Volatile nanoparticle formation and growth within a diluting diesel car exhaust

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Introduction:
Adverse health effects and the impact of particles on the earth radiation budget are major reasons to study ultrafine particles (UFP: d_p < 100 nm). Diesel vehicles are a major and continuous source of UFP. Diesel vehicle soot particle (~ 40–120 nm) emissions in number and mass are reasonably well determined for standard driving cycles (up to 120 km/h). In contrast, the assessment of volatile nanoparticle formation is difficult because the precursors of nucleating species like gaseous sulphuric acid (GSA) are still in gas-phase when leaving the exhaust pipe. Exposure measurements near busy roads indicate that volatile, secondary formed nucleation particles (~ 3–25 nm) often dominate the size distributions. Crucial for secondary particle formation and growth within a rapidly diluting turbulent vehicle exhaust plume is the dilution of precursor species and thereafter the growth stable clusters (~ 2 nm) towards detectable size ranges.
The aim of this work was to study gas particle transformation processes within the exhaust plume under real world conditions acting upon dilution and spatial scales. Moreover, the interference of volatile nanoparticle formation and growth with “solid” soot particles within the diluting diesel car exhaust was accounted as well.

Methodology:
Coupled computational fluid dynamics (CFD, www.fluent.com) and aerosol dynamics simulations (FPM, fine particle model, www.aerosols.com) have been conducted for a diesel car representing "real world" conditions. H_2SO_4-H_2O nucleation and growth, the impact of soot particles on nucleation and the possible role of low and semivolatile organic components in growth were estimated in this study. Details of the numerical set-up and aerosol physics can be found in Uhrner et al., 2007. The simulations are based on an extensive measurement program (Wehner et al., 2008) of SMPS, temperature, humidity, flow velocity, CO_2 and NO_x measurements within the plume of diesel and gasoline test cars. Tab. 1 summarises three different numerical experiments of this work. The control run (Ctrl) was based on “real world” measurements where high nucleation particle concentrations (>10^{13} m^{-3}) were recorded under extreme driving conditions such as strong acceleration or high speed (>140 km/h) and high rpm (>3800 rpm), see Tab. 1 & 2. In Exp-1 the surface area effect of a diesel particle filter on new particle formation is accounted, i.e. soot particle emissions were reduced by a factor of 100 (see Table 1). For the Ctrl and Exp-1 simulations boundary conditions for a H_2SO_4-H_2O-soot system were used, see Tables 1 and 2. In Exp-2 additional organic emissions of $1 \cdot 10^{-6}$ kgs^{-1} condensable material (gas-oil $C_{16}H_{29}$) were utilized to carry out a simplified growth study. In contrast to the H_2SO_4-H_2O system, information about organic species and their thermodynamic properties as well as interaction are actually unknown. Therefore no liquid-liquid interaction between the inorganic and organic phases was assumed, surface tensions for the organic phase not accounted.

Results:
The Ctrl run was described in detail in Uhrner et al. 2007. Due to the low sulphur content of the fuel used (< 10 ppm) high SO_2 to SO_3 conversion and additional contributions e.g. from lube oil are necessary to explain measured particle number concentrations at >140 km/h & >3800 rpm.
The prescribed reduction of soot particle emissions by two orders of magnitude resulted in about one order of magnitude larger nucleation particle concentrations within the exhaust plume (Fig.1). The particle growth in Ctrl and Exp-1 simulations is insufficient, yielding nucleation particles of a few nanometers in size. Fig. 2 and Fig. 3 show the flow and the growth pattern of Exp-2 the H_2SO_4-H_2O-organic system. Measured results and the sampling location are indicated within Fig. 2. Figures 2 and 3 indicate that the growth within the plume

is significantly affected by the flow and dilution conditions and the available condensable mass. Within the recirculation and wake zone (Fig. 3) the strongest growth was calculated illustrating the different time-scales of growth within the plume.
Urban traffic with frequent acceleration / deceleration cycles result in high engine load and engine speed operating conditions favourable for the generation of nucleation particles and strong growth on very short time scales within the vehicle exhaust plume. HC emissions could not be measured with the cited measurement set-up. In order to evaluate roughly possible organic contributions, HC measurements taken from chassis dynamometer measurements representing urban situations are used as an indicator. Fig. 4 shows HC emissions measured at a chassis dynamometer for steady state operation conditions and acceleration conditions during the NEDC cycle for 3 different Euro 3 / Euro 4 engines. Different engine power settings were reached by selecting different gears in order to obtain similar car speeds but with different engine speed. Interestingly, HC emissions are increased by up to a factor of 3.2 for higher engine speed conditions, for a similar car speed. This gives some indication that under high engine speed the amount of potential precursor gases is obviously increased. The amount of low volatile organic substances and their mixture properties impact within the particle phase are unknown.
Some interesting nanoparticle formation and growth aspects can be inferred from Fig. 5. There, measured size distributions at 45 cm and 90 cm within the exhaust plume are shown for 4 different car operation conditions. At 120 km/h & 2600 rpm (upper left panel) there is no clear indication of detectable nucleation particles (lower size limit was 7 nm). At 150 km/h and 3200 rpm (lower left panel) as well as 105 km/h and 4000 rpm (upper right panel) nucleation particles were recorded at the 45 cm distance but not at 90 cm. Based on the simulation results dilution is attributable for a factor of 2-3 between 45 cm and 90 cm. Compared to 150 km/h and 4000 rpm (lower right panel) where large nucleation particle concentrations were recorded at both measurement points the “disappearance” of nucleation particles at 90 cm is potentially attributable to the combined effects of dilution and strong growth “of a few”. The right panel size distributions of Fig. 5 measured at 45 cm indicate another interesting feature, they seem to increase in number towards the detection limit (7 nm) indicating higher concentrations below 7 nm.

Conclusions:
The simulations clearly show the complexity of nucleation and subsequent particle growth which is significantly influenced by the dilution pattern and the available condensable mass.
Simulations indicate that the in plume” growth of nucleation particles reaching ~ 10 nm in size requires two important pre-requisites: high SO2 to SO3 conversion and enough rapidly condensing, most likely organic, low and semi-volatile species. The spatial distribution in nucleation particles size and the flow pattern show clearly the interaction of flow and dilution acting upon the condensation time scale. The largest particles were simulated within the recirculation zone in the wake of the test car. Additional chassis dynamometer measurements indicate that increased diesel car HC emissions can occur at high engine speeds. It remains questionable if conditions for nucleation and subsequent growth are favourable with low fuel sulphur (<10 ppm) for typical urban traffic situations in diesel car exhaust plumes and whether the studied mechanism explains the abundance of nucleation particles which are still recorded at urban kerbsides. The results of the aerosol dynamical behaviour are summarised in Fig. 6. Most likely the abundance of nucleation particles (e.g. Wehner et al. 2008) close to busy roads is attributable to two condensation time scales. A fast one as discussed here, potentially also attributable to HDV traffic and a second and slower one which comprises the contributions of precursors of the entire vehicle fleet and complex atmospheric chemistry and aerosol dynamics.

Uhrner, U., von Löwis, S., Vehkamäki, H., Wehner, B., Bräsel, S., Hermann, M., Stratmann, F., Kulmala, M., and Wiedensohler, A. (2007) Dilution and Aerosol Dynamics within a Diesel Car Exhaust Plume – CFD Simulations of On-road Conditions. Atmos. Environ., 41, 7440 - 7461.
Wehner, B., Uhrner, U., von Löwis, S., Zallinger, M., and Wiedensohler A., 2008. Aerosol number size distributions within the exhaust plume of a diesel and a gasoline passenger car under on-road conditions and determination of emission factors, Atmos. Environ, 43, 1235-1245.

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Motivation:

- Health effects & impact on earth radiation budget of ultrafine particles (UFP: d_p < 100 nm)
- Kerbside exposure: Secondary formed nucleation particles dominate size distributions
- Diesel vehicles are a major and continuous source of UFP
  - Soot particle emission (EF) number/mass (-120 km/h + load) known
  - Nucleation particle "EF" ??? - Exhaust T > 400 – 450 K precursors (e.g. H_2SO_4) in gas-phase!

➡ AIM: STUDY TRANSFORMATION (gas-particle) in exhaust plume under impact of turbulent dilution & spatial scales & interference with "solid" particles

Methodology:

- Rapid turbulent dilution key process in volatile nanoparticle formation
- "Real World " approach by "sniff plume" measurements and simulations
- Coupled CFD (FLUENT) and aerosol dynamics (FPM) simulations within vehicle exhaust plume representing "real world" conditions
- H_2SO_4-H_2O nucleation & growth, impact of soot particles on nucleation & assessment of low and semivolatile organic components in growth

Tab. 1: Boundary conditions for the three experiments

Simulation:	Ctrl	Exp 1	Exp 2
Soot mode flux tailpipe	10^{13} s^{-1}	10^{11} s^{-1}	10^{13} s^{-1}
Condensable HC EF	0	0	10^{-6} kgs^{-1}

Tab. 2: Boundary conditions for all experiments

	V	T	H_2O	H_2SO_4	Nuc-mode	Soot-mode
Velocity -inlet	145 km/h	300 K	65% RH	0	10^{10} m^{-3} 10 nm σ : 1.5	10^{10} m^{-3} 50 nm σ : 1.8
Exhaust pipe	mfr 0.1 kgs^{-1}	550 K	6 wt%	$8.8 \cdot 10^{-8}$ kgs^{-1}	calcu-lated	sim/meas fit

Results:

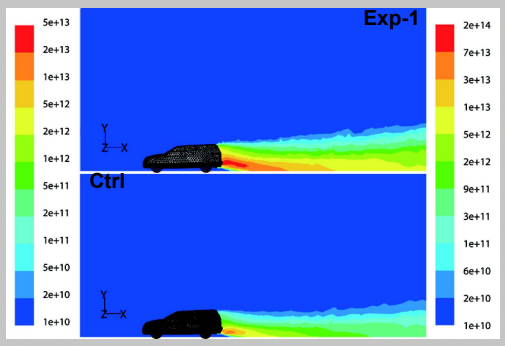


Fig. 1 Cross-section for simulated nucleation mode concentration (in #m-3) in the exhaust pipe plane for the control run **(Crtl)** lower panel & left legend.
Simulation with reduced particle flux (**Exp-1** top panel & right legend). Length of the car: 4.28 m, height: 1.51 m, sim. Operation conditions: 145 km/h, 4000 min^{-1}

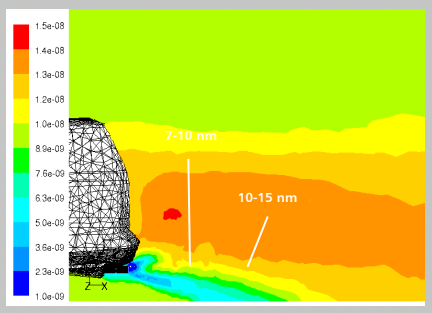


Fig. 2: Cross-section for simulated d_{gn} (in m) in the exhaust pipe plane for the nucleation particles consisting of H2SO4-H2O-organics

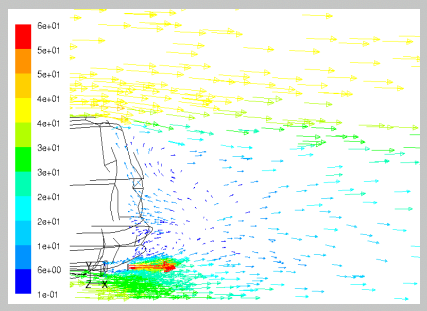
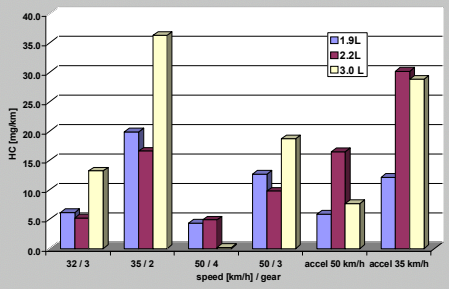


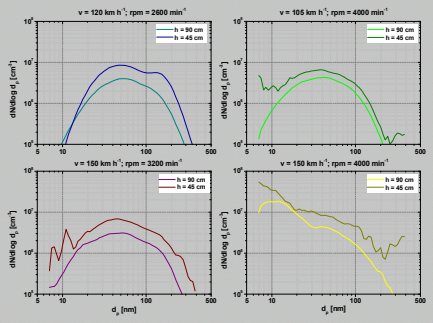
Fig. 3: Cross-section for simulated velocity vectors (in m/s) in the exhaust pipe plane

Fig. 2 & Fig. 3: Time scales matter!



← **Fig. 4:** HC emission factors measured on a chassis dynamometer for three different Euro 3 & 4 engines, at high engine speed increased HC

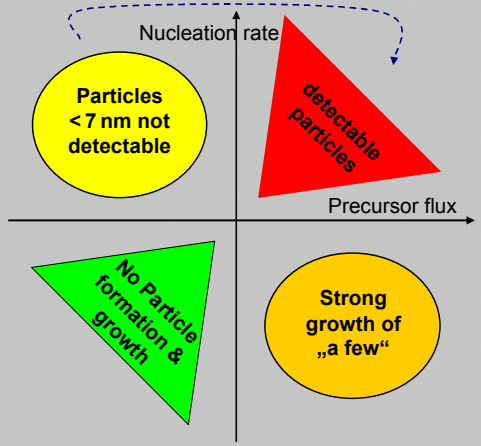
→ **Fig 5:** Measured size distributions at 45 cm and 90 cm distance behind the exhaust pipe exit for different operating conditions – 1) at high engine speed dNdlogd_p increases towards the lower detection limit, 2) nucleation particles detected at 45 cm must be > ≈10^7 cm^{-3} to be detected at 90 cm, see Fig. 5 strong growth of a few



Conclusions:

- Strong impact of dilution pattern & available condensable mass
- Reduction of soot particle emissions by 1/100 → ≈1 order of magnitude more nuclei particles
- Conditions for in plume Nucleation & Growth:
  - Low FSC 10 ppm: High SO2 to SO3 conversion → high nucleation rate
  - Sufficient precursor emissions & low flow velocity e.g. recirculation zone time to grow
  - Favourable operating conditions high vehicle and engine speed or prolonged acceleration
  - Fig. 5: Low nuc rate & sufficient precursor & rapid dilution → strong growth of a few
- Time scale matters! In plume see Fig. 2 & 3 & Fig. 6 indicating external formation path

External "slower" formation path influence of fleet precursor mix?



Abundance of nucleation particles near roads attributable to 2 condensation time scales:

1) a "fast one" leading to "in plume" volatile particle formation
2) a "slow one" comprising precursor gas "fleet mix" contributions, e.g. strong gasoline HC emission

← **Fig 6**: Schematic of results obtained from measurements and coupled CFD-Aerosol model simulations for in-plume particle nucleation and growth to detectable size ranges