values estimated from the planar fit.
Figure S2. Error of the EPI and SIMPOL planar fits as the difference between the value estimated from parameter fit and the value originally calculated by the method.