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# **The influence of particle composition upon the evolution of urban ultrafine diesel particles on the neighbourhood scale**

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42 **ABSTRACT**

43 A recent study demonstrated that diesel particles in urban air undergo evaporative shrinkage  
44 when advected to a cleaner atmosphere (Harrison et al., 2016,). We explore, in a structured and  
45 systematic way, the sensitivity of nucleation-mode diesel particles to changes in particle  
46 composition and saturation vapour pressure. We use a multi-component aerosol microphysics  
47 model based on surrogate molecule ( $C_{16}$ - $C_{32}$  n-alkane) volatilities. For standard atmospheric  
48 conditions (298 K, 1013.25hPa), and over timescales (ca. 100 s) relevant for dispersion on the  
49 neighbourhood scale (up to 1 km), the choice of a particular vapour pressure dataset changes the  
50 range of compounds that are appreciably volatile by 2-6 carbon numbers. The nucleation-mode  
51 peak diameter, after 100 s of model runtime, is sensitive to the vapour pressure parameterisations  
52 for particles with compositions centred on surrogate molecules between  $C_{22}H_{46}$  and  $C_{24}H_{50}$ . The  
53 vapour pressures of components in this range are therefore critical for the modelling of  
54 nucleation-mode aerosol dynamics on the neighbourhood scale and need to be better constrained.  
55 Laboratory studies have shown this carbon number fraction to derive predominantly from engine  
56 lubricating oil. The accuracy of vapour pressure data for other (more and less volatile)  
57 components from laboratory experiments, is less critical. The influence of a core of involatile  
58 material is also considered.

59

60 The new findings of this study may also be used to identify the Semi-Volatile Organic Compound  
61 (SVOC) compositions that play dominating roles in the evaporative shrinkage of the nucleation  
62 mode observed in field measurements (e.g. Dall'Osto et al., 2011). As well as reconciling model  
63 and observations, identifying the most significant vapour pressure regime for nucleation-mode  
64 dynamics offers a way to improve the computing efficiency of urban aerosol models by adopting  
65 simplified schemes for those less important components: e.g., an equilibrium scheme for low-  
66 carbon-number components and a linear scheme for high-carbon-number components.



## 67 1. INTRODUCTION

68 Ultrafine particles (UFP, with particle diameter  $D_p < 100$  nm) have been increasingly a focus of  
69 urban air research over the last two decades. The main source of UFP in outdoor urban air is  
70 typically road traffic (Kumar et al., 2014). Harrison et al. (2011) reported that on a busy highway  
71 in central London, UK, 71.9% of particles by number were traffic-generated; of which 27.4% are  
72 found in the semi-volatile exhaust nucleation mode, 38% are in the exhaust solid mode and the  
73 remaining 6.5% are from brake dust and resuspension (Harrison et al., 2011). The proximity of  
74 the UFP traffic source to the public, and the large number of UFP emitted by traffic, have  
75 prompted health-related research that has accrued evidence pointing to the toxicity and  
76 potentially harmful effects of UFP on human health (Atkinson et al., 2010). Experimental and  
77 modelling studies have advanced our understanding of the behaviour of urban air UFP, e.g. the  
78 relevant aerosol dynamics important to the evolution of the UFP in space and time (Allen et al.,  
79 2007; Biswas et al., 2007; Dall'Osto et al., 2011; Nikolova et al., 2011; Karnezi et al., 2014 ).  
80

81 Nonetheless, key information regarding the size-resolved composition of the UFP is missing,  
82 which limits our ability to determine the impact of gas-transfer processes on UFP evolution.  
83 Progress has been made in identifying the composition of traffic-generated particles (including  
84 the ultrafine fraction) by resolving the so-called ‘unresolved complex mixture’ (largely  
85 uncharacterised organics in traditional gas chromatography) via two-dimensional gas  
86 chromatography (GC×GC; Chan et al., 2013). Alam et al. (2016) show that emitted ultrafine  
87 diesel particles consist of a substantial amount of organic material from both unburnt  
88 diesel fuel and engine lubricating oil. They attribute the low molecular weight Semi-Volatile  
89 Organic Compounds (SVOCs, having carbon number  $< 18$ ) predominantly to the unburnt diesel  
90 fuel, whereas heavier SVOCs (carbon number  $> 18$ ) are attributed predominantly to the engine  
91 lubricating oil. A typical GC×GC separation is shown in the chromatogram (Figure 1) for diesel  
92 engine exhaust emissions in the particulate-phase Aitken mode ( $56 < D_p < 100$  nm). Compounds



93 are separated by volatility along the  $x$ -axis (first separation dimension) and by polarity in the  $y$ -  
94 axis (second dimension). Peak identification is based on retention indices and mass spectral data  
95 from the National Institute of Standards and Technology (NIST) library. The majority of  
96 chromatography peaks (identified as aliphatic alkanes, lower black polygons) are present between  
97  $C_{18}$  to  $C_{26}$ , corresponding to the compounds identified in the engine lubricating oil and particulate  
98 phase engine emissions (Alam et al. 2017). Bar charts above the chromatogram show the  
99 volatility distribution of total alkanes (red) and total identified compounds (black), indicating  
100 that, although many hundreds of individual chemical compounds are detected, the majority of the  
101 SVOCs emissions consist of alkanes. Both the alkane composition and the total composition  
102 distributions show a broad peak centred at  $C_{25}$ .

103

104 Most primary organic particle emissions are semi-volatile in nature and thus they are likely to  
105 evaporate with atmospheric dilution and moving away from the source (Robinson et al., 2007).  
106 This has been observed by Dall'Osto et al. (2011; see also Figure 1- S in Supplementary  
107 Information) as part of the REPARTEE campaign (Harrison et al., 2012). Dall'Osto et al. (2011)  
108 reported a remarkable decrease in the measured nucleation-mode peak particle diameter ( $D_{pg,nuc}$ )  
109 between a street canyon ( $D_{pg,nuc} = 23$  nm) and the downwind neighbourhood ( $D_{pg,nuc} = 8-9$  nm) ca.  
110 650 m distant in central London (UK). Nucleation formation of new particles in the atmosphere  
111 was ruled out as a possible reason for the observed behaviour. Instead, the decrease in particle  
112 diameter was attributed to the effect of evaporation and substantial mass loss from the particle  
113 surface (hereafter referred to as REPARTEE-like aerosol dynamics). Alam et al. (2016) present  
114 the composition of diesel UFP particles measured on a laboratory test-rig (cf. Figure 2-S in  
115 Supplementary Information), however the range of variability of the particle composition in  
116 emissions is still unknown. It is also not known how the organic material is distributed onto the  
117 nucleation and Aitken modes of the UFP distribution in the atmosphere.

118



119 Numerical experiments can test the plausibility of possible missing components of the system,  
120 and can advise on which experimental studies will be most likely to resolve the existing  
121 knowledge gaps. Nikolova et al. (2016) describe a modelling framework that can produce  
122 nucleation-mode dynamics consistent with observations. However, missing in that study is the  
123 identification of critical thermodynamic parameters and size-resolved composition that could  
124 determine or point to a REPARTEE-like aerosol dynamics.

125

126 In the present study, we develop a method to search the particle composition space — i.e. the  
127 volatility parameter space — to identify a group of surrogate n-alkanes in the  $C_{16}H_{34}$ - $C_{32}H_{66}$  range  
128 that could explain a decrease in the nucleation-mode particle diameter to 10 nm or below as seen  
129 in the measurements in London (Dall'Osto et al., 2011). We provide a more robust approach to  
130 identify crucial parameters responsible for the UFP behaviour in the atmosphere on the  
131 neighbourhood scale including the identification of parameter sets that are incompatible with the  
132 observed behaviour in urban air of nucleation mode UFP. We describe a new way to simulate and  
133 evaluate the role of the SVOCs composition on the atmospheric behaviour of the size-resolved  
134 urban UFP and examine more complex sets of composition involving a non-volatile core. We also  
135 assess the critical role of saturation vapour pressure on the size-resolved aerosol dynamics.

136

137 In this study we use Lagrangian box-model simulations of the evolution of urban ultrafine diesel  
138 particles on the neighbourhood scale (up to 1 km). Key results will be presented and discussed in  
139 the main text; more details are provided in the Supplementary Information. The Methodology  
140 section describes the modelling approach. The Results section presents the model output. In the  
141 Discussion and Conclusions sections, the key findings are summarised with suggestions for  
142 further work.

143

## 144 2. METHODOLOGY



145 We adopt a ‘surrogate molecule’ approach to UFP composition, based on the chemical speciation  
146 shown in analyses such as Figure 1. The composition of UFP is simulated as comprising n-  
147 alkanes from  $C_{16}H_{34}$  to  $C_{32}H_{66}$ , which are the most abundant compounds in Figure 1. Previously  
148 (Nikolova et al., 2016), we initialised the n-alkane abundance in gas and particle phases using  
149 roadside and urban background observations in Birmingham, U.K. (Harrad et al., 2003). In what  
150 follows, we retain this roadside gas-phase initialisation (see below), but choose a more general  
151 method for initialising the particle composition, in order to test the sensitivity of the results to the  
152 initialisation in a systematic way. By adopting a surrogate molecule approach, we are effectively  
153 anchoring the model volatility basis set in physico-chemical data, as discussed further below.

154

155 The SVOC mass fractions in a particle are represented by a truncated Gaussian distribution that is  
156 centred for each model run at a given n-alkane in the range from  $C_{16}H_{34}$  to  $C_{32}H_{66}$  with a standard  
157 deviation,  $\sigma$ , varying from 1 to 5. Below we call the surrogate n-alkane on which the composition  
158 distribution is centred, the *modal composition*. Example compositions are shown in Figure 2 for a  
159 Gaussian distribution centred at  $C_{24}H_{50}$ . A narrower mass distribution, with  $\sigma = 1$ , focuses  
160 predominantly (ca. 40%) on the component, j ( $C_{24}H_{50}$ ), at which the distribution is centred, with a  
161 smaller (ca. 24%) contribution from the adjacent compounds  $C_{23}H_{48}$  and  $C_{25}H_{52}$ , and a minor  
162 contribution (ca. 5%) from  $C_{22}H_{46}$  and  $C_{26}H_{54}$ . The contribution of the remaining compounds from  
163 the tail of the distribution is very low and less than 1%. However, a wider mass distribution (e.g.  
164  $\sigma = 5$ ) approximates a flat distribution and includes a contribution from the majority or all of the  
165 compounds in the n-alkane range  $C_{16}H_{34}$ - $C_{32}H_{66}$ . Monotonically decreasing distributions occur for  
166 distributions centred at either end of the  $C_{16}H_{34}$ - $C_{32}H_{66}$  range. Overall, if one excludes the  
167 compounds with less than 1% contribution, modal compositions centred at carbon number, j, with  
168  $\sigma = 1, 2, 3, 4, \& 5$ , contain surrogate compounds +/- 2, 4, 7, 9, and 11 carbon numbers of j  
169 (formally, to remain in the 16-32 carbon number range,  $[\max(16, j-2): \min(32, j+2)]$ ,  $[\max(16, j-4): \min(32, j+4)]$ ,  
170  $[\max(16, j-7): \min(32, j+7)]$ ,  $[\max(16, j-9): \min(32, j+9)]$ , &  $[\max(16, j-$





171 11):min(32, j+11)]).

172

173 We use a Gaussian distribution to represent the composition of the particles because it provides a  
174 structured and systematic way to evaluate the organic-aerosol phase partitioning and the amount  
175 of organic matter in the UFP. This is important for the behaviour and evolution of the UFP at  
176 various timescales relevant for the urban atmosphere. Although there is no reason to discount  
177 other functional forms for the composition distribution (e.g., skew Gaussian, log-normal, Pareto,  
178 linear, etc), the Gaussian distributions chosen represent a simple two-parameter approach to  
179 explore the volatility/composition space available.

180

## 181 **2.1 Box Model**

182 The model used in this study is the UFP version (Nikolova et al., 2016) of CiTTY-Street (Pugh et  
183 al., 2012); that is, a box-model configuration that accounts for the multicomponent nature of the  
184 urban ultrafine particles. The CiTTY-Street-UFP model is used with 15 discrete size bins, with an  
185 initial diameter range between 5.8-578 nm in a uniform log-scale. The model can operate in two  
186 modes with respect to the aerosol dynamics: Eulerian (fixed particle-diameter grid) or Lagrangian  
187 (moving particle-diameter grid). The Eulerian mode is selected when the UFP size distribution is  
188 evaluated in the presence of emissions and exchange of particles between boxes (Nikolova et al.,  
189 2016). The Lagrangian mode can be selected when the UFP size distribution is evaluated for an  
190 isolated air parcel, i.e., when no emissions or transport between boxes are present. In this study,  
191 the Lagrangian mode is selected in a zero-dimensional configuration with no emissions or  
192 transport in/out of the box. The UFP dynamics (only condensation/evaporation) are simulated  
193 such that particles are allowed to grow/shrink to their exact size without any redistribution onto  
194 fixed bins in a grid with bin bounds left open in a fully moving diameter scheme (see, for  
195 example, Jacobson et al., 1997). The condensation/evaporation process accounts for Raoult's  
196 Law, the Kelvin effect, and a mass accommodation coefficient  $\alpha = 1$  (Julin et al., 2014) for all



197 components. The model results are evaluated at 1, 10 and 100 s. The timescale of 100 s is based  
198 on estimate of the travel time on the neighbourhood scale (i.e., horizontal travel distances  $\ll$  1  
199 km).

## 200 2.2 Modal Composition and Initial Size-Resolved UFP distribution

201 The initial size-resolved UFP distribution is based on the measurements of Dall'Osto et al. (2011)  
202 and reproduced in Figure 1-S in the Supplementary Information. This ultrafine size distribution  
203 represents the typical street canyon bimodal size distribution found next to a traffic site, e.g. next  
204 to Marylebone Road in London (UK). The distribution has a well-defined nucleation mode with a  
205 peak number concentration at  $D_{pg,nuc} \sim 23\text{-}24$  nm. The Aitken mode appears as a shoulder attached  
206 to the nucleation mode with a peak number concentration found at  $D_{pg,aim}$  between 50-60 nm.  
207 The initial UFP size-resolved composition is represented by modal compositions in the range  
208  $C_{16}H_{34}\text{-}C_{32}H_{66}$ , as detailed above, and a standard deviation  $\sigma$  from 1 to 5. A non-volatile core is  
209 included in the ultrafine particles. While studies broadly agree on the existence of a non-volatile  
210 core in the Aitken mode (Biswas et al., 2007; Wehner et al., 2004; Ronkko et al., 2013), it is  
211 unclear if nucleation-mode particles contain some non-volatile material or if they are entirely  
212 composed of (semi-)volatile SVOC. We have tested the sensitivity to the existence of non-volatile  
213 material in the nucleation mode particles by initialising with 1%, 5% or 10% by mass non-  
214 volatile material for each modal composition (see Supplementary Information for details of the  
215 initialisation); results are discussed later in this paper. Simulations are performed by considering  
216 the initialised Aitken mode predominantly non-volatile and coated only with 10% volatile  
217 material. This is based on the observations during the REPARTEE campaign (Harrison et al.,  
218 2012) that show a fairly stable Aitken mode between the street canyon and the neighbourhood.  
219 The initial size-resolved modal compositions, composition standard deviations and non-volatile  
220 core in the nucleation and Aitken modes are detailed in Tables 1-S, 2-S, 3-S and 4-S in the  
221 Supplementary Information. We also provide information on the input parameters of the log-  
222 normal UFP size distribution for Nucleation and Aitken modes.



223

### 224 **2.3 Saturation Vapour Pressures and Gas-Phase Concentrations**

225 The driving force for condensation/evaporation is the difference between the partial pressure of  
226 each representative SVOC and its saturation vapour pressure (hereafter vapour pressure) over the  
227 ideal solution in the nucleation mode condensed phase. Figure 3 shows vapour pressures above  
228 pure, flat, supercooled liquids for n-alkanes in the range  $C_{16}H_{34}$ - $C_{32}H_{66}$ , following Chickos and  
229 Lipkind (2008), Comperolle et al. (2011), the Epi Suite calculator (US EPA, 2017), and the  
230 UmanSysProp tool (Topping et al., 2016). The UmanSysProp tool provides vapour pressure data  
231 based on the work of Nannoolal et al. (2008) and Myrdal and Yalkowsky (1997) with the boiling  
232 points of Joback and Reid (1987), Stein and Brown (1994), and Nannoolal et al. (2004). There is  
233 a very substantial range of estimated vapour pressures for the same compounds in Figure 3,  
234 especially for the high molecular weight n-alkanes. The reported data agrees within an order of  
235 magnitude between  $C_{16}H_{34}$  and  $C_{19}H_{40}$ , but discrepancies of much more than an order of  
236 magnitude are evident for the high molecular weight compounds. An enormous difference in the  
237 vapour pressure for  $C_{32}H_{66}$  (from  $2.66 \times 10^{-5}$  Pa in Epi Suite down to  $3.20 \times 10^{-15}$  Pa in A-a) is clearly  
238 seen in Figure 3. Epi Suite (U.S. Environmental Protection Agency) provides the highest vapour  
239 pressures for all selected species in comparison with the rest of the data. Nannoolal et al. (2008)  
240 and Myrdal-Yalkowsky (1997) data, both using the boiling point of Joback and Reid (1987),  
241 provide similar results and present the lowest vapour pressures among the selected n-alkanes. For  
242 the purpose of our sensitivity study, three representative datasets are nominated as an input,  
243 namely Myrdal-Yalkowsky (1997) with the boiling point of Nannoolal et al. (2004, called B-c in  
244 Figure 3 and hereafter), Comperolle et al. (2011, called Co) and Nannoolal et al. (2008) with the  
245 boiling point of Joback and Reid (1987, called A-a). Hereafter we use the legend abbreviations in  
246 Figure 3 when referring to these selected vapour pressures, which are towards the upper, mid- and  
247 lower end of the reported data. The vapour pressure from the EPI Suite calculator has been  
248 omitted from the analysis below because it has been considered in our previous study (Nikolova



249 et al., 2016).

250

251 The gas-phase concentration in the box is initialised with measured gas-phase concentrations in  
252 the  $C_{16}H_{34}$ - $C_{32}H_{66}$  range from a traffic site (Harrad et al., 2003) and reported in Table 6-S in the  
253 Supplementary Information. All model simulations are run at 298 K; the effects of temperature on  
254 vapour pressure differences as a function of carbon number are discussed in the Supplementary  
255 Information.

256

257 We have performed a total of (17 modal compositions) x (5  $\sigma$  values) x (3 non-volatile core  
258 amounts) x (3 vapour pressures) = 765 model runs to explore the sensitivity of particle dynamics  
259 on the neighbourhood scale.

260

261 The Supplementary Information contains information regarding the initial size distribution,  
262 modal composition in the nucleation and Aitken modes, and gas-phase concentrations.  
263 Accumulation-mode aerosol (particles diameter  $D_p > 100$  nm) is not considered in this study.  
264 Accumulation-mode particles have much smaller number concentrations than the nucleation and  
265 Aitken modes in polluted urban areas, and are influenced by aging and transport over larger  
266 scales.

267

### 268 3. RESULTS

#### 269 3.1 Effect of composition on Nucleation-Mode Peak Diameter

270 We consider first model runs in which the vapour pressure data follows Compornolle et al. (2011)  
271 and nucleation mode particles initialised with 1% non-volatile material. The nucleation mode  
272 peak diameter  $D_{pg,nuc}$  is evaluated at 1 s and 100 s of model run-time in runs with varying modal  
273 composition and composition standard deviations. Figure 4 shows  $D_{pg,nuc}$  (y-axis) at 1s simulation  
274 time, for each model run, plotted with respect to the modal composition and composition standard



275 deviation,  $\sigma$ .

276

277 Figure 4 maps out the effect of nucleation-mode composition at this very early stage in the model  
278 simulation. For example, at  $\sigma = 1$  and initial mass distribution centred at  $C_{20}H_{42}$  (purple solid line  
279 with a square marker), the  $D_{pg,nuc}$  decreased from 23 nm (initial diameter at  $t = 0$  s) to 12 nm in  
280 one second due to evaporation of volatile material from the particles. At  $\sigma = 2$ ,  $D_{pg,nuc} = 15$  nm, a  
281 somewhat larger diameter than for  $\sigma = 1$ , due to the inclusion of material of lesser volatility in the  
282 particle composition and, hence, a decrease in evaporation overall. For modal compositions  
283 between  $C_{16}H_{34}$  and  $C_{20}H_{44}$ , an increase in  $\sigma$  leads to a pronounced deceleration in overall  
284 evaporation and, hence, a much larger nucleation mode peak diameter at 1 s simulation time. The  
285 opposite effect occurs for modal compositions of  $C_{22}H_{46}$  and above, i.e. increasing  $\sigma$  for a given  
286 modal composition decreases  $D_{pg,nuc}$  at 1 s. This is due to the addition of quickly evaporating  
287 lower molecular weight n-alkanes.

288

289 For a modal composition of  $C_{21}H_{44}$ , increasing  $\sigma$  makes almost no difference to the model  
290 outcome at 1 s; below, we call the modal composition that shows insensitivity to  $\sigma$  for a given  
291 model output time, the *threshold modal composition*. The model output time of 1 s corresponds to  
292 the evaporation timescale of  $C_{21}H_{44}$  under the current model setting, in analogy to the e-folding  
293 time for an exponentially decaying process. That is, at this time, a significant proportion (e.g.  $1-e^{-1}$   
294  $\sim 63\%$  for one e-folding time, and  $1-e^{-2} \sim 86\%$  for two e-folding times) of the initial mass has  
295 been evaporated. Furthermore, the timescales are much shorter for those lower-carbon-number  
296 compositions (e.g.  $C_{20}H_4$ ,  $C_{19}H_{40}$ , ...) and much longer for those higher-carbon-number  
297 compositions (e.g.  $C_{22}H_{46}$ ,  $C_{23}H_{48}$ , ...).

298

299 To continue the previous example of the modal composition of  $C_{20}H_{42}$ , the case with  $\sigma = 2$   
300 includes not only less volatile materials (i.e. higher-carbon-number SVOCs), but also an equal



301 amount of more volatile materials (i.e. lower-carbon-number SVOCs), as indicated by Figure 2.  
302 One might suppose that inclusion of the more volatile material would balance the effect of  
303 including less volatile materials. However, following our argument above, most of the lower-  
304 carbon-number compounds including  $C_{20}H_{42}$  will have evaporated before the given time of 1 s  
305 due to their having much shorter evaporation timescales than  $C_{21}H_{44}$ . Thus any material  
306 repartitioned from  $C_{20}H_{42}$  to the lower-carbon-number compounds, in changing the model settings  
307 from to  $\sigma = 1$  to  $\sigma = 2$ , will not alter the total amount of evaporation and thus the shrinkage rate.

308

309 To take a second example: for  $C_{22}H_{46}$ , any material reallocated from  $C_{22}H_{46}$  to the higher-carbon-  
310 number compounds (due to changing the model setting from  $\sigma = 1$  to  $\sigma = 2$ ) will contribute  
311 negligibly to the shrinkage simply because the evaporation timescales for those higher-carbon-  
312 number components are much longer than 1 s, whilst the materials repartitioned from  $C_{22}H_{46}$  to  
313 the lower-carbon compounds will contribute significantly to evaporation in the first second of  
314 model run-time, causing the decreasing trend of the curve shown in Figure 4.

315

316 One implication of this finding is that, if a timescale of 1 s is of interest, the aerosol dynamics of  
317 the system is dominated by the threshold modal composition of  $C_{21}H_{44}$ . Those lower-carbon-  
318 number compositions evaporate in less than 1 s and are approximately in equilibrium with their  
319 respective gas concentrations in the environment. The higher-carbon-number compositions  
320 evaporate slowly and at this time of 1 s, only a small or a negligible proportion has been  
321 evaporated. A few compositions with highest carbon numbers (e.g.  $C_{31}H_{64}$ ,  $C_{32}H_{66}$ ) have  
322 evaporated almost nothing. Therefore these compositions are effectively involatile for these  
323 conditions.

324

325 Nucleation-mode particles have an initial non-volatile mass of  $2.9 \text{ ng m}^{-3}$ . Modal compositions  
326 from  $C_{16}H_{34}$  to  $C_{19}H_{40}$  and  $\sigma = 1$  will lose all their volatile mass in 1 s (Table 1). The initial  $D_{\text{pg,nuc}}$



327 decreases from 23 nm to 9 nm and no volatile material is present, i.e. particles are composed of  
328 non-volatile core only. Little or no change is simulated in terms of mass and diameter for modal  
329 composition  $C_{32}H_{66}$ .

330

331 At 100 s, the evaporation of existing mass from the surface of the particles is evident also for  
332 higher molecular weight components (Table 1). The  $D_{pg,nuc}$  at 100 s is plotted in Figure 5. The  
333 diameter has further decreased with a more pronounced drop for all  $\sigma$  and modal compositions up  
334 to  $C_{25}H_{52}$ .  $C_{25}H_{52}$  is, therefore, the threshold modal composition at this model output time.

335

336 The horizontal line drawn at 10nm on Figure 5 corresponds to evaporation approximating  
337 REPARTEE-like behaviour. At  $\sigma = 1$ , modal compositions in the range  $C_{16}H_{34}$ - $C_{23}H_{48}$  — and  
338 vapour pressures and gas-phase partial pressures as detailed in the methodology — could  
339 plausibly explain a particle diameter decrease from 23 nm to  $\sim 9$  nm. Such a narrow range of  
340 surrogate molecular compounds is incompatible with experimental observations such as Figure 1.

341 At  $\sigma = 2$  and  $\sigma = 3$ , modal compositions from  $C_{16}H_{34}$  up to  $C_{22}H_{46}$  and  $C_{21}H_{44}$ , respectively, can  
342 plausibly approximate REPARTEE-like behaviour. At  $\sigma = 4$  and  $\sigma = 5$  modal compositions from  
343  $C_{16}H_{34}$  up to  $C_{19}H_{40}$  and  $C_{17}H_{36}$ , respectively, plausibly simulate REPARTEE-like behaviour.

344

### 345 **3.2 Effect of Vapour Pressure on the Nucleation-Mode Peak Diameter**

346 We compare the simulated nucleation-mode peak diameter,  $D_{pg,nuc}$ , at 100 s using the vapour  
347 pressure parameterisations B-c, Co and A-a (cf. Figure 3). The nucleation mode particles are  
348 initialised with 1% non-volatile material in these simulations.  $D_{pg,nuc}$  at 100 s using vapour  
349 pressure parameterisations A-a and B-c (see Supplementary Information), shows the same general  
350 behaviour as for vapour pressure parameterisation Co, but with a marked change in threshold  
351 modal composition. In order of decreasing vapour pressure (Figure 3), the threshold modal  
352 composition value changes from  $C_{27}H_{56}$  for the B-c parameterisation (Figure 4-S in the



353 Supplementary Information), to  $C_{25}H_{52}$  for Co (Figure 5), to  $C_{22}H_{46}$  for A-a (Figure 5-S in the  
354 Supplementary Information). We restrict ourselves to integer values of threshold modal  
355 composition to maintain a straightforward connection back to the homologous chemical series in  
356 Figure 1, although there is nothing in principle to prevent us from attributing real number values  
357 to the threshold modal composition.

358

359 There is no composition with  $\sigma = 4$  and  $\sigma = 5$ , at the lower volatility A-a vapour pressure  
360 parameterisation, that produces REPARTEE-like behaviour; i.e., decrease of the nucleation-mode  
361 peak diameter from 23 nm to 10 nm or below. At  $\sigma = 5$ , the nucleation-mode particles can lose a  
362 maximum of  $\sim 9$  nm of their initial diameter for modal composition  $C_{16}H_{34}$  (please refer to Figure  
363 5-S in the Supplementary Information). Little or no change in mode diameter is simulated for  
364 modal compositions between  $C_{24}H_{50}$  and  $C_{32}H_{66}$  and  $\sigma = 1$ , indicating that these combinations of  
365 composition and vapour pressure parameterisation are essentially involatile for the 100 s  
366 simulation time. Modal compositions  $C_{20}H_{42}$  ( $\sigma = 1$ ),  $C_{19}H_{40}$  ( $\sigma = 2$ ) and  $C_{17}H_{36}$  ( $\sigma = 3$ ) can  
367 produce REPARTEE-like aerosol dynamics.

368

369 Vapour pressure parameterisation B-c has the highest vapour pressure for all compounds in  
370 comparison with Co and A-a. Hence, particles in the nucleation mode are subject to a more  
371 pronounced evaporation, even for modal compositions  $C_{28}H_{58}$  to  $C_{32}H_{66}$ . Nonetheless, only modal  
372 compositions  $C_{25}H_{52}$  ( $\sigma = 1$ ),  $C_{24}H_{50}$  ( $\sigma = 2$ ),  $C_{23}H_{48}$  ( $\sigma = 3$ ),  $C_{21}H_{44}$  ( $\sigma = 4$ ) and  $C_{20}H_{42}$  ( $\sigma = 5$ ) are  
373 able to produce the REPARTEE-like behaviour. Table 2 provides details on the modal  
374 compositions and composition standard deviations that approximate the REPARTEE-like aerosol  
375 dynamics for B-c, Co and A-a vapour pressure parameterisations.

376

377 The difference in 100-s  $D_{pg,nuc}$  between the highest vapour pressure (B-c) and the lowest vapour  
378 pressure (A-a) for all values of  $\sigma$ , is shown in Figure 6. The largest differences (10-14 nm)





379 between the  $D_{pg,nuc}$  occur for modal compositions between  $C_{22}H_{46}$  and  $C_{24}H_{50}$  and  $\sigma = 1, 2, 3$ . For  
380 model run-time of 100 s, the variability of the UFP shrinkage due to the uncertainty of vapour  
381 pressure data is highest for the compositions between  $C_{22}H_{46}$  and  $C_{24}H_{50}$ . From Figure 3, we see  
382 that the uncertainty of vapour pressure data increases monotonically with carbon number and is  
383 highest for  $C_{32}H_{66}$ . However this high level of uncertainty for high-carbon compositions does not  
384 exert a significant impact on the model results. We thus conclude that the accuracy of vapour  
385 pressure values for very high or very low carbon compositions are not important for  
386 neighbourhood-scale aerosol dynamics.

387

### 388 3.3 Effect of Non-Volatile Core on the Nucleation Mode Peak Particle Diameter

389 To consider how the fraction of involatile core interacts with the SVOCs composition and the  
390 vapour pressure parameterisations, we define a ‘100-s effective involatile core’: the nucleation  
391 mode peak diameter at 100 s of evaporation. Figure 7 shows results for three non-volatile  
392 fractions (initial 1%, 5% and 10% based on mass) and vapour pressures A-a, B-c and Co (cf.  
393 Figure 3), for a modal composition of  $C_{16}H_{34}$ . Results for the remaining modal compositions are  
394 not plotted here because using modal composition  $C_{16}H_{34}$  and an evaporation time of 100 s gives  
395 the maximum reduction of the nucleation-mode peak diameter for all  $\sigma$  in our model runs.  
396 However, we show the results for modal compositions  $C_{24}H_{50}$  and  $C_{32}H_{66}$  for completeness in the  
397 Supplementary Information (Figure 7-S).

398

399 Because the mass-size distribution is held constant for each model initialisation (see  
400 Supplementary Information), an increase of the non-volatile material in the nucleation mode  
401 leads to a decrease in the total amount of n-alkane SVOC available for evaporation, and hence  
402 leads to an increase in the nucleation mode ‘dry’ (i.e. involatile core only) diameter from ~9 nm  
403 to ~12 nm. For the lowest volatility parameterisation (A-a), only the lightest surrogate  
404 compounds near  $C_{16}H_{34}$  are sufficiently volatile over the timescale of the model run to drive



405 evaporation of nucleation mode particles. As  $\sigma$  increases, an increasing number of lower volatility  
406 components are added into the particle composition, causing the 100-s effective involatile core to  
407 increase.

408

409 Considering REPARTEE-like behaviour, i.e., shrinkage of the nucleation mode diameter to ca. 10  
410 nm, initial involatile core fractions of 5% or greater do not reproduce the observed behaviour.

411

412

#### 413 4. DISCUSSION AND CONCLUSIONS

414 The purpose of this study was to evaluate the importance of particle composition and saturation  
415 vapour pressure on the evolution of urban ultrafine diesel particles on the neighbourhood scale  
416 ( $\ll 1$  km) by means of numerical simulations. We present the effect of evaporation on the size-  
417 resolved ultrafine particles and looked at the evolution of the nucleation-mode peak diameter

418  $D_{pg,nuc}$  depending on particle SVOC composition, vapour pressure, and fraction of involatile core  
419 in the particles. We have used laboratory measurements of the size-resolved composition of the  
420 ultrafine particles as an additional strong constraint on the plausibility of model parameter sets.

421 We identified a group of surrogate n-alkane compounds in the range  $C_{16}H_{34}$ - $C_{32}H_{66}$  that could  
422 explain REPARTEE-like aerosol dynamics measured in London (Dall'Osto et al., 2011): i.e., a  
423 final nucleation-mode peak diameter at 10 nm or below when particles were subject to  
424 evaporation in a timescale of 100 s. Table 2 highlighted the set of parameters in terms of vapour  
425 pressure and modal compositions that produce such REPARTEE-like behaviour.

426

427 Table 2 presents the sets of model parameters consistent with diameter reduction due to  
428 evaporation. The question remains, however, to what extent these results are realistic and relevant  
429 for the real-world atmosphere. Standard deviation  $\sigma = 1$  for all vapour pressures narrows  
430 significantly the contribution from the n-alkanes ( $[\max(16, j-2):\min(32, j+2)]$  for modal



431 composition  $j$ ), present in the initial composition of the nucleation mode particles. At  $\sigma = 2$ , the  
432 main contributing compounds involved in particle composition are the modal composition  $j$  and  
433 the surrogate molecules  $[\max(16, j-4):\min(32, j+4)]$ . This means that for the given vapour  
434 pressure parameterisation, A-a, and modal composition  $C_{19}H_{40}$ , the compounds found in the  
435 particles would be between  $C_{15}H_{32}$  and  $C_{23}H_{48}$ . However,  $C_{16}H_{34}$  is the lower limit of surrogate  
436 compounds in the model, so the Gaussian distribution of composition is truncated at the low-  
437 carbon-number end in this case. At  $\sigma = 3$ , the contributing compounds found in the particles are  
438 the surrogate molecules in the range  $[\max(16, j-7):\min(32, j+7)]$ . For a modal composition  $C_{17}H_{36}$   
439 and A-a vapour pressure, the range of participating compounds is  $C_{16}H_{34}$ - $C_{24}H_{50}$ , similar to the  
440 case of  $\sigma = 2$ . At  $\sigma = 4$  and 5, the majority of the surrogate molecules in our range of n-alkanes  
441 participate in the composition of particles, thus providing a reasonable range over the  
442 contribution from diesel fuel and engine lubricating oil. The range at  $\sigma = 3$  could be considered as  
443 a transition range, while examples at  $\sigma = 2$  would have compositions that are rather more limited  
444 than available measurements in the Aitken mode (e.g. Figure 1), with a focus on the contribution  
445 from the engine lubricating oil. Overall, narrow compositions would imply a strong gradient of  
446 SVOCs across the nucleation and Aitken modes whereas broad compositions imply that SVOCs  
447 are more or less evenly distributed across the ultrafine size range.

448

449 Table 3 shows an additionally constrained range of modal compositions consistent with what we  
450 know from field and laboratory measurements combined. The lowest vapour pressure  
451 parameterisations (A-a and the very similar B-a, see Figure 3) are less likely, at any modal  
452 composition standard deviation ( $\sigma$ ), to represent the laboratory and field observations together.  
453 The results reported in Alam et al. (2016) and in Figure 1 show that diesel ultrafine particle  
454 emissions are composed of a wealth of SVOCs that are mainly identified as straight and branched  
455 alkanes in the range  $C_{11}$ - $C_{33}$ , cycloalkanes ( $C_{11}$ - $C_{25}$ ), PAHs, various cyclic aromatics, alkyl  
456 benzenes and decalins. They report emitted particulate size fractionated concentrations of n-



457 alkanes (cf. Figure 2-S in Supplementary Information) and point out that particles in the 5-100nm  
458 diameter range consist mainly of high molecular weight SVOCs ( $>C_{24}H_{50}$ ) associated with engine  
459 lubricating oil.

460

461 Vapour pressure parameterisations used in this study and plotted in Figure 3, are one of the  
462 crucial input parameters in assessing the rate at which condensation/evaporation can occur,  
463 though they are poorly constrained. We introduced a new concept of threshold modal  
464 composition, i.e. modal composition that is not sensitive to  $\sigma$  for a given model output time. In an  
465 order of decreasing vapour pressure (Figure 3) and timescale of 100 s, the threshold modal  
466 composition value changes from  $C_{27}H_{56}$  for the B-c parameterisation (Figure 4-S, Supplementary  
467 Information), to  $C_{25}H_{52}$  for Co (Figure 5), to  $C_{22}H_{46}$  for A-a (Figure 5-S, Supplementary  
468 Information). Overall, the largest differences ( $\sim 14$  nm) in the 100-s  $D_{pg,mic}$  occur between the  
469 highest (B-c) and the lowest (A-a) vapour pressure parameterisations for modal compositions  
470 between  $C_{22}H_{46}$  and  $C_{24}H_{50}$  and composition standard deviation from 1 to 3. The vapour pressures  
471 of components in this range are therefore critical for the modelling of nucleation-mode aerosol  
472 dynamics on the neighbourhood scale. For components with volatility less than that for the  $C_{22}H_{46}$   
473 surrogate compound used here, all available vapour pressure parameterisations render these  
474 compounds volatile over the 100-s timescale. These components will equilibrate with the gas  
475 phase on these short timescales. Components with volatility greater than that of the  $C_{24}H_{50}$   
476 surrogate are effectively involatile over this timescale for all vapour pressure parameterisations,  
477 and so will remain condensed and out-of-equilibrium with the gas phase on these timescales.

478

479 The other variable which will influence evaporation rate is the concentration of vapour  
480 surrounding the particles. In this work, measured roadside vapour concentrations reported by  
481 Harrad et al. (2003) are used (see also Nikolova et al., 2016). These represent an upper estimate  
482 of gas-phase partial pressures away from roadside. Mixing of cleaner urban background air into



483 the simulated air parcel would lower partial pressures and increase evaporation rates.

484

485 The 100-s effective involatile core (the nucleation mode peak diameter at 100 s of evaporation)

486 increased from ~9 nm to ~12 nm. This was attributed to the decrease in the total amount of n-

487 alkane surrogate compounds present for evaporation. As composition standard deviation  $\sigma$

488 increased, an increasing number of lower volatility components added into the particle

489 composition caused the 100-s effective involatile core to further increase. Considering

490 REPARTEE-like behaviour, i.e., shrinkage of the nucleation mode diameter to ca. 10 nm, an

491 initial involatile core of 5% by mass or greater was not capable of reproducing the observed

492 behaviour in the atmosphere. Because the higher molecular weight (lower volatility) surrogate

493 molecules in the model are essentially involatile over the modelling timescale, the nucleation

494 mode dynamics due to SVOC is confounded with that due to the size of any involatile core

495 present in the particles.

496

497 Results (Figure 7) suggest that urban nucleation mode particles should be predominantly volatile

498 in order to produce REPARTEE-like behaviour. In these numerical experiments, the nature of the

499 non-volatile core need not be specified. This core could be composed of one or more low vapour

500 pressure compounds, not affected by condensation/evaporation on the timescale of the model and

501 measurements. On the other hand, as discussed in Nikolova et al. (2016), a non-volatile core

502 could be composed mainly of carbon and possibly some contribution from metal oxides and

503 sulphates. This difference in composition could be relevant to effects on human health. Li et al.

504 (2010) show that diesel truck emissions during idle induce a high level of oxidative stress in

505 human aortic endothelial cells, due to the type of metals and trace metals found in the exhaust,

506 while Xia et al. (2015) argue that traffic-related UFP act to promote airway inflammation due to

507 the rich content of organic species. The relative importance of these particles in affecting human

508 health merits further investigations.



509

510 Laboratory exhaust diesel ultrafine particulate measurements are highly dependent on the  
511 sampling methods. Measurements of the ultrafine particle composition from a diesel-fuelled  
512 engine are still at an early stage and therefore more efforts should be put into developing  
513 sampling protocols that target the composition of the nucleation and Aitken modes particles in a  
514 realistic manner. There are no robust UFP chemical composition measurements at street scale and  
515 therefore such measurements devoted to address in detail the composition of the traffic emitted  
516 UFP in the atmosphere are urgently needed. Saturation vapour pressure is another source of large  
517 uncertainties; our study lays out a strategy to determine which vapour pressures are most  
518 significant in a given modelling scenario.

519

520

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665 **TABLE LEGENDS**

666 **Table 1.** Total mass  $M$  ( $\text{ng m}^{-3}$ ) of nucleation mode peak particles at 1 s and 100 s of  
667 simulation for modal compositions  $\text{C}_{16}\text{H}_{34}$ - $\text{C}_{32}\text{H}_{66}$  and composition standard  
668 deviations, sigma. For comparison, the initial mass of the non-volatile material in the  
669 nucleation mode peak particles is  $2.9 \text{ ng m}^{-3}$ .

670

671 **Table 2.** Modal composition ranges and composition standard deviations, sigma, producing  
672 model results that approximate REPARTEE-like behaviour (see main text), for  
673 different vapour pressure parameterisations. Initial involatile core in the nucleation  
674 mode is set to 1%.

675

676 **Table 3.** Modal composition range and composition standard deviations, sigma, producing  
677 more realistic results that approximate REPARTEE-like behaviour. Vapour pressure  
678 parameterisation follows Myrdal and Yalkowski (1997; B-c in Figure 3),  
679 Compernelle et al. (2011; Co in Figure 3), and Nannoolal 2008; A-a in Figure 3).  
680 Column 'cn' indicates the carbon number of compounds n in the modal composition  
681 with a contribution bigger than 1%.

682

683

684 **FIGURE LEGENDS**

685 **Figure 1.** A GC×GC chromatogram (contour plot) indicating homologous series of compounds  
686 identified in diesel engine exhaust emissions. Emissions from a light-duty diesel  
687 engine operating at 1800 revolutions per minute and 1.4 bar brake mean effective  
688 pressure. Compounds identified in the contour plot are indicated by the coloured  
689 polygons – Lower black polygons are n- + i-alkanes; red polygons are monocyclic  
690 alkanes; green polygons are bicyclic alkanes; pink polygons are aldehydes + ketones;



691 and upper black polygons are monocyclic aromatics. Each peak in the contour plot  
692 represents a compound present in the emissions; warmer colours (e.g. red) are more  
693 intense peaks while colder colours (blue) are smaller peaks. Contour plot were  
694 produced by GC Image v2.5. Bar charts above show the volatility distribution of total  
695 alkanes (red) and total identified species (black), indicating that the majority of the  
696 emissions consist of alkanes. For details of the compound attribution method, see  
697 Alam et al. (2017).

698

699 **Figure 2.** An example of nucleation mode UFP compositions, represented as mass fractions for  
700 surrogate compounds  $C_nH_{(2n+2)}$ ,  $n = [16:32]$ , and described by a Gaussian distribution  
701 centred on  $C_{24}H_{50}$  with standard deviation,  $\sigma$ , from 1 to 5.

702

703 **Figure 3.** Vapour pressure data for selected n-alkanes  $C_nH_{(2n+2)}$  where  $n = [16:32]$  at 298K.  
704 Abbreviations in the legend point to the source as follows: A and B refer to the  
705 vapour pressure data from Nannoolal et al. (2008) and Myrdal and Yalkowsky  
706 (1997), respectively; -a, -b and -c refer to the boiling point of Joback and Reid  
707 (1987), Stein and Brown (1994) and Nannoolal et al. (2004), respectively; ES refers  
708 to Epi Suite calculator (U.S. Environmental Protection Agency); Co to Compernelle  
709 et al. (2011); Ch to Chickos and Lipkind (2008).

710

711 **Figure 4.** Nucleation mode peak diameter  $D_p$  [nm] at 1 s of simulation depending on the modal  
712 composition and the composition standard deviation. The initial nucleation mode  
713 peak diameter is at 23nm (not shown on the figure). Vapour pressure data follows  
714 Compernelle et al. (2011).

715



716 **Figure 5.** Nucleation mode peak diameter  $D_p$  [nm] at 100 s of simulation depending on the  
717 modal composition and the composition standard deviation. The initial nucleation  
718 mode peak diameter is at 23nm (not shown on the figure). Vapour pressure data  
719 follows Compernelle et al. (2011).

720

721 **Figure 6.**  $D_{pg,nuc}$  difference between the nucleation mode peak diameter (nm) when using B-c  
722 vapour pressure and the nucleation mode peak diameter when using A-a vapour  
723 pressure for modal compositions  $C_nH_{(2n+2)}$  where  $n = [16:32]$ .

724

725 **Figure 7.** Nucleation mode peak diameter  $D_p$  [nm] at 100 s: the ‘100-s effective involatile  
726 core’ for the nucleation mode. Results are shown at 1%, 5% and 10% initial non-  
727 volatile material in the nucleation mode particles, modal composition  $C_{16}H_{34}$  and for  
728 various composition standard deviations.

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1s		C <sub>16</sub> H <sub>34</sub>	C <sub>17</sub> H <sub>36</sub>	C <sub>18</sub> H <sub>38</sub>	C <sub>19</sub> H <sub>40</sub>	C <sub>20</sub> H <sub>42</sub>	C <sub>21</sub> H <sub>44</sub>	C <sub>22</sub> H <sub>46</sub>	C <sub>23</sub> H <sub>48</sub>	C <sub>24</sub> H <sub>50</sub>	C <sub>25</sub> H <sub>52</sub>	C <sub>26</sub> H <sub>54</sub>	C <sub>27</sub> H <sub>56</sub>	C <sub>28</sub> H <sub>58</sub>	C <sub>29</sub> H <sub>60</sub>	C <sub>30</sub> H <sub>62</sub>	C <sub>31</sub> H <sub>64</sub>	C <sub>32</sub> H <sub>66</sub>
742	Centre @																	
743	Sigma																	
	1	2.9	2.9	2.9	2.9	7.4	23.6	38.1	46.8	51.0	52.6	53.2	53.4	53.4	53.5	53.5	53.5	53.5
744	2	2.9	2.9	3.2	6.9	14.3	24.1	34.0	42.1	47.0	50.3	52.1	52.9	53.3	53.4	53.4	53.5	53.5
	3	3.7	5.4	8.4	12.9	18.5	24.9	31.6	38.1	43.5	46.8	49.3	51.0	52.1	52.8	53.1	53.3	53.4
	4	8.0	10.6	13.7	17.6	21.8	26.4	31.0	35.4	39.7	43.7	46.2	48.2	49.8	50.9	51.8	52.3	52.7
745	5	12.8	15.3	18.1	21.1	24.4	27.7	31.2	34.4	37.6	40.2	43.0	45.4	47.0	48.4	49.5	50.4	51.2
100s																		
746	Centre @																	
747	Sigma																	
	1	2.9	2.9	2.9	2.9	2.9	2.9	2.9	6.1	23.8	38.9	47.5	51.3	52.8	53.3	53.5	53.6	53.6
	2	2.9	2.9	2.9	2.9	2.9	2.9	3.0	6.2	14.3	24.8	34.8	42.5	47.6	50.6	52.1	52.9	53.2
748	3	2.9	2.9	2.9	2.9	3.1	4.2	7.1	11.9	18.2	25.2	31.9	37.8	42.6	46.1	48.6	50.3	51.4
	4	2.9	3.0	3.3	4.1	5.6	7.9	11.1	15.1	19.7	24.6	29.3	33.8	37.7	41.1	43.8	46.1	47.8
749	5	3.7	4.4	5.4	6.9	8.7	11.1	13.8	17.0	20.2	23.7	27.2	30.6	33.7	36.6	39.2	41.4	43.4

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751 **Table 1.** Total mass  $M$  ( $\text{ng m}^{-3}$ ) of nucleation mode peak particles at 1 s and 100 s of simulation752 for modal compositions C<sub>16</sub>H<sub>34</sub>-C<sub>32</sub>H<sub>66</sub> and composition standard deviations, sigma. For

753 comparison, the initial mass of the non-volatile material in the nucleation mode peak particles is

754 2.9  $\text{ng m}^{-3}$ .

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	Vapour pressure Sigma	B-c	Co	A-a
770	1	$\leq C_{25}H_{52}$	$\leq C_{23}H_{48}$	$\leq C_{20}H_{42}$
771	2	$\leq C_{24}H_{50}$	$\leq C_{22}H_{46}$	$\leq C_{19}H_{40}$
772	3	$\leq C_{23}H_{48}$	$\leq C_{21}H_{44}$	$\leq C_{17}H_{36}$
773	4	$\leq C_{21}H_{44}$	$\leq C_{19}H_{40}$	-
773	5	$\leq C_{20}H_{42}$	$\leq C_{17}H_{36}$	-

774

775 **Table 2.** Modal composition ranges and composition standard deviations, sigma, producing  
 776 model results that approximate REPARTEE-like behaviour (see main text), for different vapour  
 777 pressure parameterisations. Initial involatile core in the nucleation mode is set to 1%.

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796	Vapour pressure	B-c	Co	A-a	cn
	Sigma				-/+
797	1	-	-	-	2
	2	$C_{21}H_{44}$ - $C_{24}H_{50}$	$C_{21}H_{44}$ - $C_{22}H_{46}$	-	4
798	3	$C_{19}H_{40}$ - $C_{23}H_{48}$	$C_{19}H_{40}$ - $C_{21}H_{44}$	-	7
799	4	$\leq C_{21}H_{44}$	$\leq C_{19}H_{40}$	-	9
	5	$\leq C_{20}H_{42}$	$\leq C_{17}H_{36}$	-	11

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802 **Table 3.** Modal composition range and composition standard deviations, sigma, producing more  
 803 realistic results that approximate REPARTEE-like behaviour. Vapour pressure parameterisation  
 804 follows Myrdal and Yalkowski (1997; B-c in Figure 3), Compernelle et al. (2011; Co in Figure  
 805 3), and Nannoolal et al., 2008; A-a in Figure 3). Column 'cn' indicates the carbon number of  
 806 compounds n in the modal composition with a contribution bigger than 1%.

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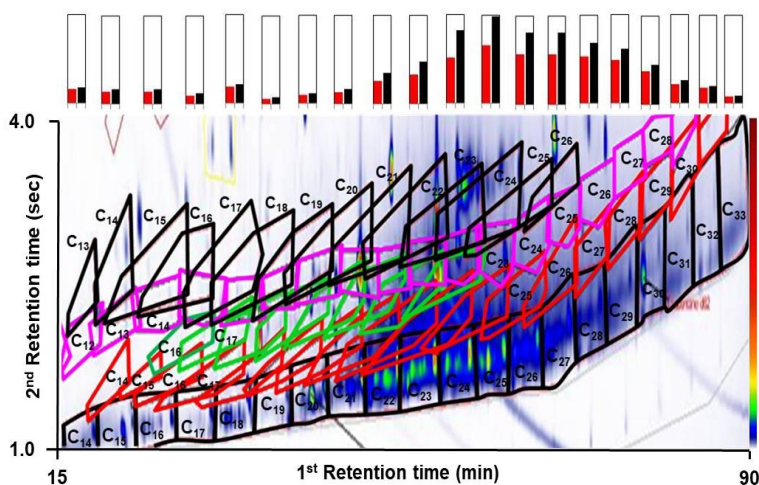
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**Figure 1.** A GC×GC chromatogram (contour plot) indicating homologous series of compounds identified in diesel engine exhaust emissions. Emissions from a light-duty diesel engine operating at 1800 revolutions per minute and 1.4 bar brake mean effective pressure. Compounds identified in the contour plot are indicated by the coloured polygons – Lower black polygons are n- + i- alkanes; red polygons are monocyclic alkanes; green polygons are bicyclic alkanes; pink polygons are aldehydes + ketones; and upper black polygons are monocyclic aromatics. Each peak in the contour plot represents a compound present in the emissions; warmer colours (e.g. red) are more intense peaks while colder colours (blue) are smaller peaks. Contour plot were produced by GC Image v2.5. Bar charts above show the volatility distribution of total alkanes (red) and total identified species (black), indicating that the majority of the emissions consist of alkanes. For details of the compound attribution method, see Alam et al. (2017).



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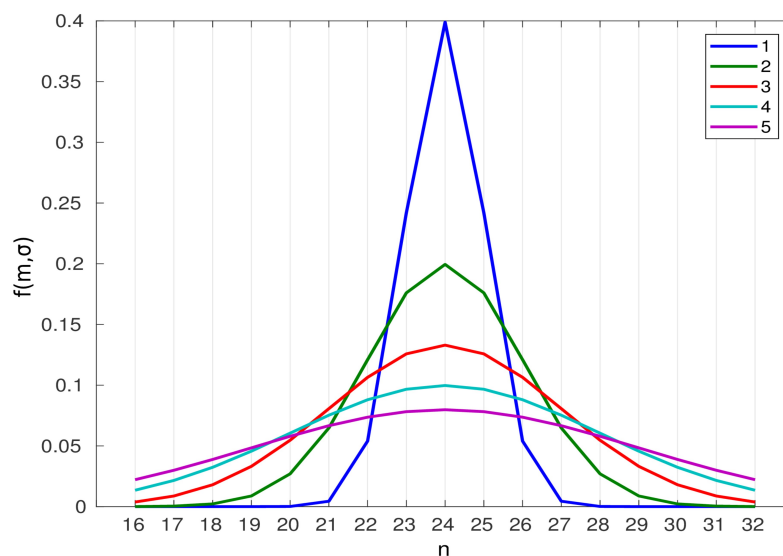
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858 **Figure 2.** An example of nucleation mode UFP compositions, represented as mass fractions for  
859 surrogate compounds  $C_nH_{(2n+2)}$ ,  $n = [16:32]$ , and described by a Gaussian distribution centred on  
860  $C_{24}H_{50}$  with standard deviation,  $\sigma$ , from 1 to 5.

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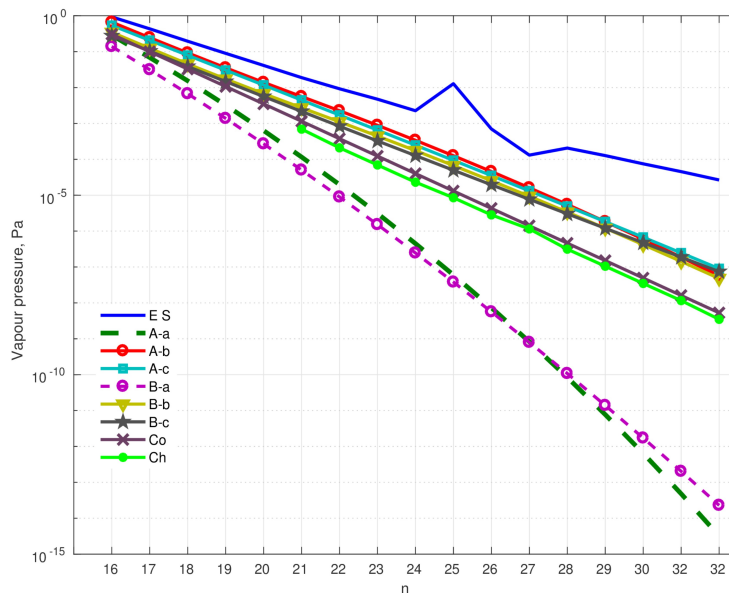
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**Figure 3.** Vapour pressure data for selected n-alkanes  $C_nH_{(2n+2)}$  where  $n=[16:32]$  at 298K.

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Abbreviations in the legend point to the source as follows: A and B refer to the vapour pressure

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data from Nannoolal et al. (2008) and Myrdal and Yalkowsky (1997), respectively; -a, -b and -c

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refer to the boiling point of Joback and Reid (1987), Stein and Brown (1994) and Nannoolal et al.

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(2004), respectively; ES refers to Epi Suite calculator (U.S. Environmental Protection Agency);

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Co to Compernelle et al. (2011); Ch to Chickos and Lipkind (2008).

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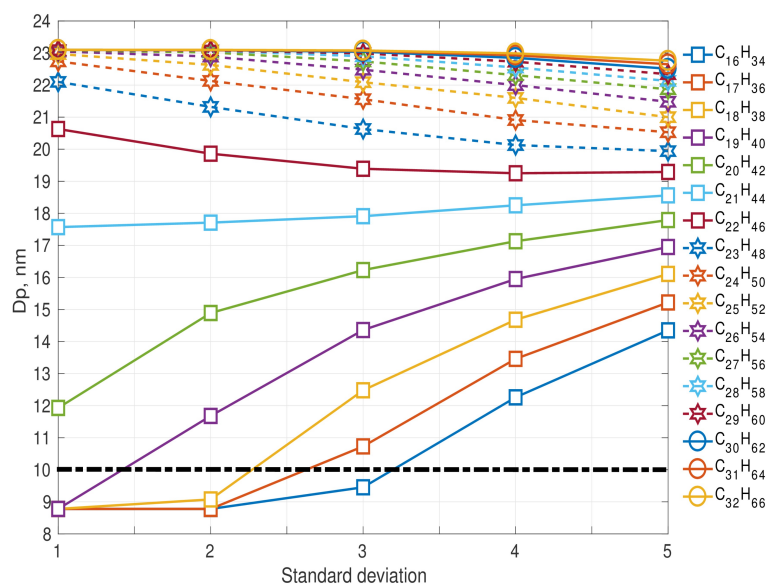
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910 **Figure 4.** Nucleation mode peak diameter  $D_p$  [nm] at 1 s of simulation depending on the modal  
911 composition and the composition standard deviation. The initial nucleation mode peak diameter  
912 is at 23nm (not shown on the figure). Vapour pressure data follows Compernelle et al. (2011).

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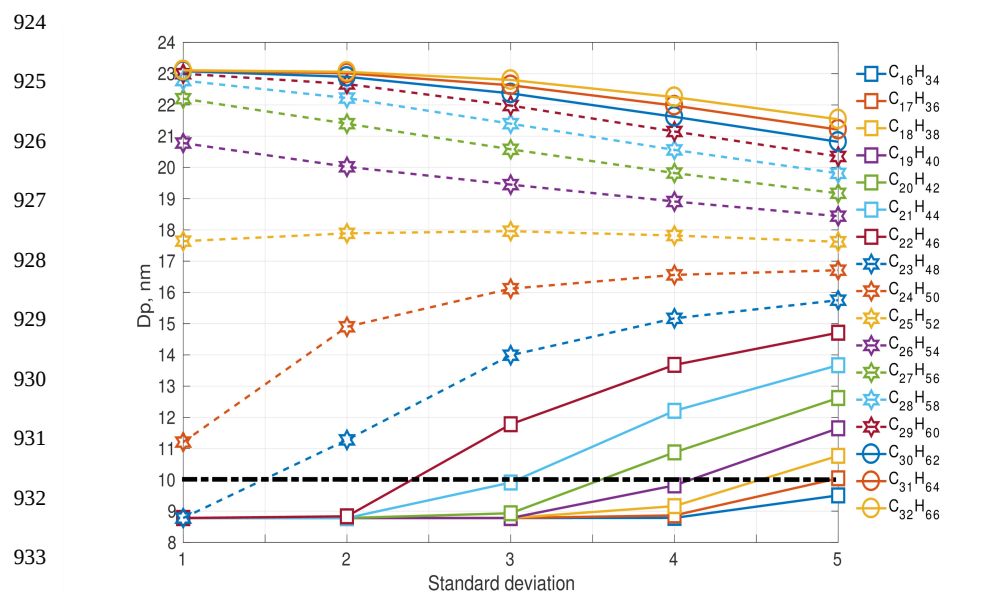
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936 **Figure 5.** Nucleation mode peak diameter  $D_p$  [nm] at 100 s of simulation depending on the  
937 modal composition and the composition standard deviation. The initial nucleation mode peak  
938 diameter is at 23nm (not shown on the figure). Vapour pressure data follows Compernolle et al.  
939 (2011).

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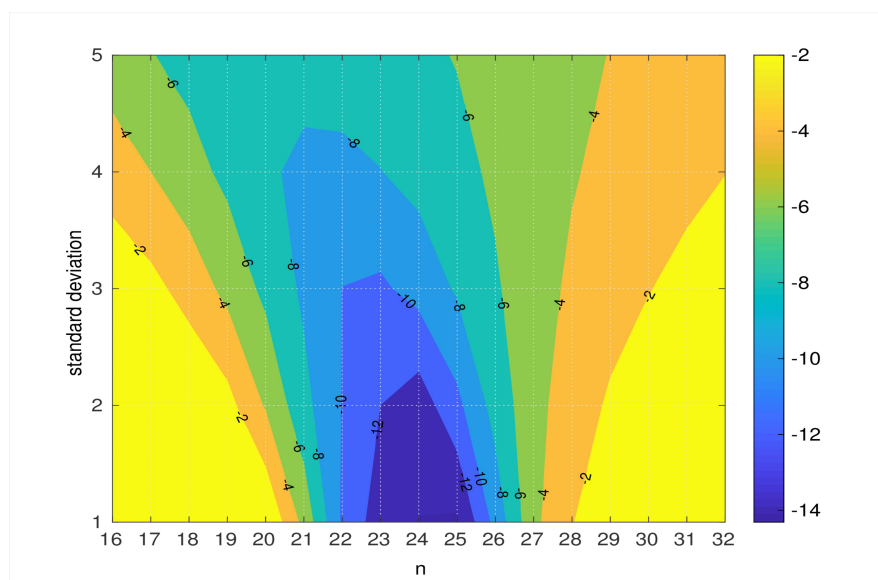
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**Figure 6.**  $D_{pg,nuc}$  difference between the nucleation mode peak diameter (nm) when using B-c

vapour pressure and the nucleation mode peak diameter when using A-a vapour pressure for

modal compositions  $C_nH_{(2n+2)}$  where  $n = [16:32]$ .

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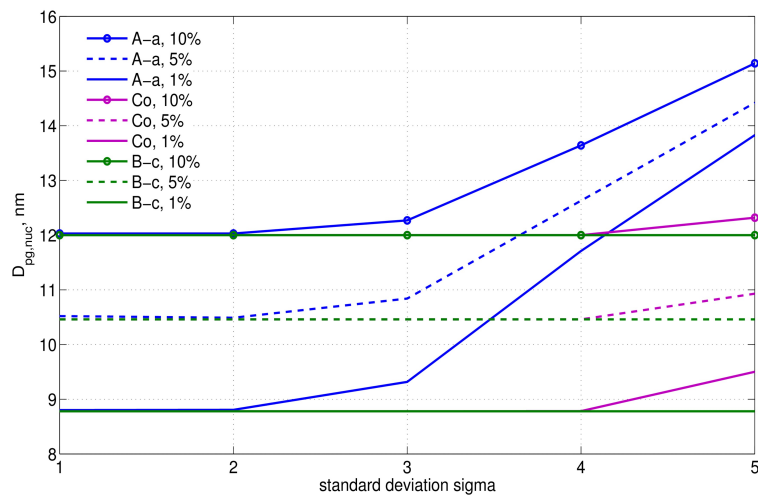
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**Figure 7.** Nucleation mode peak diameter  $D_p$  [nm] at 100 s: the ‘100-s effective involatile core’ for the nucleation mode. Results are shown at 1%, 5% and 10% initial non-volatile material in the nucleation mode particles, modal composition  $C_{16}H_{34}$  and for various composition standard deviations.