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In densely populated areas, traffic is a significant source of atmospheric aerosol particles. Due to their small size and complicated chemical and physical characteristics, atmospheric particles resulting from traffic emissions pose a significant risk for human health and but also contribute to anthropogenic forcing of climate. Previous research has established that vehicles directly emit primary aerosol particles but also contribute to secondary aerosol particle formation by emitting aerosol precursors. Here, we extend the urban atmospheric aerosol characterization to cover nanocluster aerosol (NCA) and show that a major fraction of particles emitted by road transportation are in a previously unmeasured particle size range of 1.3-3.0 nm. For instance, in a semi-urban roadside environment, the NCA represented 20% - 54% of the total particle number concentration of ambient air. The observed NCA concentrations varied significantly depending on the traffic rate and wind direction. The number emission factors of NCA for traffic were $2.4 \cdot 10^{15}$ $(kg_{fuel})^{-1}$ in a roadside environment, $2.6 \cdot 10^{15}$ $(kg_{fuel})^{-1}$ in a street canyon, and $2.9 \cdot 10^{15}$ $(kg_{fuel})^{-1}$ in an on-road study through Europe. Interestingly, the emission was not associated with all vehicles. In engine laboratory experiments, the emission factor of exhaust NCA varied from a relatively low value, $1.6 \cdot 10^{12}$ $(kg_{fuel})^{-1}$, to a high value of $4.3 \cdot 10^{15}$ $(kg_{fuel})^{-1}$. The newly discovered NCA emissions directly affect particle concentrations and human exposure on nano-sized aerosol in urban areas and they may potentially act as nano-sized condensation nuclei for the condensation of atmospheric low-volatile organic compounds.

nanocluster aerosol | atmospheric aerosol | combustion-derived nanoparticles | air pollution | traffic emission

Introduction

Detailed characterization of aerosol sources is required to understand climate impacts and health effects of atmospheric aerosols, as well as to develop technologies and policies capable of mitigating air pollution in urbanized areas. In densely populated areas one of the most significant source of particles is traffic.[1,2] Due to their small size and complicated chemical and physical characteristics[3-6], atmospheric particles resulting from traffic emissions pose a significant risk for human health[7-12] and also contribute to anthropogenic forcing of climate[13-14]. Prior research on vehicular emissions has shown the existence of soot and ash[3,15] and solid sub-10 nm core particles[4-6] in primary emissions of vehicles and engines and their variation depending on vehicle technologies[4,6], the properties of fuel and lubricant oil[15,16], and driving conditions[15-17]. In addition to particles, exhaust typically contains species that reside in the gaseous phase in the undiluted high temperature exhaust[5,17,18], but condense or even nucleate to the particle phase immediately after the exhaust is released to the atmosphere. Such aerosol is here called delayed primary aerosol, because particles' precursors exist already in the undiluted exhaust and the amount and characteristics of the resulting atmospheric particulate matter does not depend significantly on atmospheric processing or atmospheric photochemistry. In the secondary aerosol formation process driven by atmospheric photochemistry, volatile gaseous compounds emitted by traffic are chemically transformed in the atmosphere to less volatile species enabling and enhancing secondary aerosol particle formation via condensation and new particle formation[e.g.,20-22]. While the primary and delayed primary particle emissions mostly affect the air quality near the emission source, the effect of the secondary processes is more important on a regional scale.

Previous research has shown the importance of nano-sized clusters in atmospheric processes, especially in the formation of ultrafine particles.[23,24] A number of studies also indicate that nano-sized clusters have a role in engine emission formation.[4,25] Preceding research of particle number concentrations near traffic has shown highly elevated concentrations (of the order of 10^5-10^6) of ultrafine particles near roadways[2,26], also indicating the likelihood of high concentrations of nano-sized particles and clusters existing in such environments. However, until now the measurement techniques suitable for their detection have not been applied in such environments, leaving the direct observation, formation, and effects of particles smaller than 3 nm still open.

Here, we report the significant presence nanocluster aerosol (NCA) particles in a particle diameter range of 1.3-3.0 nm of urban air. Our study strongly indicates that the source of this NCA is traffic, and more specifically, the exhaust of vehicles. We also show that the significance of NCA in vehicular emissions has been

Significance

We report the significant presence of traffic-originated nanocluster aerosol (NCA) particles in a particle diameter range of 1.3-3.0 nm of urban air, determine the emission factors for the NCA, and evaluate its global importance. Our finding is important because it significantly updates the current understanding of atmospheric aerosol in urban areas: the study shows that in urban air, extremely small particles form a significant fraction of the total particle number and are a direct result of anthropogenic emissions, i.e., the emissions from road traffic. Thus it also implies that in urban areas no atmospheric nucleation process is necessary to form a large number of particles, which affect population health and climate.

Reserved for Publication Footnotes

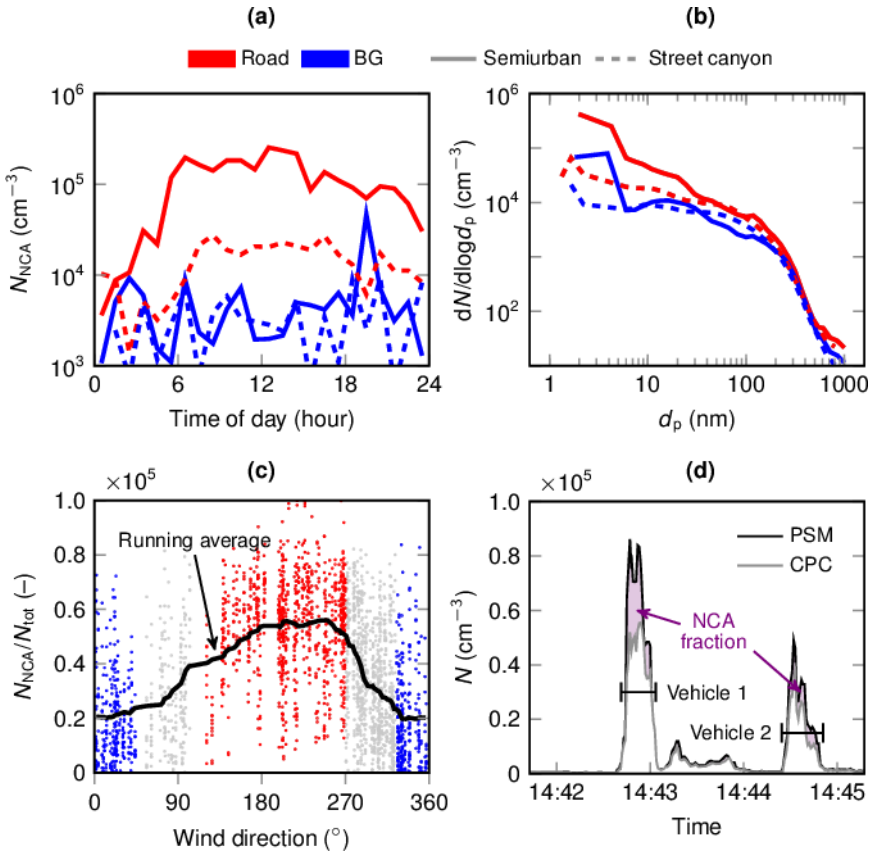

Fig. 1. Nanocluster aerosol (NCA) number concentrations in two different roadside environments, semi-urban (solid line, speed limit 80 km/h) and street canyon (dashed line, speed limit 40 km/h). (a) The diurnal variation of the NCA concentration. Two sectors, road (red, N=926) and urban background (blue, N=548) are distinguished from the data set based on the wind direction. (b) Particle number size distributions including the NCA of fresh exhaust aerosol measured in the roadside environments showing the high contribution of nanoclusters in total particle number. The road-influenced average distribution (red) and the average distribution from the clean sector (blue) representing the urban background are seen. (c) The ratio of NCA number concentration to the total aerosol number concentration as a function of the wind direction in the semi-urban environment. The nearest road is between the angles 110 – 270°. (d) An example of the time series measured with the PSM and a CPC, showing the effect of two passing vehicles on the particle concentration in the street canyon.

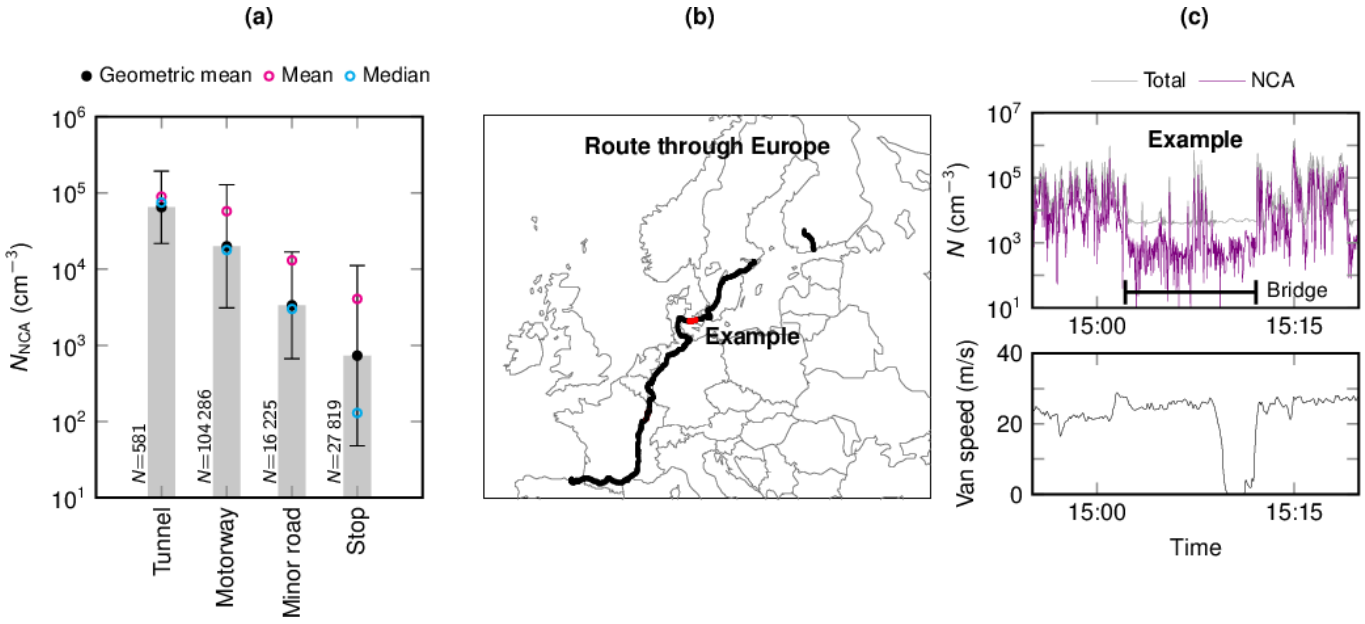

Fig. 2. Nanocluster (NCA) concentrations measured during the on-road experiment. In (a), geometric means, means and medians of NCA concentrations are shown in different experimental situations. In (b), the whole studied route is indicated by black line, location of measurements shown in (c) is indicated by red color. In (c), an excerpt of NCA and total particle concentration time series and speed profile of the mobile laboratory van is shown. Longer time series for the experiment are shown in Supporting Information.

previously underestimated due to a lack of knowledge and suitable measurement techniques. The observations reported here are based on the results from three atmospheric measurements covering a wide range of environments: stationary measurements at the roadside of a main road in a semiurban area, stationary measurements in a street canyon in an urban area, and a long-distance on-road study by a mobile aerosol laboratory. Further evidence for the existence of the NCA in traffic emissions was obtained in a laboratory study in which emissions of a modern diesel engine were characterized. The NCA measurements were

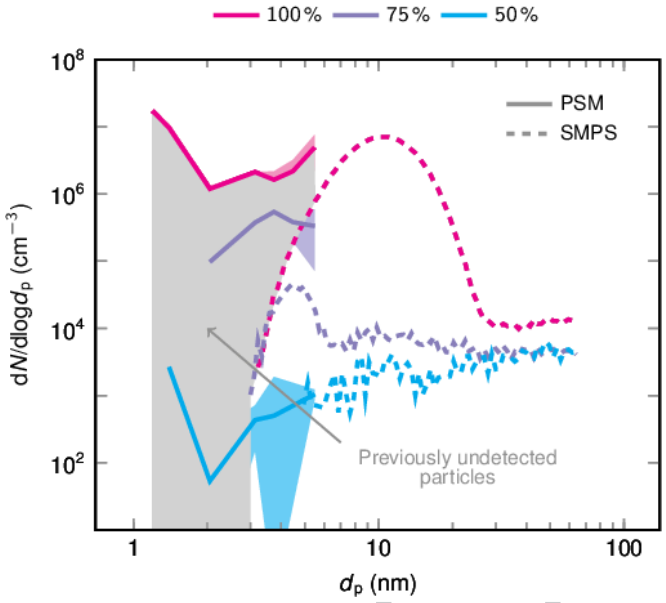

Fig. 3. Particle number size distributions of fresh exhaust aerosol measured in an engine laboratory, showing the high contribution of nanoclusters in total particle number for a diesel engine with three engine loads (50%, 75%, and 100%). The previously undetected particles are shadowed by gray color. The PSM (particle size magnifier, solid lines) and the SMPS (scanning mobility particle sizer, dashed lines) were used after the exhaust sampling and dilution system designed to mimic real-world nanoparticle formation. The shadowed areas represent the error limits for the PSM measurements formed by the standard deviations.

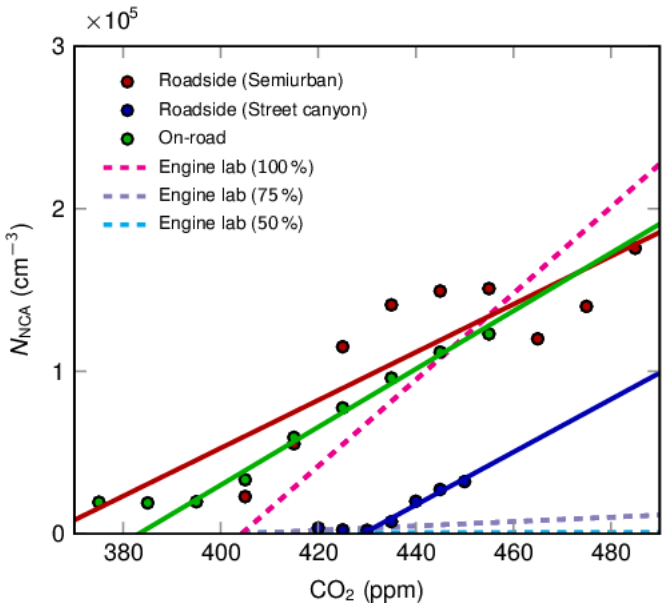

Fig. 4. The NCA number concentration as a function of simultaneously measured CO_2. Both roadside measurements, high-speed motorway driving during long-range on-road study through Europe and engine laboratory experiments are shown. The dots represent the experimental data averaged over discrete CO_2 levels. In the cases of roadside and on-road studies, the solid lines are fits for the experimental data while the dashed lines for engine laboratory results are generated based on the NCA concentration measured at by one well-defined dilution stage.

performed using a Particle Size Magnifier (PSM)[27] which uses the method for NCA detection suggested by Iida et al.[28] and enables the detection of extremely small nanoparticles. The method is currently generally adopted in nanoparticle formation studies[24].

Results and discussion

In traffic environments, high NCA concentrations were observed when the wind was blowing from the road to the measurement site. Figure 1a shows the average diurnal variation of NCA concentrations measured in a semi-urban roadside location (solid lines) and in a street canyon (dashed lines). The concentrations are given separately for two prevailing wind sectors: "BG" refers to the situations where the wind was blowing from the urban background area towards the monitoring station, whereas "Road" refers to the situation where the wind direction was from the street or road towards the monitoring station. Data for all wind directions can be found in the Supporting Material (Fig. S9). In general, when the wind was blowing from the road towards the monitoring station, the NCA concentrations reached values higher than 10^5 cm^{-3} in the semi-urban environment and 10^4 cm^{-3} in the street canyon environment. The diurnal variation of the NCA number concentration was similar in both measurements; the NCA concentration increased rapidly at early morning and decreased to very low values in the evening.

The particle size distribution analysis (Fig. 1b) indicates that in the semi-urban roadside environment the observed NCA formed a separate mode with high number concentrations. However, a clearly distinguishable NCA mode was not observed in the street canyon. Naturally, also the loading of particles larger than 3 nm was higher in the road-originated air: in the semiurban roadside environment the median number concentration was $1.3{\cdot}10^5$ cm^{-3}, compared to $7.6{\cdot}10^4$ cm^{-3} for the background sector. Like the NCA concentrations, -the fraction of NCA in the total particle concentration also depended on the wind direction. In the semiurban roadside environment, on average 38% of measured aerosol particles in number belonged to NCA, i.e., to the size range from 1.3 to 3 nm. When the wind direction was from the road to the monitoring station, the NCA fraction increased to 54 ± 18% (N = 926). This value is the mean of the red dots shown in Fig. 1c, each of which corresponds to a 5 min. average of the measured concentrations. The standard deviation and the number of data points (N) are also shown. In the background aerosol, the NCA fraction was lower, averaging 20 ± 17% (N = 548). Based on this evidence (diurnal variation and the effect of wind direction on the NCA concentration and fraction) we conclude that road traffic is a major source of NCA. Interestingly, not all vehicles emit high amounts of NCA. This is demonstrated by Fig. 1d which shows the concentration time series measured with a PSM and a condensation particle counter (CPC). The NCA concentration is obtained as the concentration difference of the two readings, and one can see that the passing of vehicle 1 resulted in a high amount of NCA (approximately 30% of the total concentration), whereas after vehicle 2, a much lower fraction of NCA was observed.

For a more regional evaluation, we conducted an on-road NCA experiment across Western Europe, from northern Spain to Finland (Fig. 2b). The experiment was mostly conducted on motorways (71% of all en-route observations) using a mobile laboratory equipped with similar instrumentation for the measurement of NCA as in the previous roadside studies. The NCA concentrations were particularly elevated in high-speed traffic environments, and lower when traffic influence was reduced, e.g., during stoppages and on minor roads (Fig 2a). The traffic influence is clearly demonstrated during the bridge crossing the Danish Straits (Fig 2c). The crossing was performed during heavy cross-wind conditions, which in practice caused the instruments to sample only marine background. At this time, both the concentration and fraction of NCA was drastically reduced. On-road observations also showed that different road environments

result in different NCA loadings (Fig. 2a) – high-speed motorways exhibited higher NCA concentration than minor roads with lower speeds, and the highest NCA concentrations were measured in traffic tunnels where the dilution of exhaust emissions is limited.

The observations presented above strongly indicate that NCA observed in urban and traffic environments is emitted by traffic rather than from atmospheric particle formation. To gain evidence of NCA as a byproduct of combustion, we performed three laboratory experiments with a modern diesel engine. We observed that, in addition to soot and nucleation mode particles larger than 3 nm, the exhaust contained a significant amount of NCA (Fig. 3). The NCA concentration depended on the engine load in a similar way than the concentration of particles in the size range above 3 nm. It should be noted that in the engine laboratory experiment the exhaust dilution and sampling system enables real-world-like nanoparticle formation[29] but does not emulate atmospheric oxidation. As discussed previously, secondary aerosol formation requires that gaseous emissions are oxidized to low-volatility compounds. Our experiments show that fresh exhaust can contain sufficient low volatility compounds that NCA formation in vehicle exhaust is possible without atmospheric oxidation. We also observed that, by using thermal treatment for the exhaust sample, the NCA disappeared at 75% engine load and nearly disappeared at 100% load (see Fig. S8). This indicates that the NCA should be considered to be delayed primary aerosol, and composed of species that were not in the particle phase in hot undiluted exhaust. However, the total NCA emission of traffic is a result of emissions from a large number of vehicles with varying technologies; this may cause significant variation the formation mechanism and composition of emitted NCA.

CO_2 is an inert gas and a product of combustion; it can, therefore, be used as a tracer for combustion-originated products in the atmosphere, i.e., to determine fuel specific emission factors for other byproducts of combustion.[30,31] Furthermore, such emission factors enable the comparison of emissions from different combustion sources. Figure 4 shows the dependence of the NCA concentration on CO_2 for each experiment conducted in this study (two roadside experiments, the on-road study and three experiments in the engine laboratory). For the roadside and on-road experiments, the figure shows the measurement data averaged over discrete CO_2 levels (at intervals of 5 or 10 ppm), and linear fits for the averaged data points above the background CO_2 level (see also Supporting Information on the background CO_2 concentrations of ambient air). For the engine laboratory experiments, the figure shows lines measured at one phase of exhaust dilution and calculated into the larger dilution scene.

For the roadside experiment conducted in the street canyon and for the on-road experiment, the NCA concentration increased linearly as a function of CO_2 concentration when the CO_2 values were above the background value. In the semi-urban roadside experiment, the linear dependence was not as clear-cut. For all three cases, slopes of the fits were similar: 1475 ± 918 $(cm^3ppm)^{-1}$ for the semiurban roadside environment, 1625 ± 1062 $(cm^3ppm)^{-1}$ for the street canyon, and 1784 ± 309 $(cm^3ppm)^{-1}$ for the high-speed motorway driving during the trans-European on-road study. Assuming a CO_2 emission of 3140 g/kg fuel (an average of conversion factors for diesel and gasoline fuels) and NTP,[30] we computed fuel specific number emission factors for the NCA: $2.4{\cdot}10^{15}$ ± $1.5{\cdot}10^{15}$ $(kg_{fuel})^{-1}$, $2.6{\cdot}10^{15}$ ± $1.7{\cdot}10^{15}$ $(kg_{fuel})^{-1}$ and $2.9{\cdot}10^{15}$ ± $0.5{\cdot}10^{15}$ $(kg_{fuel})^{-1}$ for the three environments, respectively. The error limits were formed from the 95% confidence limits obtained for the slopes of the fits (Fig. 4). For the engine laboratory experiments the fuel specific emission factors for NCA were $1.6{\cdot}10^{12}$ $(kg_{fuel})^{-1}$ at low load, $2.2{\cdot}10^{14}$ $(kg_{fuel})^{-1}$ at medium load and $4.3{\cdot}10^{15}$ $(kg_{fuel})^{-1}$ at high load (diesel fuel, thus assuming a CO_2 emission of 3160 g/kg fuel and NTP[30]). Thus, the traffic NCA emissions determined in the three field experiments were between the minimum and maximum emission factors observed in the laboratory study. When compared to other studies,[30,31] it can be concluded that the NCA emission factors of traffic are at same level with the emission factors of larger particles. In the worldwide perspective, the annual NCA emissions of road traffic are likely to exceed $4.2{\cdot}10^{27}$ per year (see Supporting Information), which represents a significant increase to the existing estimate of $17{\cdot}10^{27}$ a^{-1} for global anthropogenic particle sources[32].

Recent studies[33] have shown strong indications that a large fraction of secondary organic aerosol (SOA) formation is due to extremely low volatility vapors condensing on available aerosol surfaces. We show here that traffic-emitted NCA increases the aerosol particle number concentrations in environments near traffic. Prior research has shown that particle concentrations decrease when moving away from the roadway; this is generally attributed to coagulation and dilution[2,26,34], although also evaporation has been suggested[35]. The scavenging timescale of diluted NCA is of the order of 20 minutes to reach the levels observed for urban background aerosol. Therefore, NCA can be transported for several kilometers before removal by loss processes meaning that in urban areas the traffic-originated NCA is likely ubiquitous, and itself contributes significantly to the background. Comparing to other NCA sources, in urban environments traffic-emitted NCA is likely to exceed the number of particles formed by photochemical nucleation. High anthropogenic aerosol concentrations have typically been considered as an inhibiting factor in terrestrial boundary layer nucleation due to their effect in scavenging both condensing vapors and fresh nanoparticles from the air. Regional photochemical formation is considered to be the major source of NCA-sized aerosol in the atmosphere. Our finding updates this view, showing that human activity also directly produces nano-sized aerosol which may allow even a majority of the condensational growth events of atmospheric aerosol particles to begin in urban areas, reported, e.g., by Ahlm et al.[37], by acting as nano-sized condensation nuclei for both secondary anthropogenic and biogenic low-volatility organic compounds. Thus, the NCA has the potential to enhance tropospheric aerosol formation, and by that route, modify terrestrial cloud cover. Therefore, our finding opens new possibilities to understand atmospheric processes affecting climate, in addition to presenting a new anthropogenic NCA source that may affect urban air quality and therefore also public health.

Methods

Atmospheric measurements. The studies consisted of three atmospheric measurements covering a wide range of environments: stationary measurements at the roadside of a main road in a semi-urban area, stationary measurements in a street canyon in an urban area and a long-distance on-road study using a mobile aerosol laboratory. The nanocluster aerosol (NCA) measurements were performed using an instrument capable of detecting extremely small nanoparticles, with diameters of as small as ca. 1.3 nm (Particle Size Magnifier, PSM)[28]. NCA measurements were reinforced by measurements with other instruments.

The experiment which produced the first observation of NCA in an urban traffic environment was conducted in a roadside environment between October 19th and 30th in 2012. The measurement station was located at a distance of 5 m from the pavement of the ring road Ring 1, which is one of the main roads in Helsinki (Fig. S1). Daily traffic rate on that road during workdays is approximately 70'000 vehicles, including both heavy-duty vehicles (8%) and passenger cars. Ambient temperature and relative humidity varied between -5 and +14°C and 43-93%, respectively, and were continuously measured at a weather station located in Pasila (Fig. S1). Weather parameters were temporarily measured with a mobile laboratory[37] next to the measurement station with a good correlation with the continuous measurements. The measurement station data was classified based on the wind direction data into two relevant sectors and the sectors between these (Fig. S1b). The road-influenced sector was defined as wind directions 110-270° and the clean sector as directions 325-55° (with 0° as north).

The aerosol sample was drawn into the measurement station from the roof of the station (height 3 m) and then led to the online aerosol instruments. The combination of a particle size magnifier (PSM A09, Airmodus

Oy) and a condensation particle counter (CPC model 3775, TSI Inc.), referred simply as a PSM, measured the concentration of particles larger than 1.3 nm. It was used parallel with CPC (model 3776 TSI Inc.) that measured the number concentration of the particles larger than 3 nm in diameter. The particle size distribution was measured with a differential mobility particle sizer (DMPS) equipped with a Vienna type DMA (differential mobility analyzer) and a CPC (model 5.401 Grimm ltd). The DMPS covered a size range from 6 nm to 1 µm. Also gaseous pollutants NO_x (APNA-360, HORIBA) and CO_2 (Maihak Sidor, SICK) were monitored. CO_2 concentrations were used in the evaluation of the emission factors of NCA.

The time series of the number concentrations measured by the PSM and the CPC is shown in Fig. S2a. For the purpose of the further analysis and visualization, the data was averaged over a 5-minute time window. The concentration of the NCA, i.e., the particles from 1.3 nm to 3 nm, was defined as the difference of the concentrations measured by these two devices. The relative number concentration normalized by the total number concentration N_{tot} measured by the PSM and classified according to the road influenced and clean sectors is shown in Fig. S2b. As seen in Fig. S2a, both the PSM and the CPC measured rather high concentrations around 10^6 #/cm^3 at the maximum. The actual counting instruments, CPC model 3775 and the CPC model 3776, were concentration calibrated in the laboratory after the field campaign based on the Single Charged Aerosol Reference[38]. The calibration results were further applied in the data-analysis. Due to the material dependency of the lower detection limits of a diethylene glycol based PSM and of a butanol based CPC[39], this study may slightly underestimate the NCA concentrations.

In a street canyon environment in an urban area, the NCA concentrations were measured for three months. The measurement station was located on the pavement along a relatively busy road which leads towards Helsinki City Centre (Fig. S1). The exact address of the measurement station is Mäkelänkatu 50. The site can be classified as an avenue canyon with the aspect ratio (height/width) of 0.4 (Fig. S3). The road has 6 lanes with two tramlines and rows of trees in the middle. In total, the width of the road is 42 m. The road is flanked by 4- and 5-floor buildings. The traffic rate on Mäkelänkatu is approximately 28'000 vehicles/workday of which heavy-duty vehicles account for 9 %. Measurements were conducted between April 7th and June 26th in 2015. The temperature and relative humidity measured at the station varied between 2.1-21 ºC (avg 8.6 ºC) and 18.9-92.9 % (avg 65.1%), respectively. Wind direction measurements were performed at the weather station located in Pasila with measurement height at 53 m above ground and 78 m above sea level (Fig. S1), representing thus the roof-top wind at the measurement site. The measurement station data was divided according to the wind direction into two sectors and the sectors between these as seen in Fig. S1c. In the case of perpendicular flow, the local wind within the cavity of the canyon was assumed to be contrary to the roof-top wind. Consequently, the road influenced sector was between the angles 165-285° and the clean sector between the angles 0-105° and 345-360°.

The particle sample was drawn from the roof of the station (height 4 m) and then conducted to the online aerosol instruments in the measurement station. The setup consisted of a combination of a particle size magnifier (PSM model A10, Airmodus Oy) and a condensation particle counter (CPC model A20, Airmodus Oy), referred simply as a PSM. A bridge diluter (DR 7.55) was used in the sampling line before the PSM. The PSM was set to measure the number concentrations in a step-mode with four different cut-off sizes: 1.2, 1.5, 1.8, and 2.7 nm. The measurement duration for one step was 60 s and hence one cycle took 4 min in total. The diurnal hourly averages were calculated separately for each step and the NCA concentrations were determined from the concentration difference of the first and the last step. Sub-3 nm measurement points for the particle number size distributions were determined similarly from the step-data. Particle size distribution for larger particles was measured with a DMPS equipped with a Vienna type DMA and a CPC (model A20, Airmodus Oy). The DMPS covered a size range from 6 to 800 nm.

The on-road NCA emissions were studied with a mobile laboratory unit while driving in traffic. The mobile laboratory consists of a large van equipped with sampling systems for both gaseous and particulate compounds, a compartment where the instruments can be installed, a desktop space for the operator to control the measurement and a power source to supply the instruments. In Fig. S4a a picture of the mobile unit is shown, and a measurement situation on road is shown in Fig. S4b. The measurement route, shown in Fig. 2b (main text), started eastwards from the Atlantic coast in northern Spain. It then turned towards north form the Mediterranean coast in southern France and continued through France, Luxembourg, Belgium, the Netherlands, Germany and Denmark to the large bridges over the Great Belt and the Sound. From there the route continued through southern Sweden towards a ferry connection to Finland. The total distance covered within 6 days was ca. 3600 km. While the route consisted mainly of larger motorways, smaller highways and city traffic were also included where the schedule allowed.

The aerosol sample for the instruments was taken in front of the van from the centerline, just above the windscreen. The sampling probe was bent downstream of the flow in order to prevent insects and rain droplets entering to the sample. The sample line continued to the instrument compartment with a residence time of < 1s, where the sample was divided via a bridge diluter (DR=42) to the CPC 3776 (TSI Inc) and the PSM consisting of a Particle Size Magnifier (PSM model A10, Airmodus Oy) and a model 3775 CPC (TSI Inc.). CPC model 3776 (TSI Inc) measured the total particle number concentration for particles larger than 3 nm, while the total number concentration of particles larger than ca. 1.3 nm were measured with the PSM. CO_2 concentration was measured using an IR photometric analyzer (SIDOR, Sick Maihak). The measured data from all these instruments (shown in Fig S5) was saved with one-second time resolution. A weather station (WeatherStation 200WX, Airmar Technology Corporation) provided information on the wind speed and direction, air temperature, barometric pressure, relative humidity, GPS location, vehicle speed and vehicle direction in the sampling point. A time series of the measured air temperature (T), relative humidity (RH), barometric pressure (p) and altitude are shown in Fig S6.

Engine laboratory experiments. Laboratory experiments with a modern four-cylinder turbo-charged common rail heavy duty diesel engine (displacement 4.4 dm^3) equipped with an intermediary cooling system for the intake air, a diesel oxidation catalyst (DOC), a diesel particle filter (DPF) and a selective catalytic reduction system (SCR) were conducted to verify the traffic environment observations. The ultra-low sulfur diesel fuel (FSC < 10 ppm) was used. Thus, the technology level of the test engine corresponds to the typical modern (and even future) heavy duty diesel buses, trucks and working machines. Three experiments were conducted at an engine test bench, each at different engine loading. The driving parameters and regulated emissions of each experiment are shown in Table S1.

The measurement setup is shown in Fig. S7. To mimic real-world nanoparticle formation, an exhaust sampling system[40] that has been reported to mimic exhaust nucleation mode particle formation relatively well[29,41] was used. By using this sampling system, a part of exhaust was sampled directly from the tailpipe and, further, diluted immediately using a porous tube type primary diluter[42], led through a residence time chamber with a residence time of 2.6 seconds and, finally, diluted by an ejector secondary dilution unit. In the primary diluter the dilution air temperature was kept at 30 °C and the dilution ratio, calculated from CO_2 data from undiluted and diluted exhaust, was kept at 12. The relative humidity for the pressurized and filtered dilution air was close to zero. After the secondary dilution unit, the exhaust aerosol was led into the aerosol instruments. Because of the high stability of the particle concentrations, the PSM was used in the scanning mode, thus providing information on both the number concentration and size distribution of particles smaller than 3 nm in diameter. In order to convert the cumulative number concentration measured by the PSM to particle size distributions, calibrations for different saturator flows of the PSM was used.[25] In addition to the PSM, exhaust particle number size distributions were measured using scanning mobility particle sizer (SMPS)[43] equipped with a DMA 3085 (TSI Inc.) and a CPC 3025 (TSI Inc.), called here as Nano-SMPS, an engine exhaust particle sizer (EEPS, TSI Inc.)[44] and an Electrical Low pressure Impactor (ELPI, Dekati Inc)[45]. The EEPS and the ELPI were used to monitor the stability of the larger particle emission during the experiment. Particle volatility was studied using a thermodenuder[5] in which the aerosol sample was first heated to 265 C and, after that, led through the denuder part to collect the evaporated compounds to active charcoal.

The data presented in the current manuscript has been stored in the Finnish IDA (openscience.fi/ida) storage service. Once the manuscript has been accepted, the metadata of the dataset will be updated to reflect this, and made available in the ETSIN (openscience.fi/etsin) research data service with a permanent download link. The link will also be added to the TUT research data system TUTCRIS (https://tutcris.tut.fi/portal/en/datasets/search.html). The direct and permanent link to the data download will be provided in the final manuscript.

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