Comment on "Modelling and measurements of urban aerosol processes on the neighborhood scale in Rotterdam, Oslo and Helsinki, M. Karl et al., ACPD 15, 35157-35200, 2015

There is much current interest in the atmospheric behaviour of nanoparticles derived from road traffic emissions. These typically dominate the particle number count in urban air and there have been few studies either by experiment or model to describe their behaviour when mixing away from busy roadsides. It is recognised that there is a rapid evolution of the size distribution during the first few seconds after emission from the tailpipe and, other studies have focussed on such processes. This paper deals with the downwind dispersion and evolution of size distributions subsequent to those tailpipe to roadside processes having taken place.

We have a basic conceptual disagreement with the way in which condensation/evaporation processes have been considered in this work and would also like to highlight the very confusing information provided by the authors in relation to this aspect. To set the context, one needs first to consider the tailpipe to kerbside dilution process. The raw exhaust gases contain predominantly graphitic soot-carbon particles and the vapour of hydrocarbons deriving from unburnt fuel and lubricating oil. During the immediate dilution and cooling of the exhaust gases, semi-volatile hydrocarbons become supersaturated and condense which causes the formation of the nucleation mode seen in roadside air (Charron and Harrison, 2003) as well some condensational growth of the larger particles with a solid carbon core which typically exhibit a mode at around 70 nm in roadside air (Harrison et al., 2011 and many other published studies). Our conceptual view of this system is that because of the large surface area available for condensation, the semi-volatile organic compounds reach an equilibrium between vapour and the condensed phase. Consequently, we see no reason for further condensational growth by hydrocarbon condensation unless there is another source of vapour or a reduction in ambient temperature causing further supersaturation. We have demonstrated that both during advection and mixing with cleaner air and during vertical mixing there is a tendency for the nucleation mode particles to evaporate due to dilution of the vapour to below equilibrium concentrations (Dall'Osto et al., 2011). In a recent paper we have re-analysed some of our earlier field measurements and demonstrate clearly the evaporative process as particles are advected from a busy highway into the cleaner environment of a park (Harrison et al., 2016). As we point out in that paper, both Lipsky and Robinson (2006) and Fujitani et al. (2012b) have shown that hydrocarbons are lost from diesel exhaust particles during dilution with clean air in the laboratory. Other work by Fushimi et al. (2008) and Fujitani et al. (2012a) also gives support to the concept from their own field measurements.

In models such as that used by Karl et al., the determinant of whether nucleation mode particles shrink by evaporation or grow by condensation is the ambient vapour pressure of the semi-volatile hydrocarbons. In this context, the selection of a concentration by Karl et al. appears to be rather superficial. This is explained in their Supplementary Information which summarises total VOC concentrations (excluding VOC with less than four carbon atoms and benzene) measured in London, Copenhagen, Hamburg and Helsinki, but does not consider measured concentrations of the specific C_{22} and C_{28} n-alkanes used in the calculation. Additionally, the Supplementary Information is extremely confusing in that it uses the statement "assuming that 5-10% of the VOCs react to form condensable gas-phase products, a concentration range of 0.4-4 ppbv is obtained using the available VOC measurements". This leaves doubt as to whether the condensation process is assumed to involve the VOCs themselves or their oxidation products. The abstract of the paper refers to "condensation and evaporation of organic vapours emitted by vehicles" which suggests that it is the n-alkanes themselves, in which case it is wholly unclear what the 5-10% figure refers to. This leads the authors somewhat mysteriously to use initial concentrations of 0.25 ppb of C_{22} and 0.25 ppb of C_{28} for the reference case but they then conduct sensitivity tests in the range 1-4 ppb of each compound. There seems to be no justification whatever for these numbers. In the UK atmosphere, we have measured concentrations of vapour phase n-$C_{22}H_{46}$ of 3.97 ng m^{-3} (0.31 ppt) and n-$C_{28}H_{58}$ of 1.03 ng m^{-3} (0.06 ppt) at a roadside site (Harrad et al., 2003). The concentrations measured in that study are similar in magnitude to those reported by Pongpiajun (2006) from the UK West

Midlands, Mandalakis et al. (2002) from Athens and coastal Greece, and Cincinelli et al. (2007) for Prato, Italy, but around an order of magnitude smaller than were measured in Guangzhou, China by Bi et al. (2002) for C_{22}, although similar for C_{28}. Several of these studies demonstrate an equilibrium between the vapour and condensed phases. These concentrations are around four orders of magnitude lower than assumed by Karl et al. Consequently, we believe that some re-evaluation of the data used by Karl et al. would be appropriate.

This leaves open the question of why Karl et al. achieved a better fit to the measured data for Oslo during low dispersion conditions when assuming condensational growth, and why the data from the other sites do not imply an evaporation process during transport from roadside. In our view, the most likely explanation is that the experimental studies used comparisons between roadside and urban background sites and that further emissions of vehicle pollutants occurred between those sites which are not taken account of in the modelling approach used. This would serve to maintain the concentrations of vapour, hence suppressing the evaporation process. Alternatively, oxidised VOC (or other compounds) provided a source of condensable material.

The formulation of the dispersion model may also be significant; because the dispersion model is assumed (implied by the text of the paper) to be two-dimensional in space, plume height is thus proportional to plume volume. In other words, $H_{m,0}$ indicates the initial volume of the plume and H_m indicates the final volume of the plume. In consequence, the ratio, $H_{m,0}/H_m$, implies the volume fraction taken by the initial plume at the final stage. At the travel time of 30 min (e.g. for the results shown in Table 4), the plume is overwhelmingly taken by the background air (99.86% for 'efficient dispersion', 99.05% for 'moderate dispersion', and 88.6% for 'inefficient dispersion' calculated from Equation (1)) – see table below. Even for the travel time of 10 min, these percentages are already very high (99.6%, 98.4%, and 85.8% for the three weather conditions, respectively). It is entirely unclear whether the model collects further emissions during the travel; we assume it does not (otherwise, a specification of emission rate and composition and particle size distribution etc. should be described). These effectively lead to an approximate modelling of aerosol evolution of the background air. The results shown in Table 4, for example, have little influence from the initial traffic emissions.

In addition, it is not entirely clear how to derive the initial plume height, $H_{m,0}$, which is not described as part of fitting method (only for a and b). It is odd to have higher values for more stable conditions as shown in Table 1 and no justification is given for it. This is important for an examination of percentages of air from the initial emitted plume and from the entrained background air as discussed above.

Table 1: Ratios of plume height at source to receptor location as a function of travel time and dispersion efficiency.

	Efficient dispersion	$\boldsymbol{H_{m,0} = 0.67}$	Moderate dispersion	$\boldsymbol{H_{m,0} = 0.88}$	inefficient dispersion	$\boldsymbol{H_{m,0} = 2.59}$
	H_m	$\boldsymbol{H_{m,0}/H_m}$	H_m	$\boldsymbol{H_{m,0}/H_m}$	H_m	$\boldsymbol{H_{m,0}/H_m}$
10 min	175.9	**0.0038**	53.7	**0.016**	18.2	**0.142**
20 min	328.3	**0.002**	75.9	**0.012**	20.9	**0.124**
30 min	472.8	**0.0014**	92.9	**0.0095**	22.6	**0.114**

As part of the ERC-funded FASTER project, we are working in the laboratory to characterise the organic component of particulate emissions from diesel engines and are developing a neighbourhood scale model of the behaviour of vehicle exhaust aerosol. There are many challenges in such work, and a need for both more fundamental studies of aerosol composition and processes as well as field measurements to assist in development and validation of models.

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References:

Bi, X., Sheng, G., Peng, P., Chen, Y., Zhang, Z., Fu, J., 2002. Distribution of particulate- and vapor-phase *n*-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China, Atmos. Environ. 37, 289-298.

Charron, A., Harrison, R.M., 2003. Primary particle formation from vehicle emissions during exhaust dilution in the roadside atmosphere, Atmos. Environ. 37, 4109-4119.

Cincinelli, A., Del Bubba, M., Martellini, T., Gambaro, A., Lepri, L., 2007. Gas-particle concentration and distribution of *n*-alkanes and polycyclic aromatic hydrocarbons in the atmosphere of Prato (Italy), Chemosphere 68, 472-478.

Dall'Osto, M., Thorpe, A., Beddows, D.C.S., Harrison, R.M., Barlow, J.F., Dunbar, T., Williams, P.I., Coe, H., 2011. Remarkable dynamics of nanoparticles in the urban atmosphere, Atmos. Chem. Phys. 11, 6623-6637.

Fujitani, Y. Kumar, P., Tamura, K., Fushimi, A., Hazegawa, S., Takahashi, K., Tanabe, K., Kobayashi, S., Hirano, S., 2012a. Seasonal differences of the atmospheric particle size distribution in a metropolitan area in Japan, Sic. Tot. Environ. 437, 339-347.

Fujitani, Y., Saitoh, K., Fushimi, A., Takahashi, K., Hasegawa, S., Tanabe, K., Kobayashi, S., Furuyama, A., Hirano, S., Takami, A., 2012b. Effect of isothermal dilution on emission factors of organic carbon and n-alkanes in the particle and gas phases of diesel exhaust, Atmos. Environ 59, 389-397.

Fushimi, A., Hasegawa, S., Takahashi, K., Fujitani, Y., Tanabe, K., Kobayashi, S., 2008. Atmospheric fate of nuclei-mode particles estimated from the number concentrations and chemical composition of particles measured at roadside and background sites, Atmos. Environ. 42, 949-959.

Harrad, S., Hassoun, S., Callen Romero, M.S., Harrison, R.M., 2003. Characterisation and source attribution of the semi-volatile organic content of atmospheric particles and associate vapour phase in Birmingham, UK, Atmos. Environ. 37, 4985-4991.

Harrison, R.M., Beddows, D.C.S., Dall'Osto, M., 2011. PMF analysis of wide-range particle size spectra collected on a major highway, Environ. Sci. Technol. 45, 5522-5528.

Harrison, R.M., Jones, A.M., Beddows, D.C.S., Dall'Osto, M., Nikolova, I., 2016. Evaporation of traffic-generated nanoparticles during advection from source, Atmos. Environ. 125, http://dx.doi.org/10.1016/j.atmosenv.2015.10.077 .

Mandalakis, M., Tsapakis, M., Tsoga, A., Stephanou, E.G., 2002. Gas-particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece), Atmos. Environ. 36, 4023-4035.

Pongpiajun, S. (2006), Atmospheric chemistry of semi-volatile organic compounds in urban and rural air, PhD thesis, University of Birmingham.