

Effects of alkylate fuel on exhaust emissions and secondary aerosol formation of a 2-stroke and a 4-stroke scooter



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HIGHLIGHTS

- 2-wheelers with internal combustion engines (scooters) are strong emitters.
- The aged exhaust of scooters produces secondary organic aerosol.
- The emissions of secondary organic aerosol is reduced by using an alkylate fuel.

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ABSTRACT

Regulated and unregulated emissions from a 2-stroke and a 4-stroke scooter were characterized during a legislative driving cycle in a certified laboratory. Scooter exhaust was analyzed at the tailpipe, in a dilution tunnel, and partly collected in a mobile smog chamber for photochemical ageing. We present evidence that the photochemically aged exhaust from a 2-stroke and a 4-stroke scooter produces considerable amounts of secondary organic aerosol: from 1.5 to 22.0 mg/km, and from 5.5 to 6.6 mg/km, respectively. Tests were repeated after replacing the standard petrol and synthetic lube oil with an alkylate fuel (with low content of aromatic compounds) and ultra-clean lube oil (low ash forming potential). We observed emission reduction (with some exceptions) for several gaseous and particulate phase species, in particular for carbon monoxide (from 8% up to 38% and from 31% to 50%, for the 2-stroke and the 4-stroke scooters, respectively), particulate mass (from 32% up to 75% for the 2-stroke scooter), aromatic compounds (89% and 97% for the 2-stroke and the 4-stroke scooter, respectively), and secondary organic aerosol (from 87% to 100% and 99% for the 2-stroke and the 4-stroke scooters, respectively). We attribute the organic aerosol reduction to the low content of aromatics in the alkylate fuel.

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1. Introduction

Air pollution originates mainly from combustion systems with the transport sector being a major actor (e.g., Unger et al., 2009). Due to their agility in traffic, low price, low maintenance costs, and ease of parking Powered Two Wheelers (PTWs: mopeds and

scooters with engine displacement ≤ 50 cc, and motorcycles) are a practical and convenient means of transport, especially in urban environments at temperate latitudes. In Europe (EU27) for instance the number of circulating PTWs has increased from about 31.3 millions up to 37.4 millions from 2003 to 2011 (ACEM, 2011). PTWs are popular in urban areas where the majority of the population lives, which amplifies their negative impact on human health (WUP, 2011). They are known to be strong emitters of pollutants because of their simple engine and aftertreatment technology resulting in a partially unburned exhaust, and in the case of 2-

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stokers also because of the use of lube oil mixed with the fuel (Prati and Costagliola, 2009; Spezzano et al., 2009; Adam et al., 2010; Clairotte et al., 2012). Their typical use is for short distances, and therefore at cold engine conditions, with consequently large emissions.

From a legislative viewpoint, PTW emission limits are in most countries less stringent than those for cars, both in amount and number of limited compounds. The last update of European legislation regarding PTWs dates back to 2002 (Dir.2002/51/EC, 2002b) when the Euro 2 standard was introduced, and revisions are still in the form of a proposal (EC-COM, 2010). For comparison, the forthcoming European standard on passenger cars is Euro 6 (end of 2013 for all new type approvals; 2014 for all new registrations). In addition, information in the scientific literature about PTWs is scarce compared to passenger cars and no research about secondary organic aerosol particles (SOA) from PTWs has been reported so far.

SOA, formed in the atmosphere through the photochemical oxidation of volatile organic compounds and consequent gas to particle conversion, represents a significant fraction of the ambient tropospheric aerosol (e.g., Jimenez et al., 2009). A number of recent studies elucidated their physico-chemical properties necessary to evaluate the impact on air pollution, climate and human health. Nevertheless, significant gaps persist in our understanding of SOA formation and sources (Hallquist et al., 2009). Specifically for the air quality field, the question arises as to whether limitations on primary particle emissions from internal combustion engines are sufficient to control the ambient particle mass and number concentrations. Evidently this is not the case if vehicles are important SOA sources. There are recent indications that gasoline fuelled vehicles may be responsible for a considerable fraction of urban SOA, hence of atmospheric particulate matter burden, both from lab experiments (Platt et al., 2013; Nordin et al., 2013) and field campaigns (Bahreini et al., 2012). In contrast, Gentner et al. (2012) suggested, based on analysis of fuel samples and atmospheric aerosol (not tailpipe emissions), that diesel exhaust is seven times more efficient than gasoline exhaust at forming aerosol.

For these reasons we measured regulated and unregulated primary emissions and quantified SOA formation from a 2-stroke and a 4-stroke scooter during legislated driving cycles in a chassis dynamometer test cell hosting a mobile photochemical reaction chamber. Moreover, since aromatic compounds in fuels are known to be important SOA precursors (Odum et al., 1997; Ng et al., 2007), we also compared emissions from scooters fuelled with standard petrol and oil against the use of a reformulated alkylate fuel (almost free of aromatic compounds) and synthetic lube oil with low ash forming potential (ultra-clean oil, hereafter). These fuels are designed to produce cleaner emissions, hence reducing health risks and increasing engine lifetime.

2. Experiment and methods

2.1. Overall description

Experiments were conducted in a certified chassis dynamometer test cell (Vehicle Emissions Laboratories, Joint Research Centre of the European Commission, JRC-Ispra, Italy) combined with a mobile smog chamber (Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Switzerland) for gas/particle analysis during photochemical ageing (see Platt et al., 2013, for details on the smog chamber).

Exhaust emissions were sampled online at the vehicle tailpipe, offline after dilution (integrated, offline measurements, as required by the legislation), and part of the exhaust was injected into the smog chamber for subsequent photochemical production and characterization of secondary aerosol material, see setup diagram

in Fig. 1. Instruments and methods deployed to characterize primary emissions and SOA formation in the smog chamber are summarized in Table 1.

We have chosen, as an example of the circulating European fleet, two marketable 50 cc scooters (registration in 2010), one 2-stroker and one 4-stroker (2S and 4S), both equipped with a 2-way-catalyst (for hydrocarbon and carbon monoxide abatement). The scooters' characteristics are summarized in Table S1.

The legislated ECE-47 driving cycle (Dir.97/24/EC, 1997) (Fig. 2, dashed black curve) was run on a chassis dynamometer (Roller bench 48; AVL Zoellner GmbH, Germany) combined with a constant volume sampler (CVS) critical flow venturi dilution tunnel system (typical average dilution ≈ 27 ; typical tunnel flow $\approx 5 \text{ m}^3/\text{min}$). Depending on the country of vehicle registration, maximum speed can be limited to values lower than 50 km/h. In this study, a maximum speed of 45 km/h was reached as prescribed by the Italian legislation (actual speed, shaded grey area in Fig. 2). For legislative purposes, only the last 4 modules of the driving cycle, commonly referred to as the second phase, or hot phase (Ph2) are considered. In our analysis also the first 4 modules (the first phase, Ph1, or cold phase, hereafter) were included, since this is more representative of real-world driving, where engines are often started cold.

Scooters were fuelled either with certified reference fuel (European Emission Certification Fuel – CEC RF-02-99) and synthetic oil (API TC, Jaso FC, ISO-LEGD, 2% vol in the 2-stroker only) or with alkylate fuel (Lantmännen Aspen Petroleum AB) and ultra-clean oil (Stihl HP Ultra, 2% vol in the 2-stroker only). A comparison of basic fuels properties is given in Table 2; the fuel and oil analyses were performed independently by a specialized lab, following UNI-EN/ASTM methodologies. The alkylate fuel, commonly used in hand held machinery, is rich in short-chain single-bond hydrocarbons and has a low content of alkenes, oxygenates and aromatic compounds.

We ran a total of 15 experiments (Table S2) at stable, controlled conditions of temperature, $19.1^\circ\text{C} < T < 21.3^\circ\text{C}$, and relative humidity, $55\% < \text{RH} < 65\%$ inside the test cell (typical standard deviations for a single experiment: 0.2°C and $0.6\% \text{ RH}$). For the sake of reproducibility, all tests started at well defined cold engine conditions after a soak time of several hours ($\approx 24 \text{ h}$) at constant $T \approx 21^\circ\text{C}$ in the test cell (temperature of the engine oil $T \approx 21 \pm 1^\circ\text{C}$).

2.2. Tailpipe and CVS measurements

In most countries worldwide, vehicles have to comply with emission standards that traditionally include total hydrocarbons (THC), carbon monoxide (CO), nitrogen oxides (NO_x), particulate mass (PM) and carbon dioxide (CO_2). We refer to them as regulated compounds hereafter, even though CO_2 is not regulated by EU legislation for type approval emission tests. Instead, manufacturers are obliged to ensure that their entire light duty vehicle fleet does not emit more than an average of 130 g/km of CO_2 by 2015 and 95 g/km by 2020. No CO_2 limits are envisaged for PTWs. In particular, Euro 2 scooters have limits only on $\text{THC} + \text{NO}_x$ (1.2 g/km) and CO (1 g/km) considered only over the second half of the driving cycle (hot phase). Gaseous emissions were analyzed in accordance with Directive Dir.70/220/EEC (1970): Tedlar bags (4 bags per test, one for the first phase, one for the second phase, one for the entire cycle and one for dilution air) were filled with diluted exhaust from the CVS (Automatic Bag Sampler, CGM electronics) and CO, THC, NO_x , and CO_2 concentrations were measured with the techniques summarized in Table 1 by an integrated measurement system (AMA i60 Exhaust Measurement System, AVL). The same compounds were also measured online (at 1 Hz) at the scooter tailpipe (via a heated transfer line at $T = 191^\circ\text{C}$ to ABB Advance Optima Modular

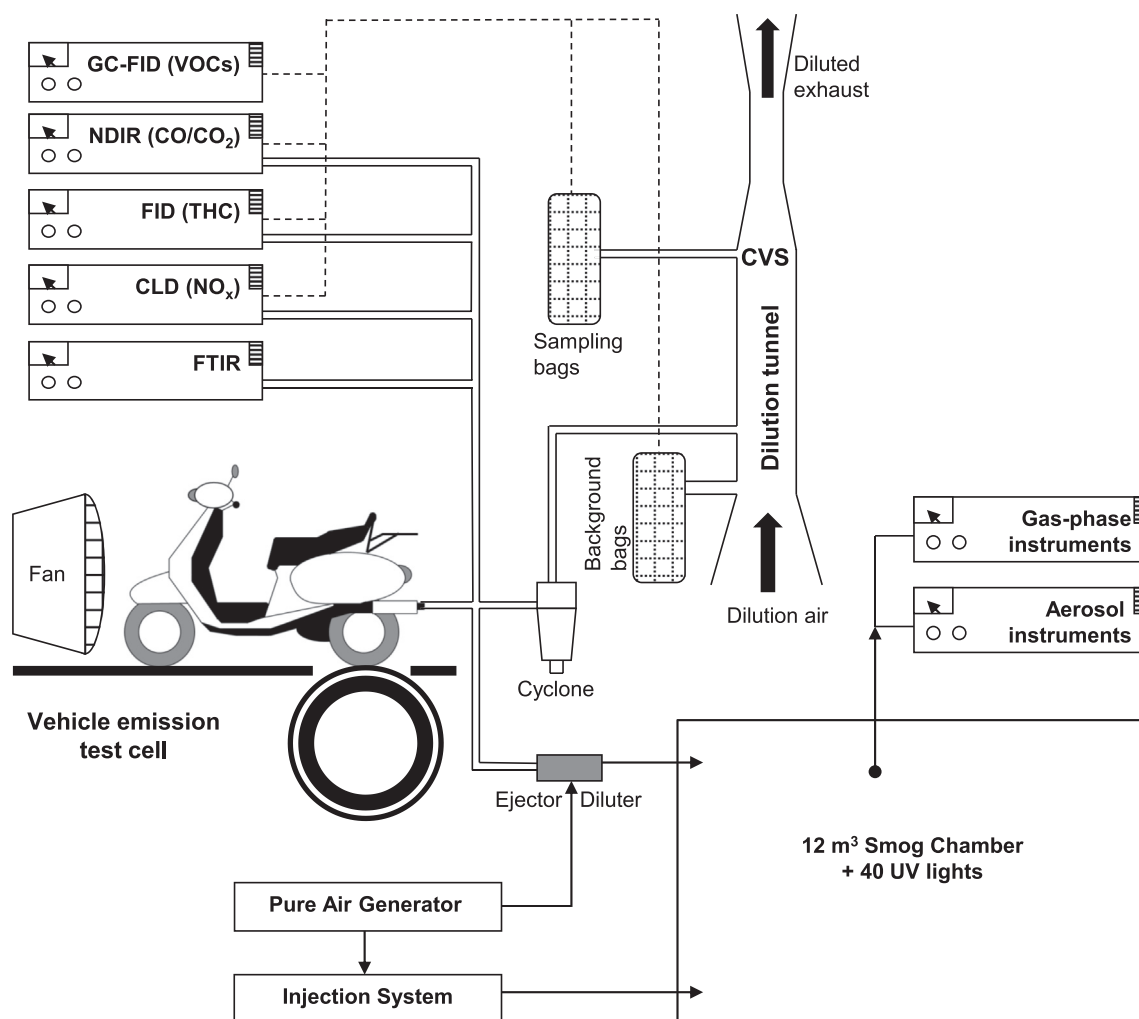


Fig. 1. Schematic of the test facility and instrumentation. The scooter exhaust is collected at the tailpipe and transferred via heated lines (190°C) to online instrumentation (FID, NDIR, CLD, FTIR - see Table 1). The exhaust is also directed to a dilution tunnel as required by the legislation for subsequent offline analysis (dashed lines). Part of the exhaust is injected into the 12 m^3 smog chamber for secondary aerosol formation.

Analyzers). The estimation of the tailpipe exhaust volumetric flow rate was based on the CVS approach. The total flow rate was maintained constant using critical flow Venturi and pressure sensors. The tailpipe exhaust volumetric flow rate was calculated by difference between the total CVS flow rate and the diluted air flow rate (see Supplement Text S1).

In addition, a heated line (191°C) conveyed tailpipe emissions to a Fourier Transform Infrared Spectrometer (FTIR, MKS Multigas analyzer 2030-HS) for online measurements (at 1 Hz) of short-chain hydrocarbons, nitrogen containing species (NO , NO_2 , N_2O , NH_3 and HCN) and other oxygenated organics (e.g., formaldehyde, acetaldehyde).

CVS diluted emissions were also collected in Tedlar bags for offline analysis of 29 volatile organic compounds (VOCs, Table S3) with dual flame gas chromatography (GC–FID, Agilent 6890 with Markes Unity 2 desorber), following the protocol described in Latella et al. (2005) and the European Directive on tropospheric ozone (Dir.2002/3/EC, 2002a).

2.3. Smog chamber

The mobile smog chamber setup and the procedure to study secondary aerosol are described in detail in Platt et al. (2013). The

chamber consists of a 12 m^3 Tedlar bag hung from an aluminium frame with a control unit to adjust the gas and particle phase conditions. It is completely independent from host facilities and is designed to be easily moved. Forty UV lamps (UV black lights Philips Ergoline Cleo-performance, peak emission at 350 nm, total power 4 kW) simulate the tropospheric photochemistry.

Tailpipe emissions are partially diverted into the smog chamber via a heated inlet system ($T = 150^{\circ}\text{C}$) powered by an ejector diluter (DI-1000, Dekati) which provides a dilution factor of around 10. Further dilution up to a total of 5000 (see Table S4) results from the clean air in the smog chamber. Concentrations with constant flow sampling versus (tailpipe) variable flow sampling are in good agreement (see Fig. S3). Around $1\ \mu\text{l}$ (20 ppbv) of butanol-D9 is injected into the chamber in order to assess photochemical ageing times using the “OH clock” methodology described in Barmet et al. (2012). Briefly, the decay rate is monitored using a Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS 8000, Ionicon) and related to photochemical age via known reaction rate with OH. The UV lights were then switched on to initiate photochemistry. A VOC/ NO_x ratio of between 5 and 38 inside the smog chamber was maintained throughout experiments by injecting NO (see Table S4). The temperature and RH inside the chamber were maintained close to those of the vehicle test cell ($T = 22 \pm 1^{\circ}\text{C}$,

Table 1

Instruments and methods. Tailpipe (TP) measurements are online at 1 Hz; Constant volume sampler (CVS) measurements are sampled in Tedlar bags and analyzed offline, integrated over the entire driving cycle and separately over the cold and hot phases. Smog chamber measurements (SC) are online (see Par. 2.3 and Platt et al., 2013, for more details).

Compound/Property	Sampling location	Technique	Model
CO, CO ₂	TP, CVS	NDIR ^a	Advance Optima, ABB (TP); AMA i60, AVL (CVS)
NO _x	TP, CVS	CLD ^b	As above
THC	TP, CVS	FID ^c	As above
PM	CVS	Filter	Pallflex TX40HI20
VOCs	CVS	GC–FID ^d	Agilent 6890
Small HC, N-species	TP	FTIR ^e	MKS 2030HS
Organic aerosol	SC	HR-ToF-AMS ^f	Aerodyne
Particle size distribution	SC	SMPS ^g	TSI 3080, TSI 3022
Particle number	SC	CPC ^h	TSI 3076
VOCs (OH-clock)	SC	PTR-ToF-MS ⁱ	Ionicon
BC	SC	Aethalometer	AE 33 Beta, Aerosol d.o.o
CO, CO ₂ , CH ₄ , H ₂ O	SC	Cavity ring down	Picarro G2401
THC	SC	FID	APHA-370, Horiba
NO _x (<200 ppb)	SC	CLD	42C Thermo Environmental
NO _x	SC	CLD	Monitor Labs 9841A
O ₃	SC	UV photometry	Monitor Labs 49C

^a Non-dispersive Infrared.

^b Chemiluminescence Detector.

^c Flame Ionization Detector.

^d Gas Chromatography.

^e Fourier Transform Infrared Spectroscopy.

^f High Resolution Time-of-Flight Aerosol Mass Spectrometer.

^g Scanning Mobility Particle Sizer.

^h Condensation Particle Counter.

ⁱ Proton Transfer Reaction Mass Spectrometer.

RH = 50–60%). Particle mass and number are measured inside the chamber with a scanning mobility particle sizer (SMPS) and a Condensation Particle Counter (CPC, TSI 3076). Aerosol concentrations before lights on were between 1 and 40 µg/m³, similar to what is typically found in the atmosphere.

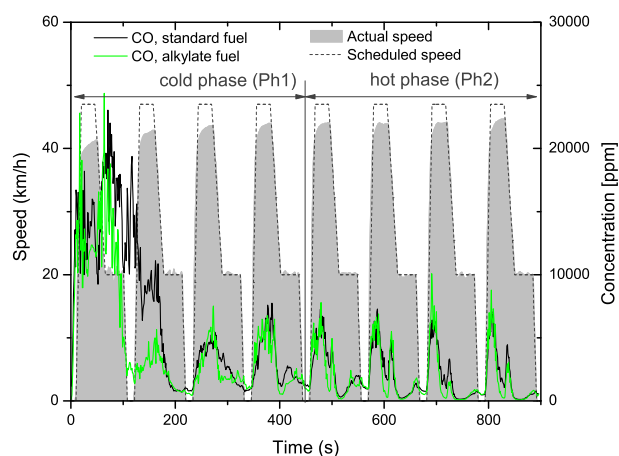


Fig. 2. Averaged tailpipe CO concentration measured at the tailpipe with FTIR for the 2-stroke scooter with standard fuel (black curve) and alkylate fuel (green curve) during an ECE-47 driving cycle. Theoretical speed (dashed black curve) reaches higher peaks than actual speed (grey shaded area) because of speed limitations enforced by legislation of the country of vehicle registration (Italy). CO emissions are largest in the first two modules of the cycle with standard fuel, followed by a repetitive pattern for the rest of the cycle. Alkylate fuel tests exhibit lower emissions especially in the cold phase. Note that only the hot phase is considered for type approval tests. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2

Fuel properties from certified ISO/ISO-EN/ASTM analysis. The uncertainty is on the last significant digit.

Property/Compound	Standard fuel	Alkylate fuel	Unit
Aromatics	29.6	<0.4	%vol
Alkenes	4.2	0.1	%vol
Alkanes	61.3	>99.6	%vol
Oxygenates	4.9	<0.1	%vol
Benzene	0.2	<0.01	%vol
H-content	13.16	15.5	%wt
C-content	85.95	84.5	%wt
O-content	0.9	<0.1	%wt
Density (15°C)	759.2	692.4	kg/m ³

Primary and secondary condensed organic matter is detected by a high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne, see DeCarlo et al., 2006). Gas phase CO, THC, NO_x, CO₂, H₂O, CH₄ (methane), O₃ (ozone), and individual VOCs concentrations are measured with dedicated monitors (see Platt et al., 2013, for details). Black carbon is monitored using an aethalometer (Aethalometer AE 33 beta, Aerosol d.o.o.). All HR-TOF-AMS data are corrected for collection efficiency (CE ≈ 0.8, in our conditions) due to particle bounce (see Text S2).

3. Results and discussion

3.1. Regulated compounds

Fig. 2 shows the time resolved tailpipe CO concentration for the 2-stroker measured with FTIR and averaged over all tests, during the ECE-47 legislated driving cycle. The CO concentration is higher in the first two modules of the cycle when the engine is colder and combustion is incomplete. Tests with alkylate fuel and ultra-clean oil combination (green curve) exhibit lower concentrations than standard fuel tests for $t = 0–200$ s. Differences become smaller and signals tend to overlap for $t \geq 200$ s. A sudden drop is visible at $t \approx 100$ s when using the alkylate fuel, indicating more complete combustion and/or better efficiency of the 2-way catalyst. Note that by only sampling the hot phase, as prescribed by the legislation, the CO abatement in the cold phase would be neglected.

Fig. 3 compares emission factors (mass/distance) of regulated compounds from the 2- and 4-stroker filled with regular and alkylated fuel, during the cold and hot driving cycle phases. For a conversion to emission factors in mass/kg fuel see Table S5. The 2-stroker emits much more CO, THC and PM than the 4-stroker, especially during the cold phase where combustion is less efficient. It emits about twice as much CO as the Euro 2 scooter studied in Clairotte et al. (2012) and up to 5 times more than the Euro 5 car in Platt et al. (2013). The 4-stroker emits ≈ 30% less CO than the 2-stroker, mainly because of more complete combustion. In particular, the scooters in our study slightly exceeded Euro 2 CO standards (uppermost right panel in Fig. 3). Emission standards are set for the registration of a prototype vehicle, and in-use vehicles do not have necessarily to comply with them. Instead, the scooters must pass a less severe periodical inspection of the tailpipe exhaust (due by law in 2014, in our case), with a warm engine CO limit of 3.5% vol. In our study [CO] ≤ 1% vol, see Fig. 2.

NO_x emissions, which are mainly thermally produced at high temperature from the nitrogen and oxygen in the combustion air, have a more levelled temporal profile (not shown here), or even opposite behaviour compared to CO, with larger amounts in the hot phase. The 2-stroker, due to its simpler engine technology and generally colder engine temperature, features less NO_x than the 4-stroker. Note that a 2-way catalyst does not act to reduce NO_x emissions, but only those of CO and THC. This contributed to the

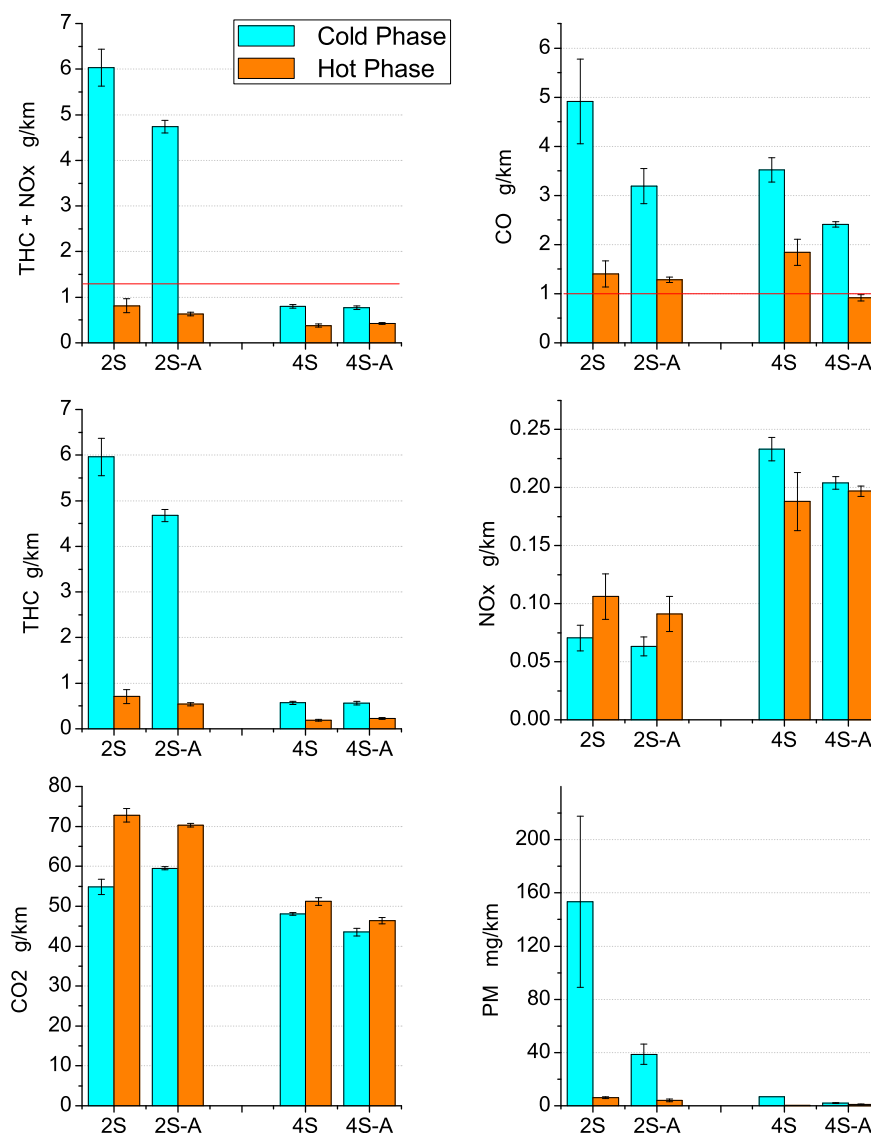


Fig. 3. Average emission factors (mass/distance) of regulated compounds grouped by scooter and fuel types, and split into cycle phases. The 2-stroker (2S) emits more THC, CO, and PM (dominated by cold phase emissions) than the 4-stroker (4S). The use of the alkylate fuel reduces THC, CO, PM and NO_x of the 2S (2S-A, where A stands for alkylate) and CO, PM, NO_x of the 4S (see text for details). THC + NO_x and CO are limited by EU legislation at 1.2 g/km and 1 g/km, respectively (red horizontal line in the uppermost panels, see text for details). All values are summarized in Table 3. Error bars are explained in Table S2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

two orders of magnitude difference between the 2-stroker NO_x emission factor and that of the modern car in Platt et al. (2013) in hot engine conditions (≈ 0.1 g/km vs ≈ 0.002 g/km), when the car could benefit from the light-off of a 3-way catalyst (which acts also on NO_x).

The use of the alkylate fuel and ultra-clean oil combination is clearly beneficial for compounds emitted mainly in the cold phase: THC, CO and PM. The effect is important for CO and PM (e.g., up to 35% and 75% reduction of CO and PM, see Table 5) and less pronounced for THC and in general in the hot phase. PM reduction is one of the main reason for using ultra-clean oil in professional 2-stroke machinery where the presence of unburned lube oil droplets in the exhaust and generally colder exhaust temperature facilitate condensation of gaseous compounds on primary particles. The certified analysis of the 2-stroke lube oils used in this study reports ash-forming material = 0.005% mass/mass for the ultra-clean oil against 0.1% mass/mass for the standard oil (method: UNI EN ISO 6245:2005). Lubricating oil formulation is suggested to

contribute up to 95% to the total exhaust particle mass (e.g., Ålander et al., 2005, and references therein).

No significant benefit was observed for CO_2 emissions which were about 75 g/km and 50 g/km, for the 2-stroker and the 4-stroker, respectively (see Text S3).

3.2. Unregulated compounds

Table 3 reports emission factors for selected unregulated species including alkanes, alkenes, alkynes, oxygenated and nitrogen containing species.

Nitrous oxide (N_2O) and ammonia (NH_3) are only present in the 4-stroker exhaust, while previous studies reported both compounds for other Euro 2 2-strokers (e.g., Clairotte et al., 2012), confirming a large degree of unpredictability for the simple technology of 2-stroke engines. N_2O is catalytically produced, especially at colder catalyst temperature, consistently with larger observed emissions during the cold phase (see Text S4). Similarly to N_2O , NH_3

Table 3
Summary of emission factors. Errors in parentheses are 1σ or half of the minimum-to-maximum range based on the number of tests in Table S2. NA: not available; nd: not detectable.

Compound	Method	2S-Ph1	2S-Ph2	2S-A-Ph1	2S-A-Ph2	4S-Ph1	4S-Ph2	4S-A-Ph1	4S-A-Ph2
Regulated (g/km)									
CO	NDIR	4.92 (0.86)	1.40 (0.27)	3.19 (0.36)	1.29 (0.06)	3.52 (0.25)	1.84 (0.27)	2.41 (0.06)	0.91 (0.06)
CO Euro2 limit	NDIR	–	1	–	1	–	1	–	1
NO _x	CLD	0.07 (0.01)	0.11 (0.02)	0.60 (0.01)	0.09 (0.01)	0.23 (0.01)	0.19 (0.02)	0.20 (0.01)	0.20 (0.01)
THC	FID	5.96 (0.40)	0.71 (0.15)	4.68 (0.13)	0.54 (0.04)	0.56 (0.04)	0.19 (0.02)	0.56 (0.04)	0.22 (0.02)
THC + NO _x Euro 2 limit		–	1.2	–	1.2	–	1.2	–	1.2
CO ₂	NDIR	54.9 (1.9)	72.8 (1.7)	59.5 (0.4)	70.3 (0.5)	48.0 (0.3)	51.2 (0.9)	43.5 (0.9)	46.3 (0.8)
PM (mg/km)	Filter	153 (64)	6.10 (0.62)	39 (8)	4.16 (0.97)	6.94	0.33	1.98 (0.34)	0.99 (0.47)
Non regulated (mg/km)									
N ₂ O	FTIR	nd	nd	nd	nd	2.16 (0.14)	1.61 (0.56)	2.14	0.69
NH ₃	FTIR	nd	nd	nd	nd	0.66 (0.12)	2.27 (0.13)	0.10	0.2
Methane (CH ₄)	FTIR	97.0 (4.8)	56 (16)	157 (8)	72 (11)	24.11 (0.01)	13.8 (1.2)	35.3	17.72
Acetylene (C ₂ H ₂)	FTIR	75 (14)	15.4 (5.4)	50.5 (2.9)	5.9 (1.6)	26.47 (0.65)	4.73 (0.81)	35.2	5.34
Ethylene (C ₂ H ₄)	FTIR	247 (12)	138 (26)	250.3 (3.8)	138.1 (9.6)	34.97 (0.78)	10.34 (0.91)	33.96	11.62
Ethane (C ₂ H ₆)	FTIR	25.7 (3.3)	17.9 (5.1)	39.9 (2.9)	26.6 (5.2)	6.61 (0.06)	3.47 (0.08)	10.91	7.65
Propylene (C ₃ H ₆)	FTIR	155.5 (7.4)	55 (11)	247.6 (9.7)	66.0 (8.9)	20.8 (2.5)	8.2 (2.1)	31.61	10.84
1-3-Butadiene (C ₄ H ₆)	FTIR	45.9 (4.8)	16.2 (4.3)	25.3 (3.4)	10.2 (3.8)	8.0 (1.4)	3.79 (0.60)	4.36	2.4
2-Methylpropene (C ₄ H ₈)	FTIR	118.7 (7.7)	28.2 (5.5)	236.5 (7.2)	48.3 (8.3)	11.6 (1.2)	5.57 (0.94)	28.28	10.84
2-Methyl-2-butene (C ₅ H ₁₀)	FTIR	258 (36)	84 (28)	245 (31)	72 (18)	NA	NA	NA	NA
Octane (C ₈ H ₁₈)	FTIR	NA	NA	NA	nd	42.89 (1.32)	16.67 (3.74)	nd	nd
o-Xylene (C ₈ H ₁₀)	FTIR	NA	NA	nd	nd	42.2 (11.81)	10.55 (8.45)	nd	nd
Isocyanic acid (HNCO)	FTIR	NA	NA	107 (34)	33.4 (7.9)	NA	NA	NA	NA
Formaldehyde (CH ₂ O)	FTIR	79.8 (7.8)	58.7 (7.9)	110.4 (4.7)	58.4 (1.8)	9.99 (0.20)	4.71 (0.24)	13.23	7.88
Acetaldehyde (C ₂ H ₄ O)	FTIR	NA	NA	73.05 (4.64)	19.85 (2.06)	10.01 (1.22)	5.20 (0.95)	11.18	5.66
Methanol (CH ₄ O)	FTIR	8.22 (0.84)	2.8 (0.4)	6.43 (0.15)	2.29 (0.52)	2.47 (0.06)	1.20 (0.19)	2.99	1.41
Ethanol (C ₂ H ₆ O)	FTIR	299 (24)	27.5 (7.3)	42 (19)	24 (14)	NA	NA	NA	NA
MTBE (C ₅ H ₁₂ O)	FTIR	297 (19)	14.9 (2.8)	145.8 (6.8)	14.5 (6.4)	7.5 (5.3)	2.6 (2.5)	15.80	7.69
OFF [g (O ₃)/km]	GC–FID	7.60 (0.51)		7.54 (0.07)		1.33 (0.73)		0.92 (0.55)	
VOCs	GC–FID	1510 (97)		1403 (139)		253 (81)		210 (27)	

is produced on the catalyst surface, via H₂ formed in the water–gas-shift reaction of CO. Higher catalyst temperatures are usually associated to larger NH₃ emissions, consistent with higher NH₃ emissions in Ph2. In particular, NH₃ concentration profiles have peaks exceeding 20 ppm (not shown here) during accelerations in the hot phase. These concentrations are even higher than the only existing EU limit on NH₃ established for heavy duty engines in the upcoming EURO VI legislation (EC-No 595, 2009).

As for the light hydrocarbon and oxygenated species monitored by the FTIR at the tailpipe, the cold phase emissions were predominant for both scooters, in agreement with the regulated THC. The effect of alkylate fuel and ultra-clean oil combination is species dependent, see Table 3. Fig. 4 displays the effect of the use of alkylate fuel on the tailpipe diluted emission (CVS sampling) of VOCs measured with GC–FID. VOCs results are broken down by aromatic and non-aromatic compounds, mainly C₂–C₈ alkanes and alkenes. Upon the use of alkylate fuel, the aromatic content of the exhaust drops dramatically for both scooters, while the other VOCs remain the same within experimental variability, as expected by the fuel formulation in Table 2. In terms of total aromatic amounts, the 2-stroker emits twice as much as the 4-stroker, mainly in Ph1.

Table 4
Black carbon (BC), primary organic aerosol (POA) and secondary organic aerosol (SOA) grouped by scooter, fuel type, and driving cycle phase. Errors are given in parenthesis (See Table S2).

Scooter	Phase	BC [mg/km]	POA	SOA
2S	Ph1 + Ph2	0.64 (0.10)	8.78 (5.21)	3.07 (1.57)
2S-A	Ph1 + Ph2	0.33 (0.04)	11.0 (2.28)	0.00
4S	Ph1 + Ph2	0.22 (0.02)	0.10 (0.01)	6.03 (0.52)
4S-A	Ph1 + Ph2	0.11 (0.03)	0.24 (0.04)	0.06 (0.06)
2S	Ph2	0.04 (0.01)	4.04 (2.62)	19.15 (2.91)
2S-A	Ph2	0.00	0.72 (0.06)	2.38 (1.79)

VOCs emission factors were used to calculate the Ozone Formation Potential (OFP) with the incremental reactivity method proposed by Carter (1994), see Table 3. As expected by the emission pattern in Fig. 4, the 2-stroker OFP is much larger than that of the 4-stroker (up to an order of magnitude), deriving mainly from the cold phase emissions. Similar values were obtained by Clairotte et al. (2012) for a 2-stroker. However, from Euro 4 and Euro 5 cars, Clairotte et al. (2013) obtained OFPs lower by an order of magnitude (0.1 and 0.2 g (O₃)/km, respectively), indicating a significant impact of scooters on ozone formation compared to other vehicles exhaust. As aromatics are only a small fraction of total VOCs and amongst the least efficient O₃ precursors, the use of the alkylate fuel has no significant effect for the 2-stroker, and up to a moderate effect for the 4-stroker.

Table 5
Benefits from the use of alkylate fuel versus standard fuel as percentage of emission factor abatement. Results are given for driving cycle phases and entire cycle. Note that only the hot phase (Ph2) of the cycle is considered for legislation.

Compound	2S-Ph1	2S-Ph2	2S-Ph1 + Ph2	4S-Ph1	4S-Ph2	4S-Ph1 + Ph2
THC	22	23	22	1	–18	–4
NO _x	11	14	13	13	–5	5
THC + NO _x	21	22	22	4	–12	–1
CO	35	8	29	31	50	38
CO ₂	–8	3	–2	9	10	10
PM	75	32	73	72	–200	59
Aromatics (VOCs)	NA	89	89	NA	NA	97
Total VOCs	NA	37	7	NA	NA	17
SOA	NA	87	100	NA	NA	99
N ₂ O	NA	NA	NA	1	57	25
NH ₃	NA	NA	NA	84	91	90
Formaldehyde	–38	0	–22	–33	–67	–44
1-3-butadiene	45	37	43	46	37	43
MTBE	51	3	49	–111	–198	–134
CH ₄	–62	–28	–49	–46	–28	–40
OFF	NA	30	0	NA	NA	31

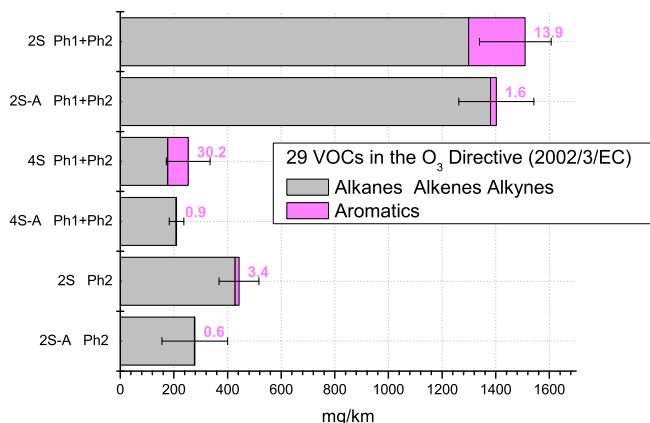


Fig. 4. Average emission factors of VOCs measured by GC-FID (see methodology in Par. 2.2) broken down by aromatic (benzene, toluene, ethylbenzene, m/p-xylene, o-xylene, 1-2-3-trimethylbenzene, 1-3-5-trimethylbenzene, 1-2-4-trimethylbenzene) and non-aromatic compounds (21 species, see Table S3). Tests are grouped by scooter type, fuel, and phase of the driving cycle (Ph1 + Ph2 = entire cycle). Sampling design is consistent with smog chamber tests in Table S2. Bar labels represent the percentage of aromatics on total VOCs. Error bars are minimum and maximum values of total VOCs based on the number of tests in Table S2.

3.3. Secondary organic aerosol

Fig. 5 shows concentrations of carbonaceous gas and condensed phase species measured from the mobile smog chamber after injection of the 2-stroker exhaust as a function of time after lights on. High resolution AMS spectra for fresh and aged emissions are shown in Fig. S1. Secondary species are produced after lights on, for example peroxy acetyl nitrate (PAN, mass 122.021, $C_2H_4NO_5^+$), benzoic acid (mass 123.047, $C_7H_7O_2^+$). The observed increase in aerosol concentration after wall loss correction is taken as the SOA production for a given emission sample. Wall loss correction factors were derived from the decay of black carbon mass (aethalometer,

880 nm channel). The organic aerosol concentration is corrected for wall losses (OA_{WLC} , green curve) via (e.g., Chirico et al., 2010; Heringa et al., 2011):

$$OA_{WLC}(t) = OA(t)/\exp(-k \cdot t), \quad (1)$$

where the BC particles average exponential decay constant k is taken from an exponential fit of BC as a function of time after lights on (average particle half-life is 2.2 ± 0.6 h). The wall loss characteristic time ($1/k$, Eq. (1)) before switching on the lamps is very similar to the one after. We had assumed this based on our previous results (Platt et al., 2013, Fig. S3): the value is 3.3 h before and 4 h after (and are equal within the accuracy of the determination of their value), even though the composition of the aerosols is different. The size distribution remained monomodal, hence we conclude that the characteristic time constant $1/k$ does not depend on the composition (see also Text S5). Primary emissions, including primary organic aerosol (POA) are taken from average concentrations measured before irradiation.

Absolute masses of both primary and secondary components are converted into emission factors (potential of production, for secondary species) per mass of fuel (EF_{MASS} , right axes) using a chemical mass balance approach (adapted from Phuleria et al., 2006):

$$EF_{MASS} = \frac{\Delta P}{\Delta C_{CO_2} + \Delta C_{CO} + \Delta C_{HC} + \Delta C_{OC} + \Delta C_{BC}} \cdot WC, \quad (2)$$

where P is the mass of pollutant, C denotes carbon mass from CO_2 , CO , gas phase hydrocarbon (HC), particle phase organic carbon (OC) from aerosol mass spectrometer measurements analysis, and BC. WC is the fuel carbon content (see Table 2). Emission factors of BC, POA, and formation potential of SOA are summarized in Table 4 and shown in Fig. 6 in mass/distance units calculated based on fuel economy e (the same results in mass/mass of fuel units can be found in Table S6):

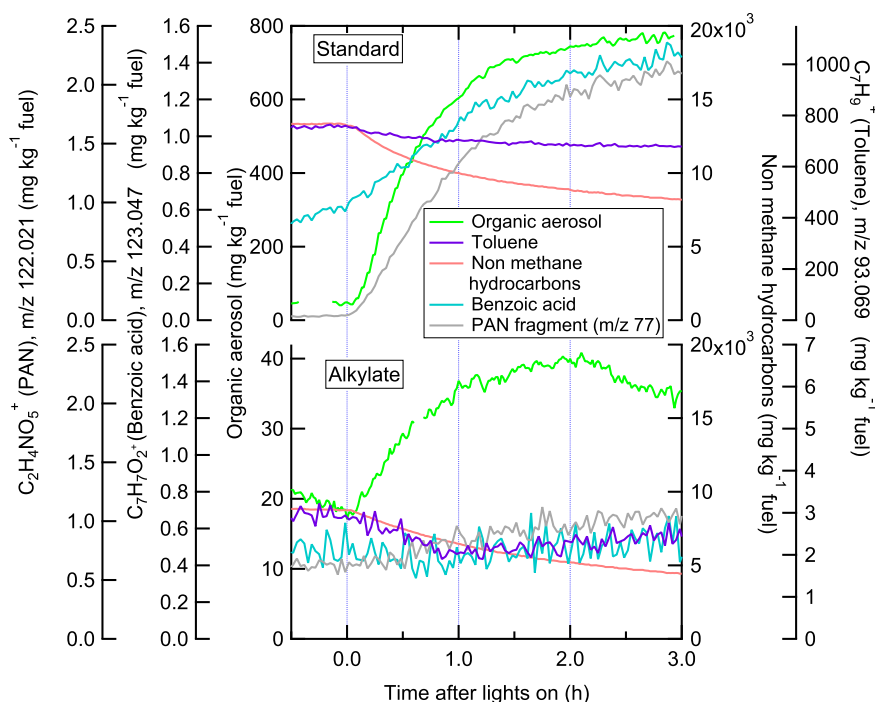


Fig. 5. Emission factors (mg/kg fuel) of various species calculated from concentrations measured inside the smog chamber as a function of time after lights on for the 2-stroker (hot phase only) using standard (top panel) and alkylate fuel (bottom panel).

$$EF_{K_m} = EF_{MASS} \cdot e \cdot \rho, \quad (3)$$

where ρ is the fuel density (see Fig. S2 for emission factors and potential of SOA production in mass/mass of fuel).

Fig. 5 illustrates the difference between hot phase emissions from the 2-stroker when using standard and alkylate fuels and ultra-clean oil combination. For the standard fuel a large mass increase is observed (800 mg/kg fuel) due to SOA formation, with aged OA/POA ratio = 16, while for the alkylate emissions, aged OA/POA = 2. In absolute mass a much smaller increase is observed (40 mg/kg fuel), suggesting that fuel composition affects SOA production. These results show that scooter emissions generated during ECE-47 driving cycles produce significant SOA, in addition to previously observed high primary aerosol emissions (e.g., Adam et al., 2010). Notably for some tests, e.g. the hot phase of the 2- and 4-stroker, SOA largely exceeds the primary emissions of POA and BC. As a consequence, our current understanding of the contribution of scooter emissions to ambient PM does not capture a significant, and possibly the largest fraction, of the total emissions.

The 2-stroker hot phase and the 4-stroker entire cycle aged exhaust produces amounts of secondary material (Fig. 6) larger than (i) primary particulate emission, (ii) PM emission factors measured with the legislated method shown in Fig. 3, and (iii) the emission limit for modern passenger cars (Euro 5 PM limit = 5 mg/km), confirming that SOA contribution to ambient PM from scooters may be important. See Text S6 for a discussion on PM discrepancies of point (ii). Furthermore, the 4-stroker shows significantly lower primary emissions, but a relatively large SOA production (a similar phenomenon is reported for a Euro 5 gasoline car in Platt et al., 2013). However, it still offers significant reduced emissions compared to the 2-stroker even when the relatively large SOA formation is taken into account. Fig. 6 shows that alkylate fuels significantly reduce SOA formation from emissions of both 2- and 4-stroke scooters, generated during a full driving cycle. We conclude that this reduced SOA formation stems from the almost complete removal of aromatic compounds from the exhaust (Fig. 4), identified by Platt et al. (2014) as predominant SOA precursors in the case of 2-stroke engines. This mitigation in total primary and

secondary particulate mass is only seen for the SOA (similar POA emissions are observed for both types of fuels), further highlighting the importance of secondary pollutants to a comprehensive understanding of vehicle emissions. Although much reduced, considerable SOA is formed from hot phase emissions of the 2-stroker run on alkylate fuel. This suggests the presence of additional, as yet unidentified, SOA precursors produced when the engine is hot. The benefit of alkylate fuels is thus seen over the course of a full driving cycle, rather than the regulatory hot phase. Therefore alkylate fuels and ultra-clean oils are of benefit not only due to the removal of toxic aromatics and olefins, but also because they have potential to reduce PM pollution.

Generally, OH exposure was in the range $(1.5-3) \cdot 10^6 \text{ cm}^{-3} \text{ h}$, corresponding to an ageing time of 1.5–3 h in the ambient atmosphere assuming a global annual mean OH concentration of $10^6 \text{ molecules cm}^{-3}$, suggesting that the already significant SOA formation quantified here may very well be a lower limit of the ambient SOA formation potential. This is further exemplified by the large fraction of unreacted toluene shown in Fig. 5 (purple curve (in the web version)). Note that OH exposure was generally higher for the alkylate emission ageing experiments and that for one smog chamber experiment with alkylate fuel an additional OH source (nitrous acid, HONO) was added to the chamber, boosting the total OH exposure to around $30 \cdot 10^6 \text{ cm}^{-3} \text{ h}$. Even with these higher OH exposures less SOA was produced from the alkylate fuel emissions. An estimation of SOA formation from aromatic emissions (for 2-stroke scooters using standard fuel) at longer OH exposure times will be presented in a forthcoming paper and further experiments are planned on these issues.

The benefit summary in Table 5 is related to the two scooters considered in this study, and should not be read to draw precise, quantitative conclusions on global atmospheric impact of PTWs. Nevertheless, strong indications for emission improvements can be expected if one reasonably assumes that standard versus alkylate fuels would have the same qualitative behaviour when tested on similar simple engines. It does not seem quite as straightforward a technological approach that of completely burning the aromatics in the fuel (to minimize SOA formation), due to their large fraction (up to 45% vol depending on the local legislation). In addition, considering that particulate pollution is one of the main concerns both in the urban environment and for the climate change, the use of alkylate fuels and low ash forming potential lube oils seem to be a promising alternative.

4. Conclusions

We have run a legislated driving cycle (ECE-47) on a chassis dynamometer for one 2-stroke and one 4-stroke scooter, monitored a range of regulated and unregulated primary compounds, and measured the secondary organic material formed during the ageing of the exhaust in a photochemical mobile smog chamber. Tests were repeated with the use of an alkylate fuel and an ultra-clean lube oil to assess benefits from the use of fuels with low content of aromatic compounds. Clearly, scooters are emitters of SOA precursors. The alkylate fuel and ultra-clean oil combination causes a large emission reduction for regulated and unregulated compounds, SOA included, with some exceptions (formaldehyde, for instance). Note that this reduction would not be caught by European legislated analysis, either because the compounds involved are not regulated or because the benefit is mainly evident in the cold phase of the driving cycle, which is not considered for legislation purposes. Our exploratory study gives clear indications for future research directions in the field of vehicle emission testing, air pollution, and legislation revisions.

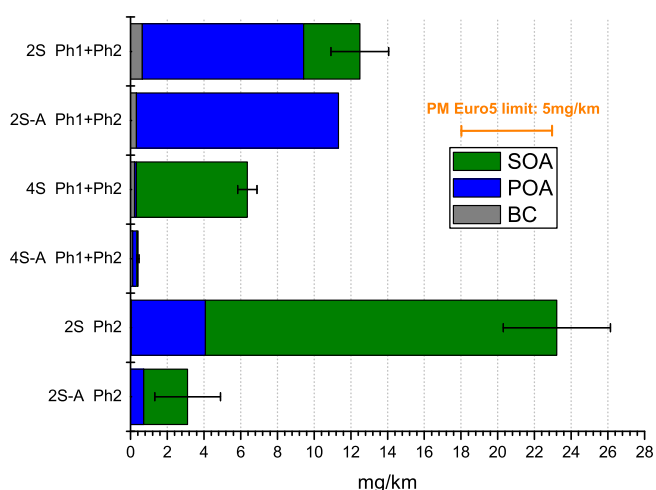


Fig. 6. Average emission factors (mg/km) of BC and POA, and SOA production from scooter emissions measured after ageing in the mobile smog chamber, grouped by vehicle type, fuel, and sampled phase (Ph1 + Ph2 = entire driving cycle). Error bars show the maximum and minimum observed values for SOA formation. For comparison, the orange bar (upper right corner) displays the Euro 5 limit for light duty passenger cars: when using standard fuel and oil SOA production from the scooters is close to or exceeds that limit. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2014.03.024>.

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