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 alkylnitriles 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*). [a]FM and RM are shown only for compounds identified in ambient samples. All other compounds used are from known standards.

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Compound	t_R[1]	t_R[2]	*Compound class*	*O/C*	*FM*[a]	*RM*[a]
n-Tetradecane	40.3	0.0	alkane	0.00		
5-Hexyldihydro-2(3H)-furanone	41.5	2.3	ester	0.20		
n-Pentadecane	42.3	0.1	alkane	0.00		
n-Dodecanoic acid	43.5	0.7	acid	0.17		
5-Heptyldihydro-2(3H)-furanone	44.2	2.8	ester	0.18		
n-Hexadecane	44.6	0.1	alkane	0.00		
5-Octyldihydro-2(3H)-furanone	47.1	3.1	ester	0.17		
Tetradecanenitrile	47.2	1.7	nitrile	-	674	740
2-Pentadecanone	47.4	1.1	ketone	0.07	800	878
n-Heptadecane	47.5	0.2	alkane	0.00		
Pristane	47.6	0.2	alkane	0.00		
Myristoleic acid	49.1	0.9	acid	0.14		
n-Tetradecanoic acid	49.4	0.9	acid	0.14		
n-Octadecane	50.6	0.2	alkane	0.00		
Phytane	51.1	0.3	alkane	0.00		
6,10,14-Trimethyl-2-pentadecanone	51.8	1.2	ketone	0.06	617	684
6-Nonyltetrahydro-2H-pyran-2-one	53.3	3.2	ester	0.14	617	684
Hexadecanenitrile	53.7	1.7	nitrile	-	876	927
2-Heptadecanone	53.8	1.1	ketone	0.06	715	767
n-Nonadecane	54.2	0.2	alkane	0.00		
Hexadecanoic methyl ester	54.6	0.7	ester	0.12	779	816
cis-9-Hexadecenoic acid	55.4	1.0	acid	0.13		
n-Hexadecanoic acid	56.0	0.9	acid	0.13		
n-Eicosane	57.4	0.3	alkane	0.00		
cis-10-Heptadecenoic acid	58.6	0.9	acid	0.12		
5-Dodecyldihydro-2(3H)-furanone	60.4	2.8	ester	0.13		
Octadecanenitrile	60.6	1.7	nitrile	-	794	824
n-Heneicosane	61.1	0.3	alkane	0.00		
(Z,Z)-9,12-Octadecadienoic acid	62.0	1.0	acid	0.11		
(Z)-9-Octadecenoic acid	62.2	0.9	acid	0.11		
n-Octadecanoic acid	63.1	0.9	acid	0.11		
n-Docosane	64.3	0.3	alkane	0.00		
5-Tetradecyldihydro-2(3H)-furanone	66.5	2.6	ester	0.11	688	724
n-Tricosane	67.5	0.3	alkane	0.00		
bis(2-ethylhexyl) hexanedioic ester	69.0	1.4	ester	0.18	859	874

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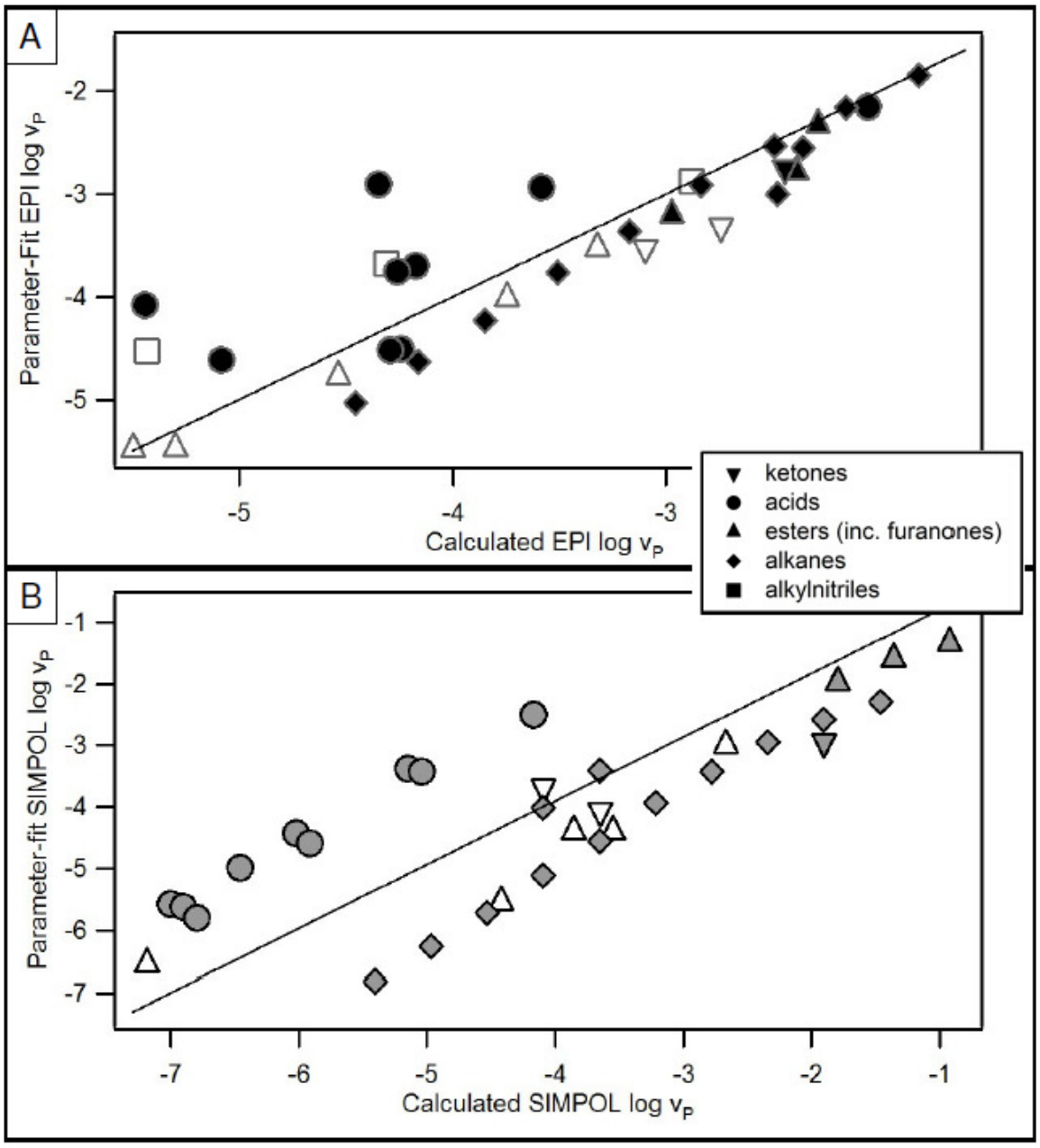

Figure S1. Vapor pressures as calculated by the (a) EPI method and (b) SIMPOL method compared to the values estimated from the planar fit.

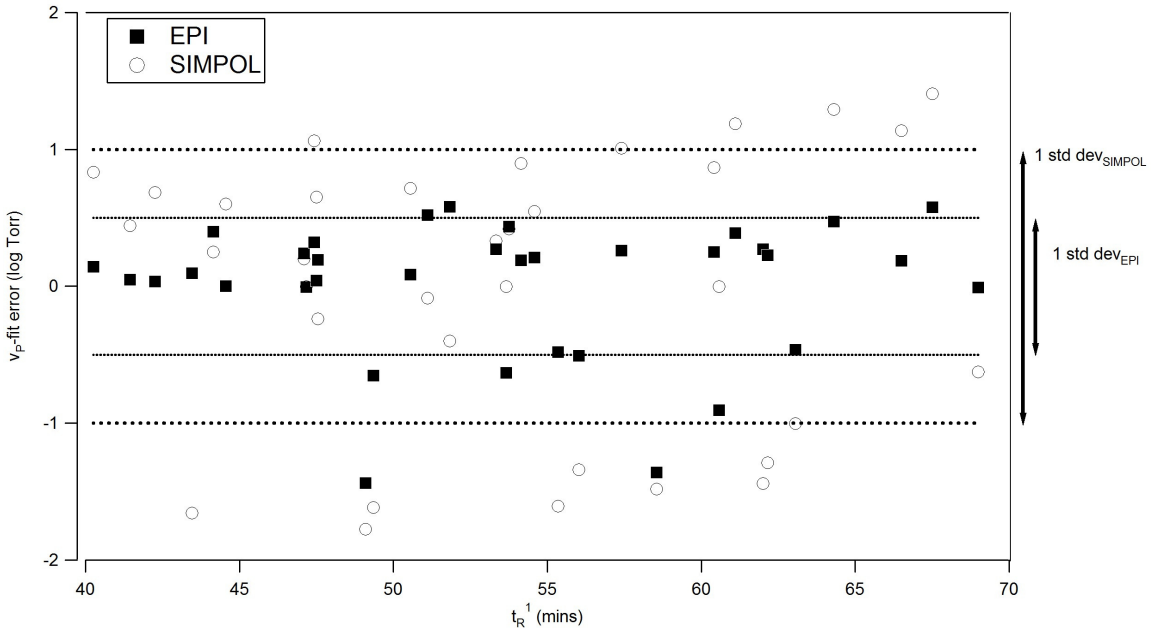

Figure S2. Error of the EPI and SIMPOL planar fits as the difference between the value estimated from parameter fit and the value originally calculated by the method.