ABSTRACT

Due to the stringent emission standards set worldwide, particulate matter (PM) emissions from diesel vehicles have been significantly curtailed in the last decade, and are expected to be reduced even further in the future. This evolution has brought forward two main issues: whether PM emissions should only be regulated for diesel vehicles and whether gasoline powered vehicles can be further neglected from PM emission inventories. This paper addresses these issues comparing the characteristics of particle emissions from a current diesel passenger car, a gasoline one and two small two-wheelers. It is shown that the gasoline car is a negligible source of particle emissions while the two-wheelers may be even more significant particle sources than the diesel car.

INTRODUCTION

Despite the significant epidemiologic and experimental research, there is still no clear view as to which particle properties are responsible for adverse health effects [1]. The main reason of the inability to establish direct associations between particle properties and health effects is, most probably, the physical and chemical complexity of the exhaust particles. This includes the wide size range reported, typically 7 nm to 1 µm, the different formation processes and hence properties (volatile, solid particles) and the confusion with additional exhaust components. However, thorough review studies from the California Air Resources Board and the US Environment Protection Agency list diesel exhaust PM as “toxic air contaminant” [2] and “likely to be carcinogenic” [3] respectively.

Recently, health effects caused by non-diesel exhaust PM have also received attention. In particular, PM emitted by two-stroke gasoline engines is of interest. It has been shown that PM emissions from diesel, gasoline and two-stroke vehicles exhibit similar mutagenic activity and toxicity [4] and that motorcycle particulates may induce acute health effects by chemical mechanisms [5]. Research on the health effects of non-diesel exhaust particulates has been initiated by the significant curtailment of diesel emissions, forced by relevant legislation world-wide. In Europe, diesel passenger car PM emissions for the years 2000 and 2005 are in the level of 50 mg km\(^{-1}\) and 25 mg km\(^{-1}\) respectively. The Year 2005 value represents an over 80% reduction compared to Year 1995 levels.

For some time now, particle emission related research has complemented mass measurements with additional metrics, including number concentration and size distribution. There is valid evidence which indicates that near-road ambient concentrations are dominated by nuclei mode particles (<50 nm) [6,7] and that vehicles are significant sources of particles in this size range [8]. Despite their large number concentration, particles in this size range cannot be quantified by mass terms, due to their small size. However, their characterization is considered important because of their penetration in the alveoli region and their higher toxicity than larger particles, possibly due to their larger specific area [9].

The characterization of nanometer particles is sensitive to the sampling and measurement conditions. This is because the main formation mechanism in this size range is the nucleation of condensable species present at the exhaust gas. Hence the saturation ratio of such species, determined by their concentration and dilution ratio and temperature at the sampling point, together with the time which is available for nucleation to occur are critical for the formation of new particles [10]. Obviously, given the sensitivity of such particles, the same “measurement” conditions need to be established when comparing particle emissions from...
different sources. “Measurement” in this case includes instrumentation, sampling and dilution devices and range of parameters utilized. Otherwise, any comparison may not actually reproduce vehicle effects but rather sampling system effects.

In this context, this paper compares particle emissions from different vehicles using an identical measurement protocol and sampling conditions. The vehicle sample consists of two small two-wheelers of improving technology, one current diesel passenger car and a gasoline one of equivalent emission standard. The comparison involves real-time characterization of a number of particle properties, including mass, number concentration, size distribution, specific surface and distinction to solid and volatile particles. Further to the establishment of absolute levels, particular emphasis is put on vehicle operation conditions, which may provide additional constraints with regard to particle emissions.

**EXPERIMENTAL**

**VEHICLES**

Table 1 shows the specifications of the sample vehicles. European legislation (97/24/EC) classifies powered two wheelers (PTWs) according to their engine capacity to mopeds (<50 cm³) and motorcycles (≥50 cm³). Our sample includes a non-catalyst moped (Mnc), an oxidation catalyst equipped motorcycle (Mcat), a diesel passenger car (D) and a gasoline passenger car (G).

The two-wheelers selected are common models in the European market. Mnc represents an average moped before any European emission standards became applicable for this vehicle category. Mcat is a somehow larger motorcycle, complying with EU Directive 97/24/EC which set the first emission standards for this vehicle category (CO: 8 g km⁻¹, HC: 4 g km⁻¹, NOₓ: 0.1 g km⁻¹). The two passenger cars are also common in the market. D is an average family car equipped with a latest technology common rail diesel engine. One oxidation pre-cat and a main under-floor oxidation catalyst are employed to allow for compliance with the strict Euro III emission standards: CO: 0.64 g km⁻¹, HC+NOₓ: 0.56 g km⁻¹, NOₓ: 0.5 g km⁻¹, PM: 0.05 g km⁻¹. G is the performance version of a small family car, equipped with an advanced gasoline engine using variable timing and lift of the valves. This vehicle also complies with Euro III emission standards (CO: 2.3 g km⁻¹, HC: 0.2 g km⁻¹, NOₓ: 0.15 g km⁻¹) by utilizing a three-way under-floor catalyst and a dual lambda sensor. The two passenger cars were of low mileage and at very good overall condition.

**FUELS**

The gasoline used was a conventional Year 2000 specifications type of fuel (according to Directive 98/70/EC). It has a RON number of 95, a sulfur content of 125±25 ppm wt., trace lead (max 5 mg l⁻¹) and no oxygenates. The Diesel fuel used exceeds Year 2000 specifications. It has a sulfur content of 31 ppm wt. and 2.4 % wt. PAH content. The lubricant oils used were synthetic (mineral in the case of D) and fulfilled manufacturer recommendations. Their chemical composition is unknown.

<table>
<thead>
<tr>
<th>Make and model</th>
<th>Plaggio Typhoon</th>
<th>Yamaha BWS</th>
<th>Renault Laguna</th>
<th>Toyota Corolla</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vehicle Coding</strong></td>
<td>Mnc</td>
<td>Mcat</td>
<td>D</td>
<td>G</td>
</tr>
<tr>
<td><strong>Category</strong></td>
<td>Moped</td>
<td>Motor- cycle</td>
<td>Pass. Car</td>
<td>Pass. Car</td>
</tr>
<tr>
<td><strong>Emission standard</strong></td>
<td>-</td>
<td>97/24/EC</td>
<td>98/69/EC Euro III</td>
<td>98/69/EC Euro III</td>
</tr>
<tr>
<td><strong>Model Year</strong></td>
<td>1999</td>
<td>2001</td>
<td>2001</td>
<td>2002</td>
</tr>
<tr>
<td><strong>Model / Engine type</strong></td>
<td>XR 50</td>
<td>BWS 100</td>
<td>1.9 dCi (F9Q718)</td>
<td>1.8 VVTI-i (2ZZ-GE)</td>
</tr>
<tr>
<td><strong>Capacity [cm³]</strong></td>
<td>49</td>
<td>100</td>
<td>1870</td>
<td>1796</td>
</tr>
<tr>
<td><strong>Cylinders / valves per cylinder</strong></td>
<td>1</td>
<td>1</td>
<td>4 / 2</td>
<td>4 / 4</td>
</tr>
<tr>
<td><strong>Max.power (kW/rpm)</strong></td>
<td>2.2 / 6750</td>
<td>5.8 / 7000</td>
<td>79 / 4000</td>
<td>141 / 7800</td>
</tr>
<tr>
<td><strong>Max.torque (Nm/rpm)</strong></td>
<td>n/a</td>
<td>9.2 / 6000</td>
<td>250 / 1750</td>
<td>180 / 6400</td>
</tr>
<tr>
<td><strong>Oil delivery system</strong></td>
<td>Metered</td>
<td>Metered</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Combustion system</strong></td>
<td>2-stroke carburator</td>
<td>2-stroke carburator</td>
<td>Common rail direct injection (max 1350 bar)</td>
<td>Port fuel-injection, variable valve timing and lift</td>
</tr>
<tr>
<td><strong>Mileage (km)</strong></td>
<td>15714</td>
<td>12170</td>
<td>23000</td>
<td>11300</td>
</tr>
<tr>
<td><strong>Transmission</strong></td>
<td>CVT</td>
<td>CVT</td>
<td>Manual</td>
<td>Manual</td>
</tr>
<tr>
<td><strong>Weight empty (kg)</strong></td>
<td>83</td>
<td>88</td>
<td>1315</td>
<td>1285</td>
</tr>
<tr>
<td><strong>After-treatment</strong></td>
<td>-</td>
<td>Oxidation catalyst</td>
<td>Oxidation pre-cat and main catalysts</td>
<td>Three-way catalyst, dual lambda sensor</td>
</tr>
<tr>
<td><strong>Type-approval cycle</strong></td>
<td>ECE-47</td>
<td>ECE-40</td>
<td>NEDC</td>
<td>NEDC</td>
</tr>
</tbody>
</table>

n/a: not available

**DRIVING PATTERNS**

In order to determine particle emissions, all vehicles have been driven according to their type-approval cycles (Figure 1). However since two-wheelers driving cycles are hot-start while passenger cars’ one is cold- start, we ran a modified version of the NEDC with hot engine at start, in order to establish similar conditions for comparison of the vehicles. The two cars were warmed up, running a full cold-start NEDC before the hot-start measurement. Comparisons were made with regard to the urban part (UDC) of the NEDC only, which is similar to the ECE40 cycle, because the PTWs driving cycle includes an urban part only. Also, two steady speed tests have been...
conducted at 50 km/h (for all vehicles) and at 120 km/h (for passenger cars only).

Despite the similarities in the driving pattern between the cycles, they impose different engine loading conditions for the cars and the PTWs. UDC is a calm urban cycle for the cars with mild accelerations and a low top speed (50 km h⁻¹). It is estimated that for the cars examined, maximum load demand is below 30 % for the engine speed range covered by the cycle. The same cycle (ECE40) corresponds to higher loads for the motorcycle which tops at about 80 km h⁻¹. Such a cycle is not considered representative of actual motorcycle driving and is soon to be amended by the World Motorcycle Test Cycle (WMTC). On the other hand, the ECE47 cycle is a demanding cycle for the small moped and incorporates full-load acceleration and driving at full speed (55 km h⁻¹). However, such a cycle fairly well represents actual urban driving of such small vehicles. In any case, the different load demands placed on the vehicles examined, ranging from low-load, low-speed for the cars, to full-load full-speed for the moped, need to be taken into account in the interpretation of the results.

MEASUREMENT SETUP

Particle samples are drawn directly at the tailpipe. A T-shape connector splits the flow to a main part which is led to the CVS for conventional pollutants analysis and a small part which is drawn by a sampling probe (Figure 2). The main characteristics of this probe have been presented elsewhere [11]. The principle of the system is that it allows rapid mixing (1 – 2 ms) of the exhaust sample with dilution air within the probe under controlled temperature conditions. This is achieved by introducing dilution air at the tip of the probe while cooling the walls with water flowing in an external jacket. A dilution ratio (DR) setting may be achieved by varying the flowrate of the dilution air with a mass flow controller, while sample flowrate is regulated by the measuring instrumentation.

This sampling system was developed in the framework of the European Commission’s “PARTICULATES” project. Its main advantage is the possibility for real-time characterization of solid and volatile particles. This is achieved by splitting the flow in two branches. One branch (named by convention “wet” branch) consists of an aging chamber with a residence time of about 2 s, where flow and nucleation mode stabilize. This is because, nucleation mode can be quite unstable during the first hundreds of milliseconds after formation. Downstream of the aging chamber, a part of the sample is further diluted by ejector dilutors (Dekati, Inc.) and is fed to a fixed voltage differential mobility analyzer (DMA – TSI model 3080L) followed by a condensation particle counter (CPC – TSI model 3010). Another fraction of the sample is fed to a diffusion charger (DC – Dekati, Inc.) used to record the “active” surface of particles. The larger part of the flow in the wet branch is sampled through a paper filter, which is used for quality control purposes, comparing this mass with the mass collected on the CVS filter.

Before reaching the aging chamber, a fraction of the flow is conditioned in a thermodenuder (Dekati, Inc.)
which removes volatile and semivolatile components. This is called "dry" branch by convention because only solid particles are sampled at the outlet of the instrument. In that respect, we consider as "solids" those particles that do not evaporate at 250°C in the thermodenuder. It has been shown that such a temperature is sufficient to separate condensable species [12]. Number weighted aerodynamic size distribution of particles is then recorded with an Electrical Low Pressure Impactor (ELPI – Dekati, Inc.). In these experiments, sintered metal collection substrates have been used in the ELPI and an end-filter connected to an electrometer channel to collect any particles evading impaction on the finest ELPI stage (7 – 25 nm aerod. diam.).

All necessary precautions were taken to ensure minimal particle losses and interference. Grounded stainless steel is used in all components of the sampling system. Thermal insulation is used in parts where thermal gradients may become significant and short conductive Tygon tubing is used for connecting the instruments to the sampling outlets. Dilution air is dehumidified in a silica gel chamber (relative humidity <5 %), volatile species are collected in a charcoal chamber and a HEPA capsule is used to remove any particle loading. Finally, ejector dilutors were calibrated before each test with CO2 recordings upstream and downstream of each dilutor. Final dilution ratios depended on the required sensitivity for each instrument, which, in turn, depends on the engine-out emission level. Differentiation of the dilution ratios was possible by modifying the primary dilution ratio and reallocating the secondary dilution units. Obviously, there are still differences between the "wet" and "dry" branches resulting in different particle losses. Also, secondary dilution units may provide some additional interference to the measurements (losses and modification of the size distribution). In average, losses in the wet and dry branches are estimated to be 10 % and 25 % respectively due to the operation of the thermodenuder in the latter case. On the other hand, since sampling set-up is almost identical for the different vehicles, losses are expected to be at the same level for all vehicles and hence no correction is applied for.

Table 2: Dilution ratios and residence times to each instrument according to vehicle tested.

<table>
<thead>
<tr>
<th>Vehicle</th>
<th>CPC/SMPS</th>
<th>DC</th>
<th>ELPI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DR (s)</td>
<td>RT (s)</td>
<td>DR (s)</td>
</tr>
<tr>
<td>Mnc</td>
<td>1200</td>
<td>3.05</td>
<td>1200</td>
</tr>
<tr>
<td>Mcat</td>
<td>150</td>
<td>3.05</td>
<td>150</td>
</tr>
<tr>
<td>D</td>
<td>10⁵</td>
<td>3.55</td>
<td>100</td>
</tr>
<tr>
<td>G</td>
<td>10⁶</td>
<td>3.55</td>
<td>100</td>
</tr>
</tbody>
</table>

*CPC dilution ratio. SMPS dilution ratio was 100.

In addition to the dedicated particle measurement protocol, conventional gaseous pollutants and PM measurements were conducted following the Constant Volume Sampling (CVS) procedure. In case of PM, the methodology relevant for diesel passenger cars was also applied for PTWs and the gasoline passenger car to establish a common reference to compare particulate emissions. Hence, pre-conditioned Teflon-coated filters were used to collect particulate samples, which were thereafter conditioned again and weighted with a Mettler Toledo balance (sensitivity 10⁻⁷ g).

RESULTS

CO2 AND FUEL EFFICIENCY

Figure 3 shows the CO2 emissions and fuel consumption of the selected vehicles. For the passenger cars there are two lines in each chart, one corresponding to the hot-start urban driving and one to the cold-start UDC. Results are an average of three repetitions for the PTWs and two repetitions for the cars. The max-min range is reported in the form of error bars, which are hardly visible due to the fair repeatability of CO2 and FC measurements.

![Figure 3: CO2 emissions (upper panel) and fuel consumption (lower panel) for hot and cold-start urban driving. Average of three measurements for PTWs and two for the cars, error bars showing the difference between max and min recordings.](image)

The chart shows the well-known lower CO2 emissions and improved fuel efficiency of the diesel over the gasoline one, which in the case examined is in the order of 20 – 25 %. CO2 emissions from the PTWs are significantly lower (4 – 8 times) despite the fact that fuel consumption is only 2 – 3 times lower. As it will be shown below, this is due to the fact that a significant fraction of fuel is not oxidized to CO2 but either is partly oxidized to CO, or is directly scavenged unburned to the environment. This results in the low thermal efficiency of the PTWs. Additionally, this is the reason for increase of the CO2 moving from Mnc to Mcat although fuel consumption decreases.
GASEOUS POLLUTANTS

Figure 4 shows the conventional, gaseous pollutant emissions from the four sample vehicles. There are dramatic differences between the vehicles and with regard to CO emissions. CO emissions from the non-catalyst moped are more than three orders of magnitude higher than the diesel vehicle, which is the lowest emitter. The catalyst operation is 80% effective in reducing CO in case of the Mcat, compared to the Mnc but still emissions from the catalyst two-wheeler are 25 times higher than the gasoline passenger car. Such high CO emissions from the PTWs are obviously the outcome of fuel-rich operation and incomplete combustion of the poorly mixed mixture. It will be shown that the same mechanisms may be responsible also for high particle emissions.

HC emissions behave similarly to CO. Again, the diesel passenger car is the lowest emitter for both cold and hot-start conditions. In general, Diesel vehicles are known for their low HC emissions and in this case the two oxidation catalysts employed bring emissions to very low overall levels. G is significant emitter only in the case of cold-start. At hot-start emission levels are 80% lower and comparable to the diesel vehicle. The two small two-wheelers emit 2 – 3 orders of magnitude more than the passenger cars. Comparison of the fuel consumption and HC emissions for the Mnc shows that almost 1/3 of the fuel consumed is emitted unburned to the atmosphere due to cylinder scavenging. However, this is a rough estimation because HC emissions also originate from lubrication oil. The oxidation catalyst is 75% effective in reducing HC but still emission is at high levels. Presently, HC emissions are probably the most significant pollution related problem for PTWs.

On the other hand, NOx emissions from the two PTWs are in significantly lower levels than either the D or the G passenger cars. D, as expected is the highest emitter, reaching more than twice the hot-start G levels and 35 times the level of the Mcat. It is not clear why oxidation catalyst equipped motorcycle is a lower emitter than the non-catalyst one. Probably this is a specific engine characteristic. In any case, given the emission levels of the passenger cars, NOx emissions from two-wheelers do not constitute a main issue for today or the future.

With regard to the repeatability of the measurements, error bars in Figure 4 show that PTWs are the most stable emitters and the G-car appears as the most variable. However, emission variations are relatively small and rather insignificant compared to the large absolute differences between the vehicles.

PM EMISSIONS

Figure 5 shows PM emissions obtained by the CVS procedure used for diesel passenger cars. PM emissions determined in this way result in higher values for both PTWs compared even to the diesel car. More specifically, Mnc emits three times and Mcat twice as high as the diesel car. This is a striking finding, given the fact that PM emissions are only regulated for cars and trucks and not for PTWs. The values reported here are similar to what is found in the literature [13]. However, diesel particulates consist of a significant fraction of soot, while PTWs particulate emissions are expected to consist up to 95% of volatiles [13,14]. The reasons for high PM emissions from two-stroke engines are primarily the high scavenging losses, which can amount to 15 – 40% of the unburned fresh charge [15], and the addition of the lubricant in the combustion chamber. Such effects result in high HC emissions, white smoke emission which is particularly obvious for such vehicles and in the collection of large amounts of volatile PM. In our case, heating of the filter papers in an inert atmosphere revealed that 62 – 86% of the total PM mass from PTWs should be attributed to volatile species.

The implications of the different formation mechanisms and chemical speciation of two-stroke particles compared to diesel ones are significant both with regard to their environmental and health consequences and with regard to the technical measures involved to reduce emissions. Therefore, one needs to be cautious when drawing conclusions by only comparing PM levels. More information on particle characteristics given in the following sections may help in such a direction.

PM emissions from the gasoline car are in the order of 2 mgkm$^{-1}$ for both hot and cold-start driving and reach the sensitivity limit of the CVS procedure. This
level is still more than ten times lower than the expected diesel standards in 2005. In principle, the current CVS requirements are only applicable to diesel cars and are not adequate to accurately determine such low mass emission rates. Thus, levels reported should only be considered as indicative. Given the constraints following a similar CVS procedure, literature reports PM emissions for port fuel injected gasoline vehicles in the range of 1 – 4 mg km\(^{-1}\) [16-19]. With such low emission levels, PM emission from gasoline vehicles are not expected to become an issue of the foreseeable future and for the driving conditions considered in today’s legislation.

Figure 5: PM emissions over hot and cold start urban driving (mg km\(^{-1}\)). For the D and G cars, the cold start emissions cannot be discriminated from the hot ones. Error bars correspond to three and two repetitions for PTWs and cars respectively.

Finally, a similar to gaseous pollutants repeatability is found for PM, over the limited number of repetitions conducted. However, such repeatability is sufficient to establish differences between the vehicles.

PARTICLE CHARACTERISTICS

A more thorough insight of the particle characteristics can be obtained from the recordings of the dedicated particle measurements, which are depicted in Figure 6. Three driving conditions are shown in this Figure: transient urban driving after a cold-start and a hot-start and steady state speed driving at 50 km\(\cdot\)h\(^{-1}\). This condition corresponds to low load condition for the cars, a moderate load/speed condition for the motorcycle and an almost full load/speed for the moped. Hence, interpretation of the results needs to take into account the significantly different engine loading in each case. Additionally, and in contrast to the legislation where PTWs regulated emissions are recorded only after hot-start, we applied the particle protocol also for cold-start driving.

The upper panel of Figure 6 shows the active particle surface. Active surface is a relatively new definition [20] for the particle surface area that is available for interaction with ions and molecules in the environment and is determined by means of electrical diffusion chargers. Active surface is supposed to be the effective surface area available for mass transfer in a kinetically limited situation and is an elegant measure of gas-to-particle transfer mechanisms occurring in the exhaust plume, in the atmosphere or the human body [8]. For particles smaller than the mean free path of the carrier gas, it corresponds to their geometric surface. Also, it does not depend on surface chemistry because it is determined by ion Brownian diffusion, except for particles less than \(~10\) nm where material properties may become important [21].

Figure 6 shows that there are differences of several orders of magnitude in the particle active surface between the different vehicles. Similarly to the PM levels, active surface from PTWs is at the same or higher level than the diesel car and in the order of 5-15 m\(^2\) km\(^{-1}\). In the case of the full load/speed condition encountered for the Mnc vehicle at 50 km\(\cdot\)h\(^{-1}\), active surface exceeds 100 m\(^2\) km\(^{-1}\). This is expected given the dense white smoke plume observed for the specific vehicle at this driving condition. On the other edge, the gasoline car has two to four orders of magnitude lower emissions than the diesel, with respect to active surface. The effect of the cold start in the G case is obvious, in contrast to the rest of the vehicles, but absolute levels still cannot be considered significant. In general, similar conclusions can be drawn when comparing PM emissions and
active surface. In this respect, active surface might be a convenient surrogate measure for PM where higher sensitivity is required.

The middle panel in Figure 6 shows the number concentration of solid particles only. It is reminded that solid particles correspond to particles recorded after the thermodenuder in the “dry” branch (Figure 2). Mnc is found at the same levels with the diesel car. Given the high CO emissions of Mnc, it is evident that the engine operates at fuel-rich condition, which results in high solid particle emissions too. Similarly to active surface, the highest emissions of all cases occur at full load of the Mnc (50 kmh⁻¹). The Mcat emissions are at lower levels with the exception of cold start. Since the catalyst is not effective in reducing the concentration of solid particles, increased emissions over cold start probably occur due to the fuel-enrichment. Cold-start effect is also evident in the G-case, increasing hot levels by one order of magnitude. Overall though, the G car emits a very low concentration of solid particles, which, under hot operation is 1000 times lower than that of the diesel car. Both active surface and solid particle number repeatability are comparable to PM and gaseous pollutants measurements.

The lower panel in Figure 6 shows the mean aerodynamic particle diameter in the range 7 nm – 1 μm. PTWs emissions are associated with smaller aerodynamic diameters than those of the two cars. In general, there is no particular effect of the driving condition on the size of the particles, which are rather vehicle specific. The results of the G car appear variable. This is probably due to the very low concentrations, which reach the sensitivity limit of the instrument and hence increase uncertainty.

STEADY STATE SIZE DISTRIBUTIONS

It is possible to obtain the size distribution of the emitted particles during steady state driving, using the SMPS. Figure 7 shows particle mobility distributions at two different speeds (upper panel 50 kmh⁻¹ and lower panel 120 kmh⁻¹). At 50 kmh⁻¹ Mnc is the highest emitter because this condition corresponds to full load for this vehicle. In this case, a bi-modal distribution forms which is obvious despite the significant variability at low sizes. Mnc is a higher emitter that the D car over all particle sizes, including both the nuclei (<50 nm) and the accumulation mode (>50 nm). The D-car forms a lognormal distribution which is very stable (low variability) and presents a peak at 70 nm. The catalyst two-wheeler is found overall below the D-car. It is difficult to obtain the exact shape of the distribution for the Mcat. This is because the nucleation mode is very sensitive and may or may not occur in some repetitions.

More repetitions of SMPS scans were conducted with the PTWs. This was because repeat steady state conditions were reached following different operations (high load or idling). In that way, we identified that the exhaust system pre-condition is responsible for this variable nuclei mode behavior: when high load conditions preceded the measurement, the nuclei mode tended to disappear and vice versa. These phenomena are rather well-known for gasoline catalyst cars [22]. Since the sampling system condition is only little affected by the vehicle operation and the transfer line from the exhaust to the sampling system is short (~0.5 m), catalyst pre-condition seems to be the most significant variable of nuclei mode abnormal behavior during steady-states. Indeed, the nuclei mode peak is more variable for the catalyst equipped motorcycle than the non-catalyst one. Hence, conclusions from steady state tests, especially from such vehicles need to be drawn carefully, given the dependence on measurement history.

Figure 7 also compares the G-car distribution with a typical ambient distribution. The ambient distribution corresponds to a concentration encountered at the engine inlet and is a typical distribution for an indoor urban environment. We have transformed this concentration to flux of particles per kilometer by multiplying with an average D and G car exhaust flowrate and dividing with the speed (50 kmh⁻¹). The picture clearly shows that, overall, the car emits lower
than ambient levels and only the concentration of the highly unstable few-nanometer particles appears higher. The particle flux from the gasoline car at 50 km h\(^{-1}\) is found 0.16\(\times 10^{12}\) km\(^{-1}\), which is in the same range with what is reported in the literature \([16,23]\) when no artifacts occur \([22]\).

At 120 km h\(^{-1}\) the diesel nuclei mode encountered in case of total particle number concentration disappears when solid particles are examined and a lognormal shaped distribution is formed instead. By comparison of total and solid particles, 62\% of the total particle number emissions appear as volatile particles because of the nuclei mode formation. However, the accumulation mode does not change significantly in concentration and size compared to 50 km h\(^{-1}\). Again, the G-concentration is at the detection limit levels.

The variability reported for the steady state tests is higher than for the transient testing. However, all scans reported correspond to repeat steady states and not a single steady state test. D size distributions appear stable with regard to both total and solid particles. PTWs emissions appear variable due to exhaust line and catalyst pre-condition effects as previously discussed. Finally, G distributions appear highly variable because concentrations reached the sensitivity limit of the sampling system.

**COLD START EFFECT**

This situation is similar in the case of 120 km h\(^{-1}\). The D-car, however, forms a repeatable bi-modal distribution in this case, despite the low-sulfur fuel used. The G-car remains below ambient levels despite the high catalyst temperature and the relatively high sulfur concentration in the fuel (~150 ppm). This evidence contrasts earlier work \([17, 18]\), which reported a dramatic increase in gasoline particle concentration at high vehicle speed and extends the conclusions of Hall et al. \([22]\), attributing high nuclei particle emissions to sampling system interference. With the controlled mini-dilution system in our case, we did not find any increase in particle emissions from the Euro III gasoline vehicle at 120 km h\(^{-1}\).

Figure 7 showed that the G-car particle emissions increase over a cold-start cycle, compared to hot-start. In order to explore this further, Figure 9 demonstrates the evolution of active surface and total number concentration for the D and G cars. For the
D-car, neither active surface nor total number differ between cold and hot-start. Differences are only found for idle levels. Observation of the idle levels at UDC sub-cycles shows that it takes about 250 s for the emissions to stabilize. However, this process is not significant in magnitude to bring any particular effect to the cycle averaged emissions.

In case of the G-car, cold start effect is clearly visible up to almost 400 s after engine start. It is seen that during the first accelerations, total number concentration reaches diesel vehicle levels. Total particle flux can momentarily reach up to trillion particles per second, compared to mean level of the order of $10^7$ to $10^8$ s$^{-1}$. This high flux refers to spikes of a couple of seconds, which only occur during acceleration. This is also observed in active surface emissions, where spikes with 3 orders of magnitude higher flux occur during the first accelerations. Nevertheless, G active surface always remains below D levels. The fact that active surface increase is less pronounced than total number increase means that the emitted particles are of smaller size than the diesel ones.

It also needs to be noted that there is in general, a distinct difference in the pattern of D and G particle number flux. Diesel emissions occur within the range of $7\times10^{10}$ s$^{-1}$ to $1.5\times10^{12}$ s$^{-1}$ and follow the cycle speed pattern. On the other hand, gasoline vehicle emissions range from $10^7$ s$^{-1}$ up to $10^{12}$ s$^{-1}$. Additionally, they do not follow the speed pattern but lie in general at very low levels ($10^7$ s$^{-1}$ equal to about 1000 particles per cubic centimeter) interrupted by the afore-mentioned spikes. However, the integral of the particle flux over the cycle is very low in absolute terms.

The increase of particle emissions over a cold-start cycle and the spiking behavior of the gasoline vehicles – even during steady-state operation – have been also observed in the literature [16, 24]. In the case of transients, the origin of particle spikes should be probably attributed to rich excursions from stoichiometry ($\lambda = 1$), which may occur at the start of an acceleration. This is further supported by the cold-start operation where fuel enrichment is required to improve drivability. In this case, spikes are more pronounced. In this respect, gasoline vehicles may be significant contributors to PM [25] during cold-start from low temperature. Although exhaust emissions at low temperature cold start are vehicle specific, fuel enrichment is expected to be more significant due to the low fuel volatility.

**DISCUSSION AND CONCLUSIONS**

Aim of this work was to report particle characteristics from different vehicles with application of the same measurement protocol. A measurement protocol involves specifications for the sampling conditions, sample handling and transfer and measuring instrumentation. It has been made nowadays clear that comparison of airborne particle emissions from different sources can only be conducted after such prerequisites have been established. In this respect, we applied such a protocol to record number concentration and size distributions of total and solid particle emissions and particle active surface from two two-stroke two-wheelers, one diesel and one gasoline passenger car. In addition PM and gaseous pollutants measurements were conducted following the CVS procedure.

With regard to gaseous emissions, it was found that the small PTWs are significantly high contributors to CO and HC, exceeding by up to 2 and 3 orders of magnitude the level of the gasoline and the diesel passenger cars respectively. An oxidation catalyst is 75 – 80 % effective in reducing emissions. NOx emissions of the PTWs are several times lower than the two cars and are not an issue for this vehicle category. The Euro III diesel car emitted more than twice the NOx levels of its gasoline counterpart. CO$_2$ emissions of the two PTWs were 4 – 8 times lower than the cars, partly because of their low fuel consumption and partly because a large fuel fraction either escapes combustion or is only partially oxidized to CO.

PM emissions collected on a filter paper following the CVS procedure were found highest for the non-catalyst moped, followed by the catalyst motorcycle. Still, the catalyst motorcycle emits twice as much as the diesel car in mass terms. However, one needs to judge the implications of particle emissions not on the basis of emission level solely but also given the fact that diesel particles are mainly soot while the majority of PTWs particles originate from unburned fuel and lubrication oil (62 – 86 % volatile fraction in our measurements). On the other edge, the gasoline vehicle emission level is at the detection limit of the CVS technique ($<2 \text{ mg km}^{-1}$). Additionally, no appreciable increase was found for a cold-start from ambient temperature. Obviously, port-fuel injected gasoline vehicles cannot be considered a significant source of particle emissions for the driving and temperature conditions imposed by today’s legislation.

The picture obtained for PM mass is repeated in the case of particle active surface area, which reproduces the relative emissions levels from all vehicles. We may conclude that active surface can be examined as an alternative to total PM mass when higher sensitivity is required.

The same, more or less, applies in the case of solid particle number. Solid particles mainly correspond to the soot emissions occurring when non-premixed combustion takes place. There are significant solid particle emissions for the diesel vehicle, as expected, in the order of $50\times10^{12}$ km$^{-1}$, which do not depend on driving condition. Solid particles form a lognormal size distribution with a mean diameter in the $120 – 140$ nm range. The small two-wheelers are also significant solid particle emitters, with emissions ranging from 5 to $83\times10^{12}$ km$^{-1}$, depending on vehicle and driving condition. This suggests that for the vehicles examined, significant fuel enrichment takes place. The catalyst vehicle was a lower solid particle emitter but this is probably due to the different fuel-air adjustment ratio rather than a catalyst effect. The
mean sizes of those particles are smaller than the diesel case, with a mean value found in the 40–70 nm range. The gasoline vehicle was found to be a negligible emitter of solid particles with concentrations reaching at maximum 500 particles per cubic centimeter. Compared to the few thousands particles per cubic centimeter encountered in typical ambient conditions, such concentration is well below urban atmospheric levels.

The observation of very low particle number emissions for the gasoline car does not change in the case of steady state tests, even when total (solid and volatile) particles are recorded. In contrast to findings of other investigators and our earlier experience [26], showing a dramatic increase of particle number concentration for gasoline cars at high speed, we never encountered such an effect in the present study, using a fuel of ~150 ppm sulfur and a well maintained Euro III vehicle. This should mainly be attributed to the mini-dilution system used for particle sampling. This induces minimal artifacts, such as condensable species accumulation and outgassing, which have been responsible for such abnormal behavior [22,27]. Only in the case of a cold-start cycle, a comparable to diesel particle flux is encountered during the first seconds of the cycle. Such fluxes appear as spikes during acceleration and do not significantly increase the average emission level over the cycle.

On the other hand, the two-wheelers are associated with high particle number emissions, exceeding the levels of the diesel car, at full load operation. There is a significant volatile fraction in these particles, reaching 95 % in the case of the non-catalyst vehicle. These emissions appear in a rather bi-modal distribution which peaks at 30–40 nm and at 100 nm. Given the volatile nature, the two-stroke combustion principles and information in the literature, one may conclude that a large particle fraction appears due to fuel and lubricant oil which are scavenged unburned from the cylinder. Total particle emissions from the diesel car were found within the range of the two-stroke vehicles. For the two conditions examined (50 km\(h^{-1}\) and 120 km\(h^{-1}\)) the diesel car shows a fairly constant accumulation mode and a stable nucleation mode at high speed.

Based on the findings of this study and with regard to the Diesel vehicle emissions, we found that particle characteristics in general follow the reduction in mass emissions. For comparison, a light duty vehicle of pre-Euro standards emitting 244 mgkm\(^{-1}\) over the New European Driving Cycle reached a concentration of 194×10\(^{12}\) particles per kilometer in the hot urban Driving Cycle [28] (covering the range 30 nm – 1 \(\mu m\)). The Euro III vehicle examined in this study, emitting 49 mgkm\(^{-1}\) over the New European Driving Cycle, reached 69×10\(^{12}\) particles per kilometer (in the range 7 nm – 300 nm). This is a consistent reduction, given the differences in size range and sampling conditions.

Small two-stroke vehicles emit particle counts, CO and HC concentrations disproportional to their size. Although, the highest fraction of these particles is volatile due to unburned fuel and lubricant oil emission, there is also a significant solid fraction of particles produced by the fuel-rich operation. A more recent technology vehicle, employing an oxidation catalyst, emits much less compared to an older vehicle. This is an indication that technology measures considered for CO and HC emission control in the future may also be effective in reducing particle emissions. This includes combustible lubrication oils, more effective aftertreatment and the possibility of direct injection to reduce scavenging losses. However, until such measures become widespread, small two-stroke engines need to be considered as a significant source of particles.

Finally, a late-model Euro III gasoline passenger (complying even with the strict Euro IV standards in HC emissions) is an overall low particle emitter. There were no particular emissions of particles for any of the cases examined – up to 120 km\(h^{-1}\) – and in general particle levels are found below usual urban ambient concentration. Additionally, solid particle emissions are negligible. There was evidence however of a cold-start effect with particle concentration spikes reaching diesel car levels. Particle emissions during cold start increase due to fuel enrichment, aftertreatment inefficiency and, possibly, exhaust system warm-up. This needs to be given more attention in the future in parallel to the efforts to control CO and HC emissions at sub zero temperature (–7°C testing enforced by European Directive 98/69/EC for all new types since January 2002).

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