Primary Emissions and Secondary Aerosol Formation from a 2-stroke and a 4-stroke Scooter Fuelled with Standard and Alkylate Petrol

Zardini AA[1], Platt SM[2], El Haddad I[2], Clairotte M[1], Temime B[3], Marchand N[3], Jezek I[4], Mocnik G[4], Slowik JG[2], Prevot ASH[2], Astorga C.[1]

[1]*European Commission - Joint Research Centre, Institute for Energy and Transport, Sustainable Transport Unit, Ispra (Va), Italy.*

[2]*Paul Scherrer Institute, Laboratory for atmospheric Chemistry, Villigen, Switzerland.*

[3]*Laboratoire Chimie et environnement, Universit de Provence (Marseille, France).*

[4]*Aerosol d.o., Ljubljana, Slovenia.*

Rationale. Atmospheric aerosol particles have significant effects on climate, human health and air quality in general. The largest uncertainties in quantifying the Earth radiative forcing are connected to atmospheric aerosols [1]. Organics have been identified as important constituents of the atmospheric particulate matter, especially over continental regions and include thousands of species from non-toxic to carcinogenic and mutagenic ones. Secondary organic aerosols (SOA) matter, formed in the atmosphere by photo-oxidation of some volatile organics and consequent conversion to particle phase, represents a large fraction of the total fine particle mass [2]. Even though SOA have been the focus of several studies in the last decade, many of their properties remain unexplained, e.g., gas precursors and nucleation mechanisms, detailed yields, aging paths, and toxicity. In particular, we noticed a lack of documentation regarding SOA formation from internal combustion engines emissions. For these reasons we designed experiments where the primary emissions from a series of vehicles are photochemically aged to produce SOA. Here we present gaseous and particulate characterization from primary and photochemically aged exhaust of a 2-s and a 4-s scooter over a legislative ECE47 driving cycle. Chassis dynamometer experiments, combined with a photochemical reaction chamber, were carried out at the Vehicle Emission Labs of the European Community Joint Research Centre. Powered two wheelers (PTW) and in particular those with engine displacement less than 50 cm3 are a good fraction of urban vehicle fleets in Southern Europe and Asia (see for instance [4], [5] and references therein). They generally emit more pollutants per km than modern cars. Nevertheless, the latest update on their emission standards in Europe, EURO2, dates back to 2002. We tested the performance of alkylate gasoline and ultra-clean oil, normally used in professional, non-road small engines, and investigated potential wider use in scooters. The alkylate fuels, almost free of aromatics, are designed to produce cleaner emissions, hence reducing health risks and increasing engine lifetime. Aromatics are known to be important SOA precursors [3]; we therefore expect a lower SOA yield when alkylate fuels is used.

Experimental. Besides the regulated compounds (CO, THC+NOx), we monitored a range of exhaust constituents, both in gas and particle phases, with online and offline state of the art techniques: aerosol (HR-ToF-AMS, Aerodyne) and proton transfer reaction (HR-ToF-PTR-MS, Ionicon) mass spectrometers; Fourier transformed infrared spectroscopy (MKS-2030-HS); gas and liquid chromatography. Details on the PSI mobile smog chamber, AMS and other instruments can be found at:
http://www.psi.ch/lac/instruments-and-tools. Details on the PTR-MS can be found at: http://www.ionicon.com. Details on the Vehicle Emission Laboratories of the European Community can be found at:
http://iet.jrc.ec.europa.eu/clean-and-efficient-vehicles-cleeve.

Preliminary Results. Preliminary results can be summarized as follow:

- Alkylate fuel reduces Particle Mass considerably
- Beneficial effect on NH3 emissions (4-s moped)
- Mopeds produce a large amount of secondary organic aerosol
- Alkylate fuels significantly reduces SOA and the ratio secondary/primary aerosols

Since SOA is comparable or larger than primary with standard fuel, SOA must be considered when comparing particle mass ambient levels to vehicle emissions. Also, considerable primary particle mass and SOA reduction with alkylate fuel are observed, suggesting that alkylate fuels specifically designed for PTW would have a strong beneficial effect on air quality. Results on NH3 might be related to the different 2-s/4-s technology and will not be commented further at this stage of the analysis.

References

[1] IPCC Working Group I: http://www.ipcc.ch/

[2] Zhang et al. GRL, 34, 2007.

[3] Odum et al. Science 276, 96, 1997.

[4] Adam T. et al., Env. Sci. Tech., 44, 2010.

[5] Clairotte et al., Analytica Chimica Acta, 717, 2, 2012.

Primary Emissions and Secondary Aerosol Formation from a 2-stroke and a 4-stroke Scooter Fuelled with Standard and Alkylate Petrol

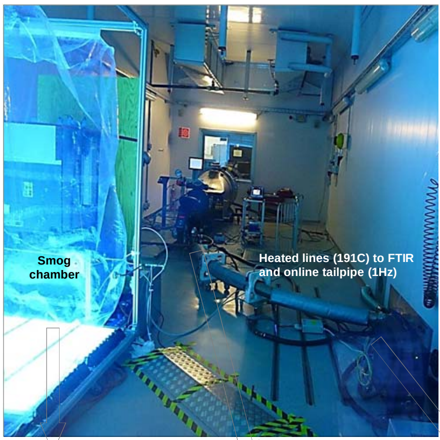
Alessandro A Zardini[1], Platt S.M.[2], El Haddad I.[2], Clairotte M.[1], Temime B[3]., Marchand N.[3], Jezek I.[4], Mocnik G.[4], Wolf R.[2], Slowik J.G.[2], Baltensperger U.[2], Prevot A.S.H.[2], Astorga C.[1]

[1]European Commission - Joint Research Centre, Institute for Energy and Transport, Sustainable Transport Unit, Ispra (Va), Italy. [2]PSI, Villigen, Switzerland.
[3]Laboratoire Chimie et environnement, Université de Provence (Marseille, France). [4]Aerosol d.o., Lubjana, Slovenia.

1. Introduction

Powered two wheelers (PTW) with engine displacement less than 50 cm^3 are a good fraction of urban vehicle fleets in Southern Europe and Asia. They generally emit more pollutants per km than modern cars. Nevertheless, the latest update on their emission standards (EURO2) dates back to 2002 and the scientific literature about PTW is scarce compared to passenger cars (e.g., [1,2] and references therein). In particular, no research about secondary organic aerosol (SOA) from PTW has been reported so far. Besides the regulated compounds (CO, THC+NOx), we monitored a range of exhaust constituents, both in gas and particle phases, with online and offline techniques: aerosol (HR-ToF-AMS, Aerodyne) and proton transfer reaction (HR-ToF-PTR-MS, Ionicon) mass spectrometers, Fourier transformed infrared spectroscopy (MKS-2030-HS), gas and liquid chromatography (GC-FID, HP-LC). We aged the primary emissions in a photochemical smog chamber and investigated the secondary condensed material. We tested the performance of alkylate gasoline and ultra-clean oil, normally used in professional, non-road small engines, and investigated its potential for wider use with scooters. The alkylate fuels, almost free of aromatics, are designed to produce cleaner emissions, hence reducing health risks and increasing engine lifetime.

2. Facility and instrumentation



Vehicle Emission Lab (VELA1) at JRC. A 2-s and a 4-s moped are tested on legislated driving cycles (chassis-dyno) with controlled ambient conditions. Primary gaseous and particulate emissions are measured at the tailpipe and in dilution tunnel. Tailpipe exhaust is also injected in a photochemical aerosol **mobile smog-chamber** and Secondary Aerosol is characterized.

Mobile Smog Chamber: 9m² Teflon bag; 40x100W UV lights; pure air generation; controlled T and RH. (PSI, Switzerland).

Sampling: Real time (1Hz) and offline/integrated at 3 ports: Tailpipe, Dilution Tunnel, and Smog Chamber.

Smog-chamber
- AMS: SOA
- MAAP: BC
- Aethalometer: BC
- PTR-MS: organics
- SMPS: sizing
- THC, NOx, CO

Tailpipe
- FID, CLD, NDIR: THC, NOx, CO
- FTIR: N-compounds and organics

Dilution Tunnel
- FID, CLD, NDIR: THC+NOx, CO Regulated compounds
- HP-LC: Carbonyls
- GC-dual FID: VOCs

3. Primary emissions

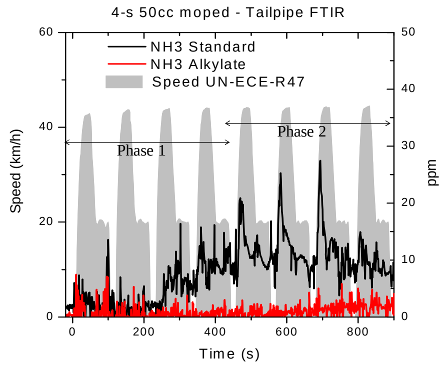
Major fuel compositional differences and effects of alkylate fuel on primary emissions:

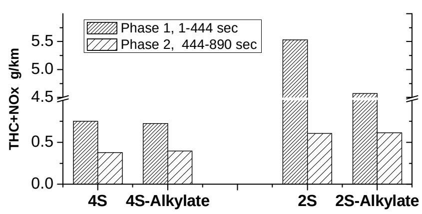
1) (Real time) **ammonia** emissions: alkylate fuel is **beneficial**.

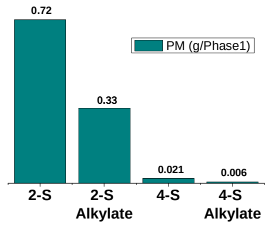
2) **THC+NOx** (Regulated: 1.2 g/km, phase 2): no significant effect.

3) **Particulate Mass**: **beneficial**

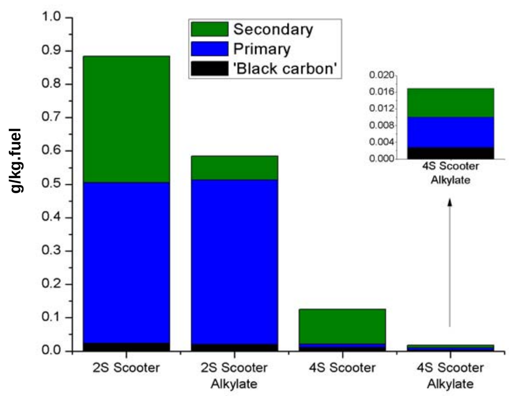
Composition (vol%)	Standard fuel	Alkylate fuel
Aromatics	29.6	0.1
Olefins	4.2	0.1
Benzene	0.2	0.01







4. Secondary Aerosol Formation



Aerosol composition after aging of primary tailpipe exhaust emissions.

1) Secondary organic aerosol (SOA) is formed from gas phase photochemistry.
UV exposure: 5-hours ca.

2) **SOA is comparable or larger than primary**, with standard fuel
→ SOA must be considered when comparing PM ambient levels to vehicle emissions.

3) Considerable **SOA reduction with alkylate fuel.**

5. Conclusions

- **Alkylate fuel reduces Particle Mass considerably**
- **Beneficial effect on NH_3 emissions (4-s moped)**
- **Mopeds produce a large amount of secondary organic aerosol**
- **Alkylate fuels significantly reduces SOA and the ratio secondary/primary aerosols**

Basic References
[1] Adam T. et al., Env. Sci. & Tech., 44 (2010), p.505.
[2] Clairotte M. et al., Analytica Chimica Acta, Volume 717, 2, 2012, p. 28-38.

Acknowledgment
The authors would like to thank Urbano Manfredi and the VELA staff.

Joint Research Centre

Contacts
Alessandro A. Zardini
alessandro.zardini@jrc.ec.europa.eu
Covadonga Astorga-Llorens
covadonga.astorga-llorens@jrc.ec.europa.eu