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Experimental vapour pressures of eight n-Alkanes $(C_{17}, C_{18}, C_{20}, C_{22}, C_{24}, C_{26}, C_{28}$ and C_{31}) at ambient temperatures

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- 37 ABSTRACT
- We present direct room-temperature vapour pressure measurements for eight semi-volatile n-38 alkanes of atmospheric importance. Measured vapour pressures range from 8.4 \pm 1.6 x 10⁻³ Pa for 39 C_{17} , to 1.7 ±0.6 x 10⁻⁸ Pa for C_{31} . The new measurements for C_{17} - C_{18} are in reasonable agreement 40 but at the lower end of values in the literature; the new measurements for C_{28} and C_{31} are one-to-41 42 two orders of magnitude higher than most literature values, but six orders of magnitude higher than 43 the lowest values in the literature. Our measurements are suitable for atmospheric aerosol 44 modelling and interpretation of environmental measurements, interpolated in carbon number where 45 necessary, and extrapolated over temperatures relevant to the atmospheric boundary layer using the 46 Clausius-Clapeyron equation with literature values of the enthalpy of vaporisation. 47

Keywords: Physico-chemical properties; vapour pressure; n-alkanes

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50 1

INTRODUCTION

51 The equilibrium saturation vapour pressure (henceforth vapour pressure, p) of a compound is an 52 intrinsic physical property related to its molar entropy and molar volume, and which plays a crucial 53 role in determining a compound's transport behaviour in industrial, environmental, or biological 54 media. Vapour pressure is defined as the pressure exerted by a pure substance, at a given 55 temperature, in a system containing only the vapour and condensed phase (liquid or solid) of the substance at equilibrium (Calvert, 1990). The vapour pressure of a substance is highly dependent 56 57 upon temperature through the Clapeyron and Clausius-Clapeyron equations (e.g. Atkins et al. 2018), 58 and varies for different compounds of the same molecular mass due to molecular interactions (inter-59 and intramolecular in the condensed, and intramolecular in the vapour phase). For a substance to be in phase equilibrium, it must be in chemical, thermal and mechanical equilibrium (Bilde et al., 60 61 2015).

62

Many compounds of environmental interest - e.g., sulphuric acid, persistent organic pollutants, and 63 64 (our focus in the current study) organic compounds derived from crude-oil fractionation — have small but environmentally important vapour pressures, the accurate measurement of which poses a 65 significant experimental challenge, particularly for semi-volatile (1 to 10^{-6} Pa at room temperature) 66 and 'non-volatile' ($p < 10^{-6}$ Pa) organic compounds. Given the exponential increase in the number of 67 unique isomers possible as a function of carbon atoms in an organic molecule, the number of 68 organic compounds in an atmospheric sample could be in the range of $10^3 - 10^4$ (Goldstein and 69 70 Galbally, 2007). Comparing these relative numbers with the experimental saturation vapour 71 pressure literature available for atmospherically relevant organic molecules, it is evident that very 72 limited data are available for low volatility and polyfunctional molecules, largely due to 73 measurement challenges (Barley and McFiggins, 2010; Compernolle et al., 2011; Bilde et al., 74 2015). There are, however, well established experimental methods that provide good results at low pressures; for example the transpiration (Verevkin et al., 2000) and the Knudsen effusion techniques 75

(Dekruif and Vanginkel, 1077; Hallquist et al., 1997). Vapour pressure measurements have been
conducted at ambient temperatures for few organic compounds using different techniques based
upon the rate of evaporation of a compound under well controlled conditions (Razzouk et al., 2009;
Cappa et al., 2007; Koponen et al., 2007). The majority of studies however, estimate *p* from
experiments performed at high temperatures (Sawaya et al., 2006; O'Meara et al., 2014 and refs
within), with subsequent extrapolation to ambient temperatures.

82

83 Ultrafine particles (UFP, with particle diameter Dp < 100 nm) in the urban atmosphere are dominated by particles composed of semi-volatile organic compounds (SVOC) (Harrison et al., 84 85 2011; Kumar et al., 2014). Accumulating evidence indicates that UFP are toxic and have potentially harmful effects on human health (Atkinson et al., 2010). In order to understand and model the 86 atmospheric behaviour of SVOC, it is necessary to specify their chemical composition, their phase 87 88 partitioning and the size distribution of the particulate fraction, and the vapour pressures of the 89 constituent molecules (Harrison et al., 2019; Nikolova et al., 2018). Diesel exhaust vapour and particulate phases consist of SVOC in the range $C_{12} - C_{34}$ (Alam et al., 2016). Many of these SVOC 90 91 in UFP have solid-liquid phase transitions at temperatures well above room temperature but are 92 usually regarded as being present in UFP as super-cooled liquid mixtures. Thus, vapour pressures, 93 at atmospherically relevant temperatures (i.e., approximately 240-310K for the near-surface 94 atmosphere), are of fundamental importance for developing atmospheric and thermodynamic models Clegg et al., 2008). For unstudied compounds (usually those without industrial 95 96 applications), numerous vapour pressure estimation techniques are available in the literature, based, 97 for example, on structure-activity relationships. For compounds with industrial applications, 98 experimental data for vapour pressures and thermodynamic quantities may exist but at much higher 99 temperatures than found in the atmosphere (Barley and McFiggans, 2010). Vapour pressure 100 estimation and extrapolation methods have recently been reviewed (Bilde et al., 2015; O'Meara et al., 2014; Barley and McFiggins, 2010). Since the measured thermodynamic property data are 101

102 ACCEPTED MANUSCRIPT scarce and mostly unavailable for atmospherically relevant compounds, these estimation methods 103 are widely used as an approximation.

104 n-Alkanes are important constituents of the atmosphere, arising from both anthropogenic and 105 biogenic sources (Dunmore et al., 2015; Harrad et al., 2003; Sartin et al., 2002; Fraser et al., 1997). 106 Compounds from C_{10} to C_{30} partition between the vapour and condensed phases, and hence influence concentrations of airborne particulate matter (Fujitani et al., 2012; Lipsky and Robinson, 107 2006). C_{10} to C_{30} n-alkanes are important components of vehicle emissions, deriving from both 108 109 diesel fuel and lubricating oil (Sakurai et al., 2003; Karjalainen et al., 2016; Alam et al., 2016). 110 Prediction of the atmospheric behaviour of diesel exhaust particles requires knowledge of the 111 physico-chemical properties of their chemical constituents, of which n-alkanes are among the most 112 abundant (Harrison et al., 2016; Alam et al., 2018).

113

114 The majority of literature values of vapour pressure of the n-alkanes were estimated from extrapolation of vapour pressures measured at higher temperatures (Chirico et al., 1989; Morgan 115 116 and Kobayashi, 1994; Sawaya et al., 2006; Razzouk et al. 2009). Very few studies have measured vapour pressures of n-alkanes at 298 K (Chickos and Hanshaw, 2004a; Chickos and Hanshaw, 117 2004b) and more recently extended measurements (and estimations) for n-alkanes up to $n-C_{92}$ 118 (Chickos et al., 2009). Although variability amongst reported vapour pressures is relatively small 119 120 for the more volatile compounds, literature values for the lower volatility compounds can vary by more than five orders of magnitude for a single compound (see Figure 3 of Nikolova et al., 2018 121 and cf. Figure 1, below). With such a large range of extrapolated vapour pressures for a given 122 compound, the behaviour of atmospheric models will depend greatly on which set of vapour 123 124 pressures is adopted (Nikolova et al., 2018).

125

In this study, the transpiration method is adopted to make new measurements of vapour pressures of eight low volatility n-alkanes (C_{17} , C_{18} , C_{20} , C_{22} , C_{24} , C_{26} , C_{28} and C_{31}) at close to ambient temperatures. In the transpiration method, a stream of nitrogen is slowly passed over the headspace above the pure n-alkane, picking up and transferring any material which is then trapped by a sorbent and analysed using comprehensive gas chromatography time-of-flight mass spectrometry. The vapour pressure is then calculated based on the mass of the compound transferred by the nitrogen gas stream (Verevkin et al., 2000).

133

134 **2. EXPERIMENTAL**

135 2.1 Experimental Setup

136 The experimental methodology was adopted from Verevkin et al. (2000) and is briefly described 137 here. Individual n-alkane standards, C₁₇, C₁₈, C₂₀, C₂₂, C₂₄, C₂₆, C₂₈ and C₃₁ were purchased from Sigma Aldrich, UK (purity >99%). Approximately 0.5 g of the individual n-alkane was dissolved in 138 dichloromethane (DCM, purity ≥99.9%; VWR International Ltd, UK) and ultrasonicated for 180 139 140 min at 298 K. The n-alkane was then coated onto 1 mm diameter glass beads; microscopy revealed the liquid coating to be present as a super-cooled liquid. Super-cooled liquid has a higher saturation 141 vapour pressure than the more thermodynamically stable, but presumably kinetically hindered, 142 crystalline solid. The coated beads were packed into a U-tube of length 20 cm and inner diameter 143 0.5 cm, and kept at a constant temperature of $298(\pm 2)$ K, using a dry bath/block heater. A gentle flow 144 of nitrogen (CP grade (N5.2) BOC, purity 99.9992%) was passed through the U-tube, such that 145 146 contact time with the coated beads was long enough to allow the vapour to equilibrate with the pure liquid phase, after which the saturated vapour was stripped out of the nitrogen gas flow in a 147 148 stainless steel thermal adsorption tube. Adsorption tubes (designed to collect SVOC from C_7 to C_{40}) 149 were packed with 1 cm quartz wool, 300 mg Carbograph 2TD 40/60 (Markes International Ltd, 150 UK), and were analysed using 2-dimensional Gas Chromatography Time of Flight Mass 151 Spectrometry (GC×GC-ToFMS). The optimum flow rate of nitrogen used in these experiments was between 15.6 - 31.2 cm³ min⁻¹, in order to not be too slow, thus avoiding transportation of material 152 from the U-tube due to diffusion, and not too fast, to ensure saturation of the nitrogen flow with the 153

n-alkane (Verevkin et al. 2000). Assuming that the saturated nitrogen flow was subject to Dalton's
law of partial pressures, the vapour pressure, *p* was calculated by assuming the validity of the ideal
gas law (eq 1).

157

$$p = \frac{mRT}{V(total)MW} \approx \frac{mRT}{V(N_2)MW}$$

(eq1)

159

158

Where *p* is the vapour pressure (Pa), *m* is the mass of the measured n-alkane (g), *R* is 8.3144598 J $K^{-1} \text{ mol}^{-1}$, *T* is temperature (K), *V(total)* is the total volume of gas sampled, which is closely approximated by *V(N₂)*, the calculated volume of N₂ (m³) and *MW* is the molar mass (g mol⁻¹). The vapour pressure, *p*, was calculated from the mass of the n-alkane collected on the adsorption tube after the sampling time period. Each experiment was repeated five times with the exception of n-C₃₁ (completed four times) as the time taken for this experiment was >10 days. Blanks were also sampled and all were below detection limit.

- 167
- 168 2.2 Analytical Instrumentation

169 Adsorption tubes were desorbed using thermal desorption (Unity 2, Markes International Ltd, UK) 170 and subsequently analysed using a gas chromatograph (GC, 7890A, Agilent Technologies, USA) equipped with a Zoex ZX2 modulator (Houston, USA). The first dimension was equipped with a 171 172 non-polar capillary column (SGE DBX5; 30 m, 0.25 mm ID, 0.25 µm - 5% phenyl polysilphenylene-siloxane), and the second dimension was equipped with a mid-polar capillary 173 column (SGE DBX50; 4.0 m, 0.1 mm ID, 0.1 µm – 50% phenyl polysilphenylene-siloxane). The 174 175 GC×GC was interfaced with a BenchTOF-Select, time-of-flight mass spectrometer (Markes International Ltd, UK) with a scan speed of 50 Hz and mass range 35 – 600 m/z. All data produced 176 177 was processed using GC Image v2.5 (Zoex Corporation, USA). The adsorption tubes were spiked with 1 ng of deuterated internal standards, eicosane- d_{42} and pentacosane- d_{52} (Sigma Aldrich, UK), 178

179 for quantification and desorbed onto the cold trap at 380°C for 15 min (trap held at 20°C). The trap 180 was then purged onto the first dimension column at 380°C and held for 3 min. The initial 181 temperature of the primary oven was 80°C and then increased by 2.5°C min⁻¹ to 320°C and held for 182 5 min. The initial temperature of the secondary oven was 80°C and was increased by 2.5°C min⁻¹ to 183 150°C and then increased by 3.0°C min⁻¹ to 330°C and held for 8 min. Helium was used as the 184 carrier gas at a constant flow rate of 0.8 L min⁻¹.

185

186 Compounds were identified based on the NIST mass spectral library, known retention times and in 187 conjunction with authentic standards. The quantification for n-alkanes was performed by the linear 188 regression method using seven-point calibration curves established between the authentic 189 standards/internal standard concentration ratios. The calibration curves for all n-alkanes were highly 190 linear (r^2 >0.99).

191

192 **3. RESULTS AND DISCUSSION**

The observed experimental vapour pressures are presented in Table 1, and illustrate the repeatability of the transpiration technique for measuring individual vapour pressures of n-alkanes. Due to the slight deviation in the temperature (296 – 300 K), the observed vapour pressures were adjusted to 298 K for each compound using the Clausius-Clapeyron equation, integrated assuming the enthalpy of vaporisation is independent of temperature over the range of the temperature correction (eq 2).

$$p_{298k} = \frac{p_i}{exp^{\left(\frac{\Delta H_{vap}}{R}\right)\left(\frac{1}{298} - \frac{1}{T_i}\right)}}$$

(eq 2)

200

199

201 Where p_{298K} is the vapour pressure at 298 K, p_i is the measured vapour pressure of n-alkane (*i*) at 202 observed T (K), ΔH_{vap} is the enthalpy of vaporisation (obtained from Chickos and Hanshaw,. 203 2004a), or calculated using $\Delta H_{vap} = -3.82(\pm 0.03) \ln p_i + 70.0(\pm 0.2)$ adopted from Goss and 204 Schwarzenbach (1999), *R* is the universal gas constant (8.3144598 J K⁻¹ mol⁻¹) and *T_i* is the 205 measured temperature during the experiment for specific n-alkane (*i*).

The ΔH_{vap} is a function of temperature and is not constant. Therefore, extrapolation of vapour pressures to higher temperatures or extrapolation from higher temperature data for a given compound to ambient temperatures leads to significant uncertainty. Unlike the majority of previously published literature (discussed herein), the experimental vapour pressures presented in Table 1 are made close to ambient temperatures (296 – 300 K) for all compounds and so the Clausius-Clapeyron equation can be used to adjust the presented vapour pressures to 298 K.

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213 **3.1** Comparison with Published Data

214 Figure 1 illustrates the absolute difference of log_{10} saturation vapour pressure between literature 215 data and measurements made in our lab. Although, the vapour pressure data presented in this study 216 are amongst the lowest for n-C₁₇ and n-C₁₈ alkanes in comparison to the literature, they are in reasonable agreement (see Figure 1). Similarly, the vapour pressure of $n-C_{20}$ alkane is lower than the 217 218 selected literature, but in excellent agreement with the estimation methods of Nannoolal et al. 219 (2008) and Myrdal and Yalkowsky (1997) when using the boiling point of Joback and Reid (1997). 220 There is very good agreement for n-C₂₂ and n-C₂₆ alkane vapour pressures when compared to the estimation method of Compernolle et al. (2008) and the experimentally determined pressures of 221 222 Goss and Schwarzenbach (1999), Chickos and Hanshaw (2004a) and Morgan and Kobayashi 223 (1994). For n- C_{24} and n- C_{28} alkanes, the experimental saturation vapour pressures are higher than 224 the saturation vapour pressures among the selected literature and these two compounds do not well 225 fit the linear trend seen in Figure 2. Their measured vapour pressures were, however, very repeatable (Table 1) and we have no reason to doubt the quality of the data. The saturation vapour 226 227 pressure of $n-C_{31}$ is in very good agreement with the estimation method of Compernolle et al. (2001) and the experimentally determined pressure reported by Chickos and Hanshaw (2004b), but 228

are relatively much higher than those estimated by Kudchadker and Zwolinski (1966), Nannoolal et
al. (2008) and Myrdal and Yalkowsky (1997); the latter two studies using the boiling point of
Joback and Reid (1987).

232 Kudchadker and Zwolinski (1966) report some of the lowest vapour pressures among the selected 233 literature (see Figure 1). They use an extrapolation of existing experimental data (measured by the 234 chemical and petroleum industries, at unreported but presumably much higher temperatures) for n-235 alkanes based on Antoine constants and the Kreglewski-Zwolinski correlation. The extrapolation 236 capabilities of the Antoine equation are limited; particularly for low pressures and near the triple 237 point, and it is usually utilised over a limited temperature range. Extrapolation of vapour pressure 238 data using the Antoine equation should be avoided when temperature intervals for correlation 239 exceed 50 K (Ruzicka and Majer ,1996). Their vapour pressures however, are in good agreement with those estimated by Nannoolal et al. (2008) and Mrydal and Yalkowsky (1997) when using the 240 241 boiling point of Joback and Reid (1987). Ruzicka and Majer (1996) investigated four types of empirical relationships frequently used for correlation of vapour pressure data, including Antoine, 242 Wagner, Quasi-polynomial and Cox equations. They demonstrated that the use of different types of 243 244 correlation equations can considerably affect the results of the extrapolation, and indicated that the Antoine equation revealed the poorest performance, which is related to over-fitting of the vapour 245 246 pressure data; a typical effect observed when using simple extrapolations with too many parameters. 247 Morgan and Kobayashi (1994) reported direct vapour pressure measurements of ten n-alkanes in the $C_{10} - C_{28}$ range, at temperatures between 323 and 588 K. Their data for n- C_{22} is in good agreement 248 249 with this study but there is less agreement for the less volatile n-alkanes (n- C_{24} and n- C_{28}). This is 250 due to the vapour pressures of the latter alkanes being measured at elevated temperatures (n-C₂₄: 251 453–588 K and n-C₂₈: 483–588 K). Vapour pressure data measured at the conditions of interest (298 252 K) have lower uncertainty than data that are extrapolated from significantly larger temperatures. The authors discuss that the accuracy of low pressure direct measurements can be affected by the 253 254 inadequacy of the experimental method, phenomenological effects, and thermal decomposition.

Vapour pressure data can also be affected by small impurities within the pure n-alkane, particularly 255 for the less volatile hydrocarbons, or vapours that may interfere with the measurements (e.g. 256 257 impurities present in the carrier gas). Thermal decomposition is known to limit the accuracy of 258 critical property measurements such as the critical pressure, critical temperature, melting and 259 boiling points (Morgan and Kobayashi,1991). The study also used the Wagner vapour pressure 260 equation to extrapolate between mid-pressure range data towards low reduced temperatures which 261 limits the flexibility of the relationship in low-pressure extrapolations. Many studies have identified 262 the Cox equation as the most reliable for extrapolation towards low temperatures as they offer the 263 possibility of changing both the number of parameters and the reference temperature and pressure 264 (Ruzicka and Majer, 1996). It is, therefore, not surprising that the reported vapour pressures in Chirico et al. (1989), Chickos and Hanshow (2004a) and Ruzicka and Majer (1993) are very 265 266 similar, and in excellent agreement, particularly for the low molecular weight n-alkanes.

267

As the chain length of the n-alkanes increases, the intermolecular van der Waals forces increase, up 268 269 until a chain length at which the sample can be vaporised only through rupture of the C-C bonds 270 (Morgan and Kobayashi, 1991). This occurs typically close to C_{100} , where samples will have a 271 melting point but no longer have a triple point. Most of the estimation methods reported in the literature require a normal boiling point that is used to extrapolate down to atmospherically relevant 272 273 temperatures (Barley and McFiggans, 2010). Due to the high boiling point, small errors in the slope can produce substantial differences in the predicted vapour pressure, particularly for the low 274 275 molecular weight compounds.

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277

3.2 **Use by Atmospheric Science Community**

278 A number of estimation methods to calculate vapour pressures have been used in the atmospheric science community (Myrdal and Yalkowsky, 1997; Nannoolal et al., 2008; Compernolle et al., 2011; 279 280 O'Meara et al., 2014). Myrdal and Yalkowsky, 1997 and Nannoolal et al. (2008) calculate vapour

ACCEPTED MANUSCRIPT pressures using the temperature boiling points of Joback and Reid (1987), Stein and Brown (1994) 281 (2004). example 282 and Nannoolal et al For UmanSysProp 283 (http://umansysprop.seaes.manchester.ac.uk) is an online web-based facility for the prediction of 284 properties of individual organic compounds (including sub-cooled liquid vapour pressure) using specific functional groups ((Topping et al., 2016). Under standard atmosphere conditions, the 285 methods of Myrdal and Yalkowsky (1997) and Nannoolal et al. (2008) using Joback and Reid 286 287 (1987) boiling points produce the lowest vapour pressures for the n-alkanes studied in comparison to the same methods but using the boiling point of Stein and Brown (1994), see Figure 2. The 288 289 discrepancy is more evident for n > 20, where the deviations of the sub-cooled vapour pressure 290 become very large. Many studies have reported that the method of Joback and Reid (1987) tends to 291 over-predict the boiling points of the compounds measured in this study, and hence underestimates the slope of the vapour pressure curve (Clegg et al., 2008; Barley and McFiggans, 2010; 292 293 Compernolle et al., 2011). On the other hand, the estimation of vapour pressure by Myrdal and Yalkowsky (1997) using the boiling point of Nannoolal et al. (2004) tends to overestimate vapour 294 pressures (2010). Figure 2 illustrates the substantial range of estimated (and measured) vapour 295 296 pressures for the studied n-alkanes. The disagreement between estimated vapour pressures of the 297 same compound at high molecular weight (over 9 orders of magnitude) illustrates the need to directly measure vapour pressures at the conditions of interest, and show the difficulties in 298 299 accurately extrapolating and predicting data at ambient temperatures. This is further discussed in 300 Nikolova et al. (2018).

301

A new vapour pressure estimation method ('EVAPORATION') for zero-, mono- and polyfunctional groups has recently been published (Compernolle et al., 2011). Although this method is particularly developed for oxidised biogenic molecules, it has been reported to produce accurate (O'Meara et al., 2014). O'Meara et al. (2014) in their assessment of vapour pressure estimates have compared the vapour pressure error of organic compounds based on seven methods, including

- 307 EVAPORATION. They show that the error in the vapour pressure among the 90 organic compounds
- 308 is relatively small for the EVAPORATION method (running close to zero).

309

310 Overall, the technique described in this study gave repeatable measurements and vapour pressures 311 intermediate between the highest and lowest values available from the literature, suggesting that the 312 literature data were subject to random error, exacerbated by the large temperature extrapolation, 313 rather than systematic bias. For atmospheric aerosol modelling and interpretation of environmental 314 measurements we recommend direct use of our data, interpolated in carbon number where 315 necessary, and extrapolated over temperatures relevant to the atmospheric boundary layer using 316 equation (2), above. Of the existing parameterisations, we have used Compernolle et al. (2011) as 317 base case in a recent modelling study (Nikolova et al., 2018) because it follows our direct 318 measurements reasonably well.

319

320 DATA ACCESSIBILITY

321 Data supporting this publication are openly available from the UBIRA eData repository at
 322 https://doi.org/10.25500/eData.bham.00000292

323

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328

329 CONFLICTS OF INTEREST

330 There are no conflicts to declare.

331 **REFERENCES**

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508 **TABLES LEGENDS**

ACCEPTED MANUSCRIPT

- 509**Table 1:**Saturation vapour pressure measurements for eight n-alkanes at ambient temperatures510(K). Vapour pressures at 298K were calculated using (eq2) and the average vapour511pressures reported with 1 σ standard errors including error propagation through equation5122 of the main text. Vapour pressures at 298K were calculated with the use of ΔH_v^a 513(experimental: Chickos and Hanshaw (2004a)) and ΔH_v^b (calculated: Goss and514Schwarzenbach, 1999).
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516 FIGURE LEGENDS

- 517 **Figure 1:** Absolute error of log₁₀ saturation vapour pressure between literature and our study. The 518 n-alkanes are detailed in the legend. Abbreviations in the x-axis are as follows: 519 (subscript 'e' denotes experimental studies): KU - Kudchadker and Zwolinski (1996), 520 CHR - Chirico et al. (1989), MO - Morgan and Kobayashi (1994), RU - Ruzicka and Majer (1993), GO – Goss and Schwarzenbach (1999), CH1 – Chickos and Hanshaw 521 522 (2004a), CH2 – Chickos and Hanshaw (2004b), N – Nannoolal et al. (2008), MY – 523 Myrdal and Yalkowsky (1997), CO – Compernolle et al. (2011). Abbreviations in parenthesis point to the boiling point method, as follows: (JR) – Joback and Reid 524 (1987), (SB) – Stein and Brown (1994), (N) – Nannoolal et al. (2004). 525
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Vapour pressure data for selected n-alkanes at 298 K. Abbreviations in the legend are as 528 Figure 2. follows: (subscript 'e' denotes experimental studies): KU – Kudchadker and Zwolinski 529 (1996), CHR - Chirico et al. (1989), MO - Morgan and Kobayashi (1994), RU -530 531 Ruzicka and Majer (1993), GO - Goss and Schwarzenbach (1999), CH1 - Chickos and 532 Hanshaw (2004a), CH2 – Chickos and Hanshaw (2004b), N – Nannoolal et al. (2008), MY – Myrdal and Yalkowsky (1997), CO – Compernolle et al.(2011), EPI Suite – U.S. 533 534 Environmental Protection Agency calculator. Abbreviations in parenthesis point to the 535 boiling point method, as follows: (JR) – Joback and Reid (1987), (SB) – Stein and Brown (1994), (N) – Nannoolal et al. (2004). 536

Table 1. Saturation vapour pressure measurements for eight n-alkanes at ambient temperatures (K). Vapour pressures at 298K were calculated using 537

538

(eq2) and the average vapour pressures reported with 1σ standard errors including error propagation through equation 2 of the main text. Vapour pressures at 298K were calculated with the use of ΔH_v^{a} (experimental: Chickos and Hanshaw(2004a)) and ΔH_v^{b} (calculated: Goss and Schwarzenbach, 539 540 1999).

			n-C ₁₈ Alkane					
		$\Delta \mathbf{H_v}^{\mathbf{a}}$ (KJ/mol)	$\Delta \mathbf{H_v^b} (\mathbf{KJ/mol})$			$\Delta \mathbf{H_v}^{\mathbf{a}}$ (KJ/mol)	ΔH_v^{b} (KJ/mol)	
		86.3 (±1.2)	88.86 (±0.28)			91.1 (±1.3)	93.02 (±0.29)	
		At 298	3 K		At 298 K			
	Vapour Pressure, p / Pa (10 ⁻³)					Vapour Pressure, p / Pa (10 ⁻³)		
297.5	5.30	5.62	5.63	300.0	2.78	2.18	2.17	
296.0	6.06	7.66	7.72	299.0	2.13	1.89	1.88	
296.5	8.36	9.97	10.02	298.5	2.59	2.43	2.43	
297.0	8.89	9.99	10.03	298.5	2.53	2.38	2.38	
296.5	7.23	8.63	8.67	297.0	1.87	2.12	2.12	
298		8.37 (±1.63)	8.41 (±1.64)	298		2.20 (±0.20)	2.20 (±0.20)	
		n-C ₂₀ Alkane				n-C ₂₂ Alkane		
		ΔH_v^a (KJ/mol)	ΔH_v^{b} (KJ/mol)			$\Delta \mathbf{H}_{\mathbf{v}}^{\mathbf{a}}$ (KJ/mol)	ΔH_v^{b} (KJ/mol)	
		101.9 (±1.4)	99.21 (±0.32)			111.9 (±2.7)	103.25 (±0.34)	
		At 298 K			At 298 K			
	Vapour Pressure, p / Pa (10 ⁻⁴)				Vapour Pressure, p / Pa (10 ⁻⁴)			
297.0	6.48	7.44	7.42	298.0	0.75	0.75	0.75	
297.0	2.50	2.87	2.86	298.0	1.61	1.61	1.61	
297.0	5.29	6.08	6.06	298.0	2.49	2.49	2.49	
298.5	4.52	4.22	4.23	298.5	2.07	1.92	1.93	
298.0	5.49	5.49	5.49	298.5	1.71	1.59	1.60	
298		5.22 (±1.57)	5.21 (±1.56)	298		1.67 (±0.56)	$1.67 (\pm 0.57)$	
		n-C ₂₄ Alkane				n-C ₂₆ Alkane		
		$\Delta \mathbf{H}_{\mathbf{v}}^{\mathbf{a}}$ (KJ/mol)	$\Delta \mathbf{H_v^b} (\mathbf{KJ/mol})$			$\Delta \mathbf{H}_{\mathbf{v}}^{\mathbf{a}}$ (KJ/mol)	ΔH_v^{b} (KJ/mol)	
		121.9 (±2.8)	101.63 (±0.32)			131.7 (±3.2)	115.58(±0.39)	
	At 298 K				At 298 K			
	Vapour Pressure, p / Pa (10 ⁻⁴)				Vapour Pressure, p / Pa (10 ⁻⁶)			
297.0	1.81	2.14	2.08	298.0	4.05	4.05	4.05	
297.0	2.23	2.63	2.56	299.0	6.15	5.15	5.26	
297.0	2.86	3.38	3.29	299.0	5.85	4.90	5.01	
297.0	2.74	3.24	3.15	299.0	8.29	6.94	7.09	
			19					

297.0	2.81	3.32	3.23	298.0	8.02	8.02	8.02	
298		2.94 (±0.48)	2.86 (±0.47)	298	0.00	5.81 (±1.45)	5.89 (±1.45)	
		n-C ₂₈ Alkane				n-C ₃₁ Alkane		
		$\Delta \mathbf{H_v}^{\mathbf{a}}$ (KJ/mol)	$\Delta \mathbf{H_v^b} (\mathbf{KJ/mol})$			$\Delta \mathbf{H_v}^{\mathbf{a}}$ (KJ/mol)	$\Delta \mathbf{H_v^{b}} (\mathbf{KJ/mol})$	
		141.9 (±4.9)	108.66(±0.36)			157.3 (±1.2)	139.00 (±0.48)	
		At 298 K				At 298 K		
	V	/apour Pressure, p / Pa		Vapour Pressure, p / Pa (10 ⁻⁸)				
298.0	4.75	4.75	4.75	297.0	0.76	0.94	0.91	
297.5	4.75	5.23	5.12	296.5	0.93	1.29	1.24	
297.5	3.55	3.90	3.82	298.0	2.37	2.37	2.37	
297.5	3.10	3.41	3.34	297.5	1.88	2.09	2.06	
297.5	3.47	3.82	3.74			5		
298		4.23 (±0.67)	4.15 (±0.67)	298		1.67 (±0.58)	1.65 (±0.59)	

542 Footnote:

543 Column 1 - Temperature of each experiment

544 Column 2 - Vapour Pressure calculated at that temperature (in Column 1), using eq 1.

545 546 547 Column 3 - Vapour pressures at 298K using ΔH_v^a and Clausius-Clapeyron equation (eq 2). ΔH_v^a determined experimentally by Chickos and Hanshaw³⁴ (which are almost identical to

the literature recommendations).

Column 4 - Vapour pressures at 298K using ΔH_v^b and Clausius-Clapeyron equation (eq 2). ΔH_v^b determined by using the simple equation in the manuscript text (Goss and

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548 Schwarzenbach³⁷.

ACCEPTED MANUSCRIPT 550 551 C₁₇H₃ C18H38 ▲ C₂₀H₄₂ **X C₂₂H₄**6 C24H50 C26H54 + C28H58 C₃₁H₆₄ 2 X li X 1 -**ж** ж ж 0 ۸ + + + ж +ж ж + ++ + + -5 + ٠ \$ -6 -7 Kue MY(JR) N(SB) CHRe Moe Ru_e CH1_e CH2_e N(JR) MY(SB) N(N) MY(N) со GOe

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Figure 1. Absolute error of log_{10} saturation vapour pressure between literature and our study. The n-553 554 alkanes are detailed in the legend. Abbreviations in the x-axis are as follows: (subscript 'e' denotes experimental studies): KU - Kudchadker and Zwolinski (1996), CHR - Chirico et al. (1989), MO -555 Morgan and Kobayashi (1994), RU – Ruzicka and Majer (1993), GO – Goss and Schwarzenbach 556 557 (1999), CH1 – Chickos and Hanshaw (2004a), CH2 – Chickos and Hanshaw (2004b), N –

Nannoolal et al. (2008), MY – Myrdal and Yalkowsky (1997), CO – Compernolle et al.(2011). 558

Abbreviations in parenthesis point to the boiling point method, as follows: (JR) – Joback and Reid 559

560 (1987), (SB) – Stein and Brown (1994), (N) – Nannoolal et al. (2004).

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Figure 2. Vapour pressure data for selected n-alkanes at 298 K. Abbreviations in the legend are as
follows: (subscript 'e' denotes experimental studies): KU – Kudchadker and Zwolinski (1996),

569 CHR – Chirico et al. (1989), MO – Morgan and Kobayashi (1994), RU – Ruzicka and Majer

570 (1993), GO – Goss and Schwarzenbach (1999), CH1 – Chickos and Hanshaw (2004a), CH2 –

571 Chickos and Hanshaw (2004b), N – Nannoolal et al. (2008), MY – Myrdal and Yalkowsky (1997),

572 CO – Compernolle et al.(2011), EPI Suite – U.S. Environmental Protection Agency calculator.

573 Abbreviations in parenthesis point to the boiling point method, as follows: (JR) – Joback and Reid 574 (1987), (SB) – Stein and Brown (1994), (N) – Nannoolal et al. (2004).

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Experimental Vapour Pressures of Eight n-Alkanes (C_{17} , C_{18} , C_{20} , C_{22} , C_{24} , C_{26} , C_{28} and C_{31}) Measured at Ambient Temperatures

Mohammed S. Alam, Irina Nikolova, Ajit Singh, A.R. MacKenzie and Roy M. Harrison

HIGHLIGHTS

- High MW alkanes are semi-volatile and vapour pressure is an important property
- Reported individual vapour pressures range over up to 8 orders of magnitude
- New measurements are made at tropospheric ambient temperatures