

## Reply to Short Comment

We thank Prof. Roy M. Harrison and his co-workers for substantiated comments to the manuscript. We acknowledge that evaporation can be an important process altering the particle size distribution, probably as a result of reduced vehicular emissions of semi-volatile organic vapors in Europe. Following the Reviewers' remarks, significant changes will be made in the manuscript in order to improve the evaluation of nanoparticle loss by evaporation as well as the description of the initial plume stage.

- 1. 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.***

### Response:

The concept regarding condensation and evaporation between roadside and ambient environment applied in our study is based on the work of Zhang and Wexler (Zhang and Wexler, 2004; Zhang et al. 2004).

Hundreds of condensable organic vapors could form in vehicle exhaust with varying concentrations. Determination of their physicochemical parameters such as bulk-phase vapor pressure, molar volume and surface tension, required for modelling, poses an enormous challenge. Due to the lack of composition measurements at roadside, we had to assume a lumped, average composition for the condensable material in the gas-phase. In the applied approach, the effective behavior of condensable organic vapors with respect to changes of the particle number concentration and the particle size distribution was modeled by introducing two different volatility classes: C22 representing semi-volatile vapors and C28 representing low-volatile vapors. This has been mentioned in section 2.1, page 35162, lines 9-11.

For the included roadside locations and campaigns, concentration of n-alkanes and other condensable organic vapors have not been measured and therefore it is not known whether they were in equilibrium with the (bulk) particle phase or not. Such measurements are still rare and not complete regarding the full volatility spectrum of condensable organic vapors. Based on theoretical considerations, Zhang and Wexler (2004) concluded that during the second dilution

stage, between roadside and a few hundred meters distant from the road, particles can still grow by condensation, although with decreasing growth rates when the air parcel moves away from the road.

We have assumed that gas-phase organic compounds at roadside are in excess, even after the first dilution stage between tailpipe and roadside, potentially enabling further growth in accordance with the study by Zhang et al. (2004) that shows growth of sub-6nm particles until 30-90 m downwind. It was also assumed that the roadside concentration of condensable organic vapors is several orders higher than their concentration in the urban background. In fact, the background concentration of C22 and C28 had been set to zero in our study, forcing maximum dilution of the condensing vapors.

The following text will be added in section 2.1:

“The concept regarding condensation and evaporation between roadside and ambient environment applied in this study is based on the work of Zhang and Wexler (Zhang and Wexler, 2004; Zhang et al. 2004). The effective behavior of condensable organic vapors from vehicular exhaust with respect to changes of the particle number concentration and the particle size distribution was modeled by introducing two different volatility classes: the n-alkane C<sub>22</sub>H<sub>46</sub> (abbreviated as C22) representing semi-volatile vapors and the n-alkane C<sub>28</sub>H<sub>58</sub> (abbreviated as C28) representing low-volatile vapors.”

Subsequent to section 2.2, the term “n-alkanes”, meaning representatives of two volatility classes, will be replaced by “condensable organic vapors”.

- 2. 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 C22 and C28 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.***

**Response:**

The applied aerosol dynamics model makes no assumption regarding equilibrium. If the gas-phase concentration of an organic compound is below the saturation concentration, the compound will evaporate from the particles, if it is above the saturation concentration, the compound will condense to the particles. During the road-to-ambient process, some compounds may continue condensing, while others begin evaporating, depending on the relative magnitude of their vapor pressures. In addition, the vapor pressure of the model compounds C22 and C28 is further modified by their molar fraction in the particle phase, according to Raoult's law, and by

their molar volume and surface tension according to the Kelvin effect. This in particular has an impact on the growth or shrinkage of particles in the nucleation mode.

We agree that the estimation of 5-10 % conversion of VOC into condensable organic compounds is not relevant for the roadside, since the figure refers to the oxidative conversion yield of reactive hydrocarbons, such as toluene and alkenes. At roadside, the “fast” photochemical equilibrium will be dominating while the photochemical reactivity of VOC is generally reduced.

The estimation of the 5-10% conversion was removed from the Supplementary Information.

The following text will be added to section 2.2 to better explain the applied concept regarding condensation and evaporation:

“The applied aerosol dynamics model makes no assumption regarding the equilibrium between organic vapor and the condensed phase at the roadside. If the gas-phase concentration of an organic compound is below the saturation concentration, the compound will evaporate from the particles, if it is above the saturation concentration, the compound will condense to the particles. During the road-to-ambient process, some compounds may continue condensing, while others begin evaporating, depending on the relative magnitude of their vapor pressures. In addition, the vapor pressure of the model compounds C22 and C28 is further modified by their molar fraction in the particle phase, according to Raoult’s law, and by their molar volume and surface tension according to the Kelvin effect.”

- 3. 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 C22 and 0.25 ppb of C28 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-C22H46 of 3.97 ng m<sup>-3</sup> (0.31 ppt) and n-C28H58 of 1.03 ng m<sup>-3</sup> (0.06 ppt) at a roadside site (Harrad et al., 2003).***

#### **Response:**

C22 and C28 are thought to be representative of the non-oxidized condensable material in the gas-phase of the vehicle exhaust. It has already been clarified in the manuscript that the concentrations do not refer to the individual chemical species, but are intended to represent the total concentration of two volatility classes. It was decided to keep the initial concentrations at 0.25 ppb of C22 and 0.25 ppb of C28 (i.e. in total 0.5 ppb), potentially allowing for continued growth downwind the road. This is not unreasonable since for instance the particle size distribution from the SAPPHIRE Case I campaign shows a clear increase of the nucleation mode diameter between roadside measurement and background measurement. It is noted that Pohjola et al. (2007) obtained best fit between modeled and measured particle size distribution on a distance scale of 125 m near a major road in Helsinki when using roadside concentrations of one condensable organic vapor of the order of 10<sup>10</sup> molecules cm<sup>-3</sup> (ca. 0.4 ppb).

Mandalakis et al. (2002) reported a total n-alkane (C14 – C33) concentration of 50.43 ng m<sup>-3</sup> in the vapor phase and of 38.65 ng m<sup>-3</sup> in the particulate phase, from measurements in the urban center of Athens (Greece). C14 – C23 n-alkanes were mainly in the vapor phase while C25 – C33 n-alkanes were mainly in the particulate phase; C24 was equally present in both phases. Summing up vapor concentrations for C14 – C23 and particulate phase concentrations for C25 – C33 and the phase averaged concentration for C24 gave a concentration of total condensable n-alkanes of 73.5 ng m<sup>-3</sup>, corresponding to 5.1 ppt when using the averaged molecular weight of C22 and C28. Similar total n-alkane concentrations were reported by Harrad et al. (2003) for an urban traffic site (Birmingham, UK), by Doskey and Andren (1986) for a rural site (North Wisconsin, WI, USA), and by Pietrogrande et al. (2011) for a suburban site (particulate phase only, Augsburg, Germany). Total n-alkane concentrations were several times higher at an urban industrial site (Prato, Italy) in a study by Cincinelli et al. (2007). Total n-alkane concentrations were more than one order of magnitude higher at an urban site in China (Bi et al., 2002). Although a concentration of 5 ppt of condensable n-alkanes seems to be typical for the urban environment, higher concentrations may occur. Other condensable organic compounds such as PAH, n-alkanols, and dicarboxylic acids are also emitted from vehicles and may contribute to the total concentration of condensable organic vapors at the roadside, represented by C22 and C28 in our study.

The sensitivity tests in the range 1-4 ppb (for the sum of C22 and C28, not for each compound as suggested by the Prof. Harrison) were now replaced by a test series with smaller concentrations for the sum of C22 and C28, stepwise decreasing by one order of magnitude between 500 ppt (i.e. 0.5 ppb, reference case) and 5 ppt, closer to the reported measurements of the sum of n-alkanes available for condensation. Since evaporation depends on the volatility of the nanoparticles in the exhaust post-emission, the OC fractions in the modeled nucleation mode were changed to 100% C22 in an additional test. Results from the new tests on condensation and evaporation were added to section 3.4. Two new figures (Figures S3 and S4) showing the particle number and mass size distributions in 240 m distance from roadside for Helsinki LIPIKA and for UFP-Oslo Winter with different concentrations of condensable organic vapors will be included in the Supplement.

The following text will be added to section 2.2:

“For the included campaigns, gas-phase concentration of n-alkanes and other condensable organic compounds have not been measured at the roadside locations. Measurements of n-alkane vapor concentrations in urban environments indicate typical concentrations of 5 ppt for the sum of the n-alkanes, but higher concentrations may occur (for more details see section S2 in the Supplement). Pohjola et al. (2007) obtained best fit between modeled and measured particle size distribution on a distance scale of 125 m near a major road in Helsinki when using roadside concentrations of one condensable organic vapor of the order of 10<sup>10</sup> molecules cm<sup>-3</sup> (ca. 0.4 ppb). Based on this, initial concentrations of 0.25 ppb C22 and 0.25 ppb C28 were used in the reference case (all campaigns and dispersion conditions). The background concentration of C22 and C28 was set to zero, forcing maximum dilution of the condensable organic vapors during travel of the air parcel away from the roadside.”

The above description of reported n-alkane measurements will be included in Section S2 of the Supplementary Information.

4. **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.**

**Response:**

We do not exclude alternative explanations for the diameter increase of nucleation mode particles between roadside and background measurements during the Oslo UFP Winter campaign. Vehicle emissions models suggest that in cold climates the majority of volatile organic compounds (VOC) emitted by vehicles occur during engine cold starts. Vehicle emissions of hydrocarbons from gasoline vehicles during cold start might be up to 35 times higher at -20°C than at room temperature (Weilenmann et al., 2009). It is possible that oxidation of extra-emitted VOC from gasoline vehicles provided an additional source of condensable material during the travel between roadside and the neighborhood.

The alternative explanations given by Harrison and co-workers will be included in the discussion of the Oslo winter case in section 3.4 and in the new section 3.6 “Uncertainties of the aerosol treatment in the idealized scenario”.

5. ***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).***

**Response:**

We thank Prof. Harrison and co-workers for compiling the ratio  $H_{m,0}/H_m$  for 10 min, 20 min and 30 min in form of a table in their short comment.

Exponential decay observed for the total PN concentration during dispersion of the particles between 1 m from road to several hundred meters from road, is dominated by the atmospheric dilution. Lähde et al. (2014) demonstrated that an exponential dilution function,  $c(x) = B + D \exp(kx)$  can be applied to various PN roadside dispersion studies. Although relative concentrations of the background (B) and of the emission source (D) differed, the decay coefficient  $k$  was similar for all sites. This confirms the result of our study, that for efficient dispersion conditions between roadside and neighborhood scale, total PN can be modelled as passive tracer.

- 6. 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.**

**Response:**

No additional emissions are collected during transport from roadside to ambient in this idealized scenario. The background concentration of particles has an essential influence on the dilution time scale. The scenario calculations are constrained by the measured background particle concentration and size distribution. If there had been other sources of ultrafine particles between the roadside and the urban background, these are integrated in the shape of the particle size distribution of the urban background, which is imposed on the calculated aerosol evolution of the model.

Table 4 is intended to illustrate the relative importance of the different aerosol dynamics processes, in changing the total particle number concentration between roadside and the neighborhood scale, assuming no additional emissions and a homogeneous underlying surface.

The obtained percentage changes of PN due to aerosol dynamics (coagulation and dry deposition) are comparable to those found previously with urban dispersion models.

The following sentence will be added in section 2.2.:

“No additional emissions of particles or vapors are collected during transport from roadside to ambient in this idealized scenario.”

- 7. 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.**

**Response:**

Wind speed and direction are important in determining the dispersion of ultrafine particles near busy roads. Zhu et al. (2002) observed a linear dependence of the total particle number concentration on wind speeds, 30 m downwind of a motorway in Los Angeles. With increasing wind speed the atmospheric dilution effect will be stronger. Therefore wind speed was included to characterize the dispersion cases of our study. Wind speed  $U$ , perpendicular to the road, was 1.0 m/s, 3.0 m/s, and 4.0 m/s, respectively, for the inefficient dispersion, moderate dispersion, and efficient dispersion cases; indicated in Table 1 of the manuscript.

The initial stage of the exhaust plume was described with the simple plume dispersion model by Vignati et al. (1999). This was done independently before the actual scenario calculation. We apologize that the derivation of  $H_{m,0}$  has not been mentioned in the manuscript.

The expression by Vignati et al. (1999) for the evolution of the plume cross section was applied:

$$S(t) = \left( \sqrt{S_0} + t \sigma_w(0) \right)^2 - (t \alpha u_0)^2$$

Where  $S$  is the cross sectional area of the plume or, in more statistically oriented way, it can be interpreted as being proportional to the variance of the Gaussian plume distribution, i.e.

$S \propto \sigma_y \sigma_z$ .  $S_0$  is the size of the plume at the exhaust pipe (assumed to be equal to the cross-sectional area of the exhaust pipe, here using a radius of 0.020 m),  $\sigma_w(0)$  is the initial entrainment velocity at  $t = 0$  and  $u_0$  is the initial exhaust gas velocity. The proportionality constant  $\alpha$  is given a value of 0.1, which corresponds to typical levels of mechanically induced turbulence (Berkowicz et al., 1997). For  $\sigma_w(0)$  a value of  $0.25 \text{ m s}^{-1}$  was adopted (Fig. 6 in Kastner-Klein et al., 2000), typical for traffic on working days between 8 a.m. and 7 p.m. in situations where traffic-induced turbulence dominates. For the initial exhaust gas velocity  $u_0$  a value of  $0.23 \text{ m s}^{-1}$  typical for light-duty vehicles was taken (Kurkela et al., 1994). Further,  $t$  is the time from the release, here expressed as  $t = x/U$ . A fixed distance from the release point of  $x_{st} = 9 \text{ m}$  was chosen for the PN measurement, resulting in an arrival time  $t_{st}$  at the measurement location which differs for different wind speeds. Solving the above expression for the initial plume height at roadside, assuming circular plume cross-section, gives:

$$H_{m,0} = 2 \sqrt{\frac{S(t_{st})}{\pi}}$$

For the wind speeds 1.0 m/s, 3.0 m/s and 4.0 m/s we obtained an initial plume height,  $H_{m,0}$ , of 2.6 m, 0.9 m, and 0.7 m at the roadside ( $H_{m,0}$  values are now given with one significant decimal).

Description will be added as new section S1 in the Supplementary Materials.

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