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Interactive comment on "The influence of particle composition upon the evolution of urban ultrafine diesel particles on the neighbourhood scale" *by* Irina Nikolova et al.

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The paper presents a targeted model study on the evaporative shrinking of diesel particles over timescales representative for the dispersion on the neighbourhood scale. The model study explores the sensitivity of nucleation-mode diesel particles to the volatility of the initial chemical composition represented by a mixture of surrogate molecules, the higher n-alkanes, in a very systematic manner. Gaussian distributions of the n-alkanes with carbon numbers between 16 and 32 with various bandwidths are systematically tested for three different vapour pressure datasets. The influence of a non-volatile core with various mass fraction in the nucleation mode is also tested. A new concept of

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threshold modal composition is introduced which allows identification of the components for which an accurate vapour pressure estimation is most critical. The paper is well written for the most part and results are presented in a structured way. Input datasets and model results of the study are well documented and easily accessible. It is claimed that the method has the potential to improve the efficiency of urban aerosol models. I had expected to see a comparison of the suggested simplifications with the full model and an estimate of the computational savings. The main problem is that the analysis was restricted to the process of condensation/evaporation alone. My reservations are expressed in the following.

Specific Comments

1.) The exhaust size distribution from laboratory test-rig measurements (Figure 2-S) shows a broad distribution of n-alkanes in the diameter range < 10-18 nm with a maximum at C29H60 and a range of +/-7 corresponding to sigma = 3. In contrast, most realisations of the current model setup resulted in solutions with a narrow distribution of n-alkanes with carbon number < 18 (this includes all solutions for vapour pressure datasets A-a and B-c) to explain the REPARTEE-like behaviour. These n-alkanes are predominantly in the gas-phase under ambient atmospheric conditions. Only for vapour pressure dataset B-c, which has the highest vapour pressure for all n-alkanes, the model gives solutions with carbon number > 20 and broad distributions (sigma =3 to 5) for the REPARTEE-like behaviour (P.15, lines 372-373). It looks like other processes, consistent with an initial nucleation mode composition of higher-carbon-number compounds, are relevant.

2.) Coagulation was obviously not included in the model setup (P.8, line 192). Coagulation is enhanced through the shrinking of particles by evaporation (Jacobson et al., 2005). As particles shrink, their coagulation rates with larger particles will increase. Although evaporation has a greater effect on the evolution on the particle size distribution in the first second, coagulation will become more important towards longer time scales and may be dominant at 100 s. When evaporation and coagulation are treated

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together, there will be a feedback of coagulation on the composition of nucleation mode particles. This is because coagulation affects the vapour pressures of n-alkanes in particles of a given size through the Raoult's Law. This feedback may well influence the calculated nucleation mode peak diameter.

3.) P.5, lines 114-116: The range of volatility of the particle composition in the diesel exhaust emissions is not known. However, formation of a volatile nucleation mode is evident in a laboratory system that mimics real-world dilution of diesel exhaust (Arnold et al., 2012; Rönkkö et al., 2013). Aerosol dynamics models show that low volatile and extremely low volatile organic compounds are required to explain the evolution of the volatile nucleation mode during cooling and expansion of the exhaust (Rönkkö et al., 2013; Pirjola et al., 2015).

4.) P.8, line 184: A higher number of bins representing the small particles would give a more accurate result for the relevant part of the size distribution. How does a larger number of size bins, for instance 25, change the result on the REPARTEE-like behaviour?

5.) P.9, line 197: how fast is the dilution in the first second? Preferably, the dilution ratio of the modelled total particle number after 1 s should be given and compared to literature data.

6.) P.11, line 251: Gas-phase n-alkanes C16H34 and C17H36 can be oxidized by the OH radical leading to oxygenated products with lower vapour pressures (Jordan et al., 2008). An estimate should be given how much gas-phase oxidation can affect the modelled size distribution on the time scale of 100 s.

7.) P.17, lines 409-410. Which assumptions were made regarding the mixing with the non-volatile core? If the non-volatile component is able to influence the gas-particle partitioning, for example due to its absorptive nature, then the evaporation rate will be affected by a decrease of the vapour pressure of the volatile compounds in the mixture through the Raoult's Law. If the non-volatile core is not in a mixture with the

n-alkanes, there is no Raoult's Law depression of the vapour pressure of the volatile compound. The assumption about the non-volatile core will also affect the conclusion about its chemical composition in the nucleation mode (organic carbon or lubricant oil metal compounds).

Technical Corrections

Abstract p.3, line 52-54. Mention the uncertainty range of the vapour pressures for n-alkanes between C22H46 and C24H50 based on the vapour pressure datasets displayed in Figure 3.

P.4, line 71: Add information on size range.

P.4, line 79: Jacobson et al. (2005) and Karl et al. (2016) should be included in this list.

P.7, line 168: missing ", respectively" at end of this line.

P.10, line 227-232 and Figure 3: the vapour pressure data from Lemmon and Goodwin (2000) should be included in Figure 3 to facilitate comparison with previous studies on the volatility of exhaust particles near roadways (Zhang and Wexler, 2004; Zhang et al., 2004; Karl et al., 2016).

P.10, line 237: A-a is mentioned before it is defined in the text.

P.11, line 270: Please add the abbreviation (Co) for this vapour pressure dataset here.

P.12, line 291: Here the concept of threshold modal composition is introduced for the first time. It would be good to add a paragraph on the reasoning behind this concept.

P.15, line 358: Although the model results with the vapour pressure dataset Co are explained in detail in section 3.1, it would help the reader to give a short summary of Co results regarding the REPARTEE-like behaviour before A-a and B-c results are discussed.

P.19, lines 472-477. There seems to be something wrong with the logic of the two

sentences. The second sentence contradicts with the statement on p.30, lines 492-493.

Figure 1: Contours of the GCxGC chromatogram are hardly visible due to the overlay with the coloured polygons. For clarity, it would be better to show the original chromatogram beneath the current figure plot. Annotate x-axis and y-axis of the upper bar charts.

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