

## Primary and Secondary Organic Aerosol Emissions from 2-stroke Mopeds

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### Introduction

Road vehicles are a major source of particulate matter (PM) in urban areas [1]. PM has significant, sometimes lethal, health effects [2]. A large fraction, 20-90%, of the total PM consists of organic aerosol (OA) [3]. OA may be classified as primary (POA), from direct emissions, or secondary (SOA), formed via gas-phase reactions. These reactions also involve semi volatile compounds partitioned between the particle and the gas phase and remain poorly understood [4].

Mopeds are a popular means of transport in many countries, particularly in Southern Europe and Asia. Many mopeds on the road today have two-stroke (2-S) engines; known emitters of unburnt fuel and lubricating oil [5], and may therefore contribute significantly to both POA and SOA in urban areas. Characterisation of POA and SOA emissions from mopeds is therefore required to understand their health impact and to design effective future vehicle pollution regulations.

### Methods

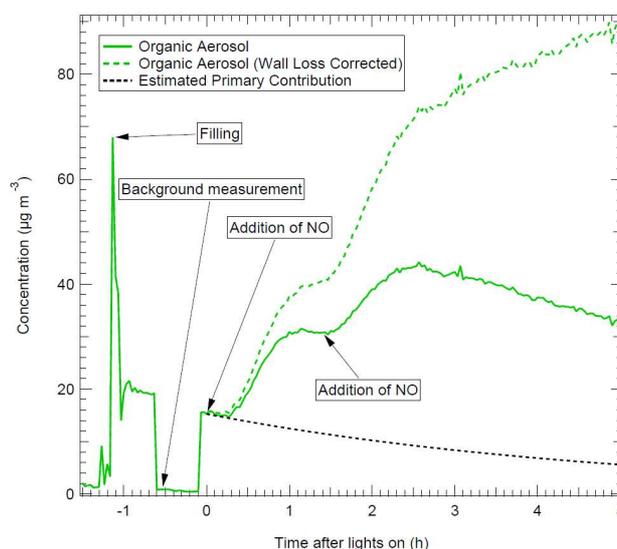
Emissions factors (EF) ( $\text{g OA kg}^{-1}$  fuel), of POA and SOA were determined during smog chamber experiments, at the Paul Scherrer Institute (PSI), Villigen, Switzerland, for a EURO1 2-stroke moped and a EURO2 2-stroke moped.

Much of the experimental set up used for these experiments is described in detail elsewhere [6]. Briefly, moped exhaust was introduced into the chamber via a heated ( $150^{\circ}\text{C}$ ) injection system and ejector diluter. High resolution Fourier-transform infrared (HR-FTIR) spectroscopy of the undiluted exhaust during injection was used to quantify the emissions of CO, CO<sub>2</sub>, and gaseous hydrocarbons. An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was used to quantify OA in the smog chamber (for information concerning this instrument, see [7]). Measurements of total hydrocarbon, CO, O<sub>3</sub>, and NO<sub>x</sub> concentrations were also performed. SOA formation in the chamber was initiated using UV lights. Moped POA EFs determined from the OA concentrations in the smog chamber using a carbon mass balance based on [8].

During the smog chamber experiments, online quantification of particle bound reactive oxygen species (ROS), a proxy for human health effects, was performed. Online particle bound ROS analysis utilised the fluorescence probe 2,7-dichlorofluorescein (DCFH) in solution. Particles were collected and continuously extracted on a wetted hydrophilic filter. The particle collector samples air at up to 5 litres per minute (lpm) and collects particles larger than an aerodynamic diameter of 50 nm with greater than 95% efficiency. Particles are collected and extracted in an aqueous solution of horseradish peroxidase (HRP) (0.5 units per ml) that allows immediate reaction of ROS on collection. The concentration of ROS is characterised following subsequent reaction of the oxidised HRP with DCFH (5  $\mu\text{M}$ ) for 10 minutes at 40°C, yielding the fluorescent product DCF in the continuous flow set-up. The concentration of DCF is measured using fluorescence spectroscopy in a flow-through cell and calibrated to ROS concentration with hydrogen peroxide. More information on this method may be found in [9].

## Results

Figure 1 shows a time series of a typical smog chamber experiment. After an initial spike in OA concentration following sample injection, a time of twenty minutes was allowed for equilibration of the exhaust in the chamber and the concentration of OA at this point was regarded as the initial primary organic aerosol (POA) emission. After background measurements with the AMS to correct for concentrations of gas phase species four Xenon arc lamps and a battery of UV black lights were switched on to initiate photo-oxidation and secondary organic aerosol (SOA) formation. The first experiment (on 15.11.10) showed that SOA formation was sensitive to the presence of  $\text{NO}_x$  (as would normally be present in the ambient atmosphere) and subsequent experiments were carried out with a steady injection of  $\text{NO}$  whereby  $\text{NO}_x$  was maintained at around 20 ppb.



**Figure 1: Time series of a typical moped smog chamber experiment (15.11.10). The green line indicates the concentration of organic aerosol in the smog chamber with respect to time after lights on as measured by the aerosol mass spectrometer. The dashed green line is the wall loss corrected aerosol mass concentration based on the loss rate of the primary organic aerosol (see text), shown in black.**

The data on OA concentration was corrected for wall loss in the chamber using the decay rate of the initial POA and used along with concentrations of gas phase hydrocarbons, CO, and CO<sub>2</sub> to calculate emission factors.

The calculated EFs from the smog chamber studies were comparable to those calculated in previous moped emissions studies at the Joint Research Center (JRC), Ispra, Italy. Moped EFs determined at both JRC and PSI are several orders of magnitude higher than those of other vehicle classes, including diesel and gasoline cars and heavy duty trucks. Furthermore, these emissions contain large quantities of volatile hydrocarbons, as reflected by the fact that SOA comprised the main fraction of the OA after only a few hours. A large fraction of the hydrocarbons in the smog chamber remained unreacted, indicating that EFs for SOA may be even higher.

Online ROS measurements show that ROS concentrations are linked to the formation of SOA.

## Conclusions

We conclude that emission of OA by mopeds may be a major public health consideration in many urban areas and may represent a large contribution to the burden of organic aerosol globally.

## References

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5. Spezzano, P., P. Picini, and D. Cataldi, *Contribution of unburned lubricating oil and gasoline-derived n-alkanes to particulate emission from non-catalyst and catalyst-equipped two-stroke mopeds operated with synthetic lubricating oil*. Journal of Environmental Monitoring, 2008. **10**(10): p. 1202-1210.
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7. DeCarlo, P.F., et al., *Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer*. Anal. Chem, 2006. **78**(24): p. 8281-8289.
8. Phuleria, H.C., et al., *Size-resolved emissions of organic tracers from light- and heavy-duty vehicles measured in a California roadway tunnel*. Environmental Science & Technology, 2006. **40**(13): p. 4109-4118.
9. Venkatachari, P. and P.K. Hopke, *Development and laboratory testing of an automated monitor for the measurement of atmospheric particle-bound reactive oxygen species (ROS)*. Aerosol Science and Technology, 2008. **42**(8): p. 629-635.

# Primary and secondary organic aerosol emissions from 2-stroke mopeds

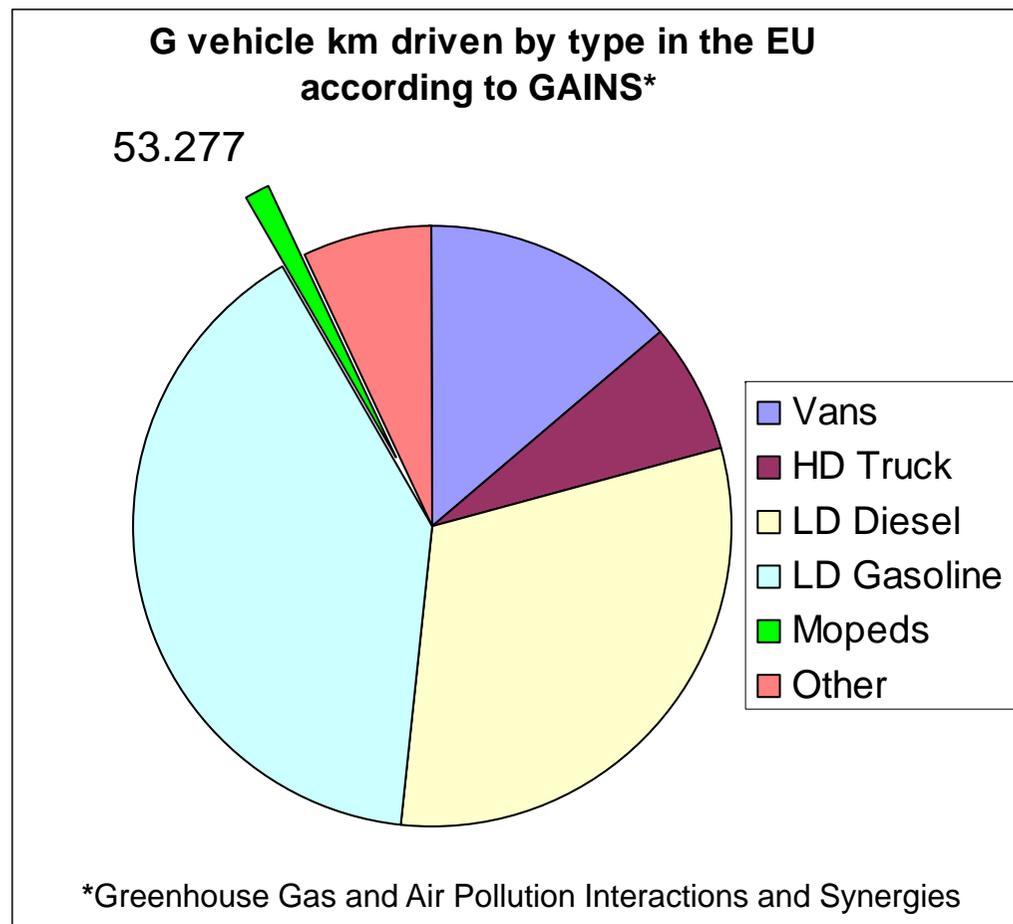
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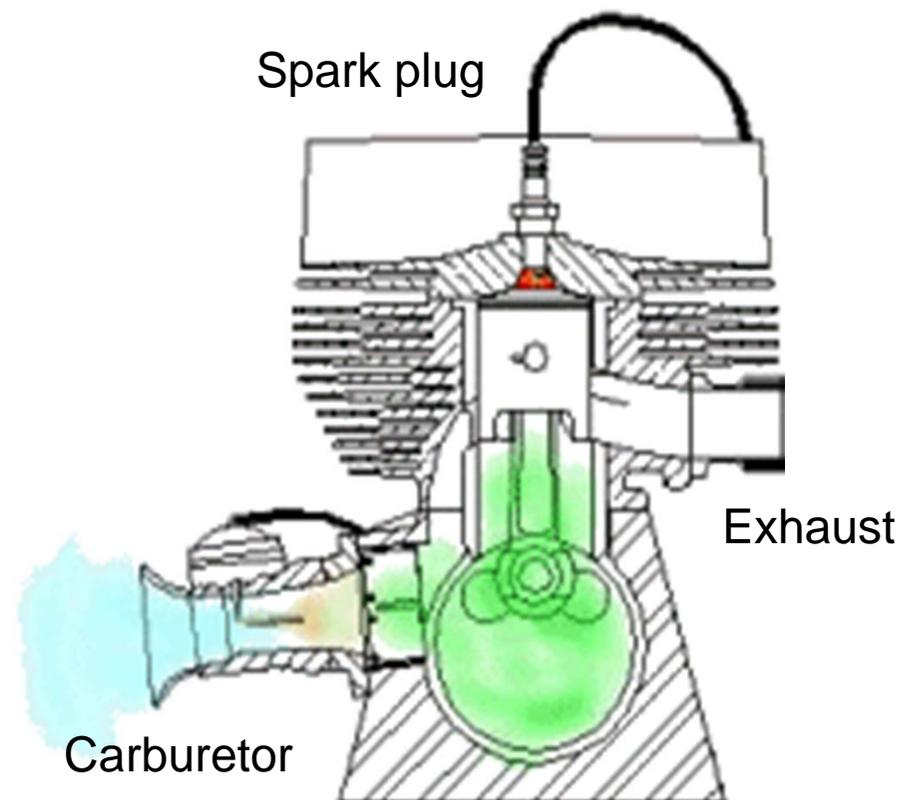
Are particulate emissions from 2-stroke mopeds a problem?

- How do their particulate emissions compare to those from other vehicles?
- What happens to these emissions in the atmosphere, do we get secondary formation?
- Might their emissions have health implications?

- Need for effective pollution control
- 2-stroke mopeds relatively small contribution to km driven
- Regulations: Euro2 (mopeds) vs. Euro5 (cars)
- Issues with 2-stroke?



- Lubricant oil
- High hydrocarbon when open to atmosphere
- High primary aerosol emission
- Secondary aerosol from hydrocarbons?

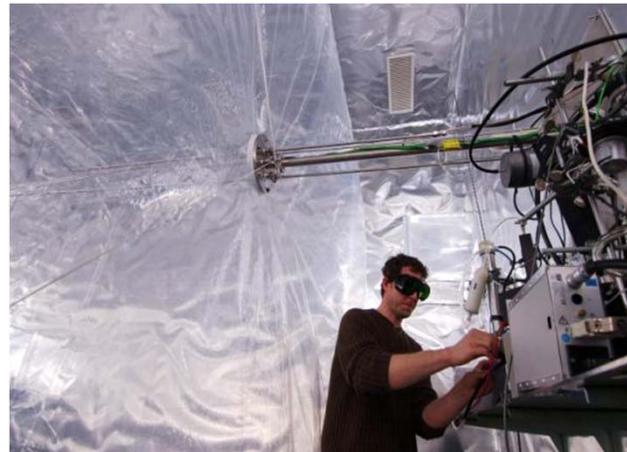


(Goes much faster than this...)

## Combined approach:



Test bench  
measurements on  
primary emissions



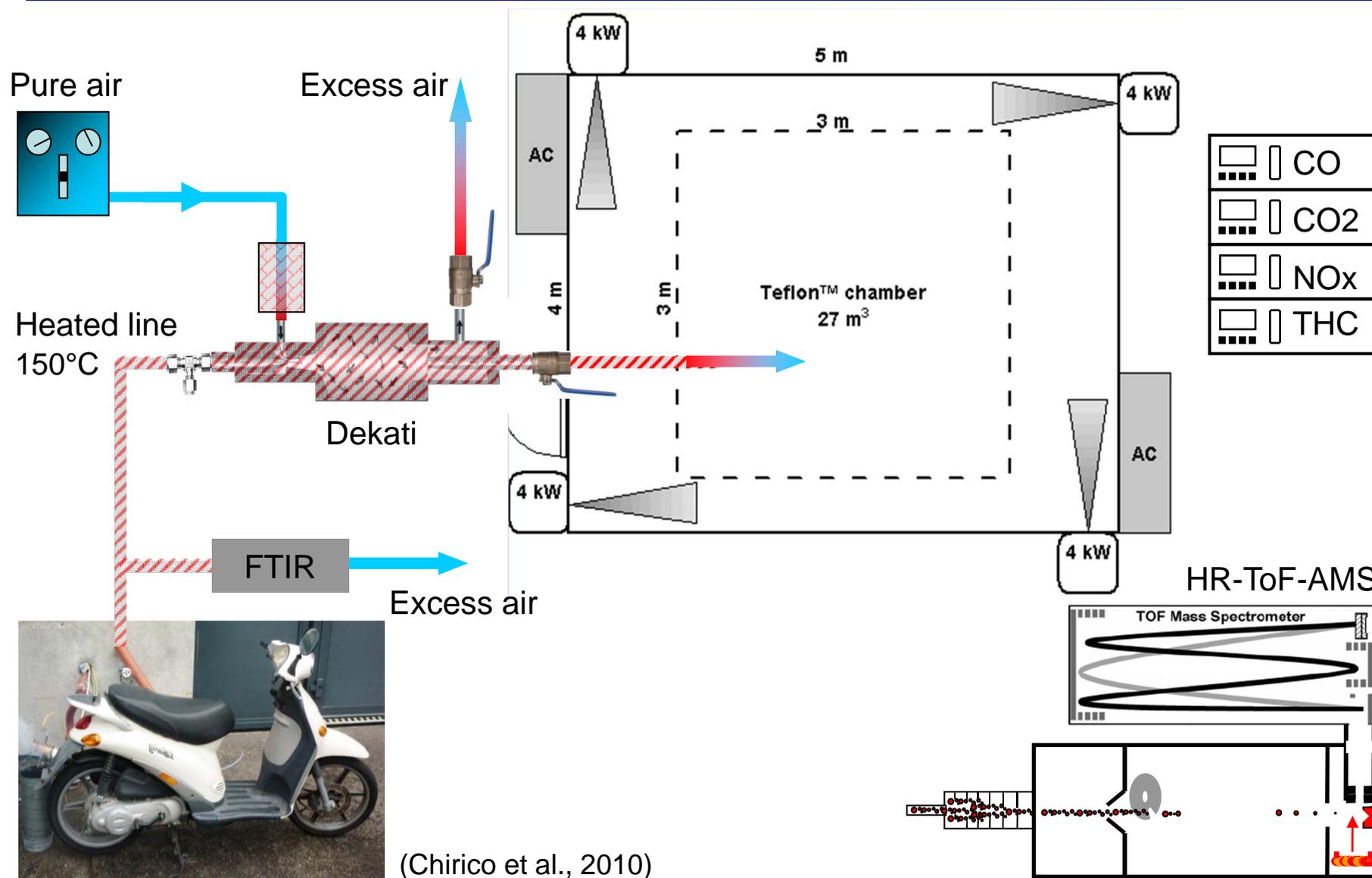
Smog chamber study on  
secondary aerosol  
formation



Online analysis of  
water soluble  
reactive oxygen  
species 'ROS'

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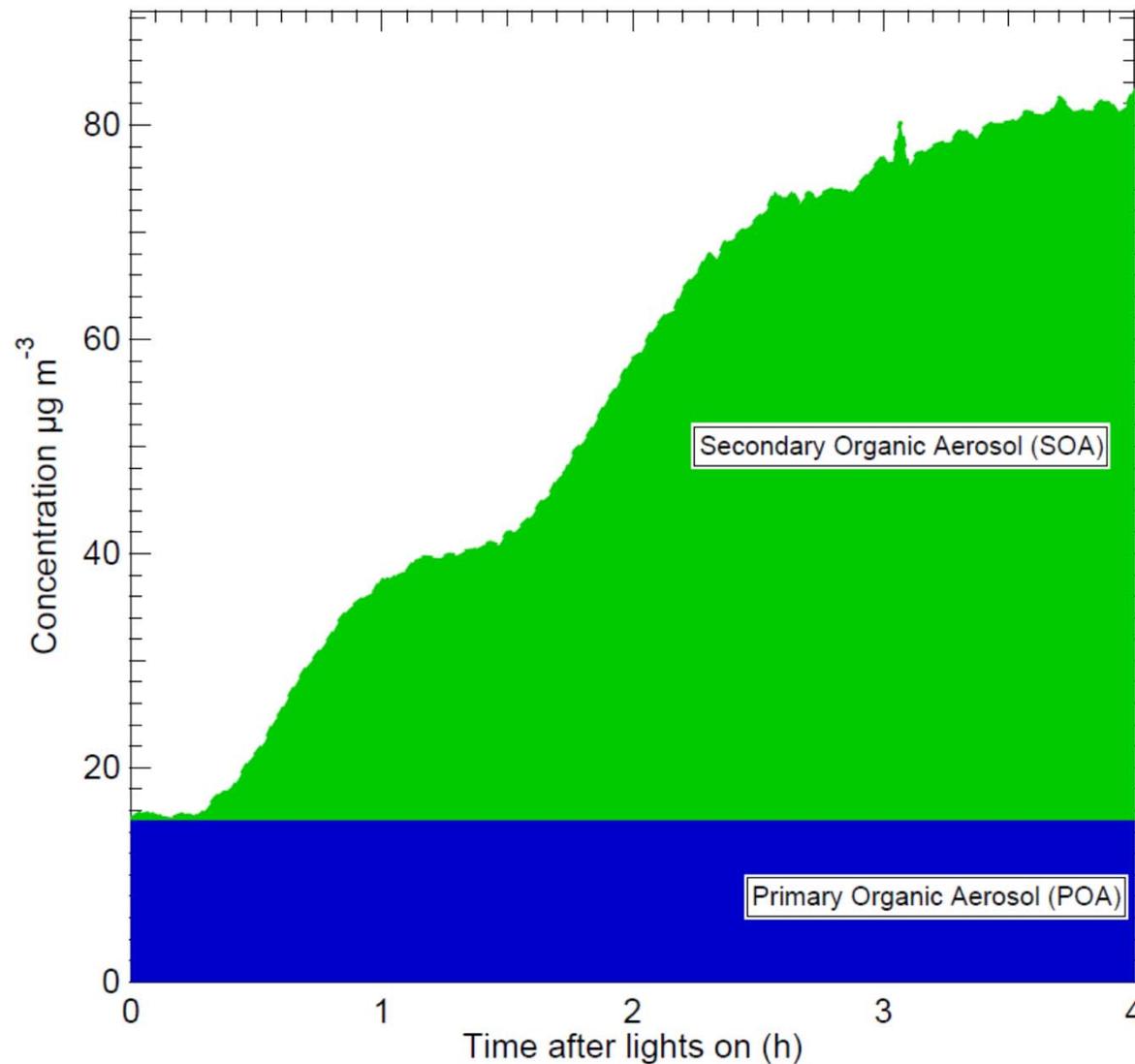
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(Chirico et al., 2010)

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- Organic aerosol from HR-ToF-AMS
- Secondary organic aerosol (SOA) after lights on
- $\text{NO}_x$
- Wall loss correction



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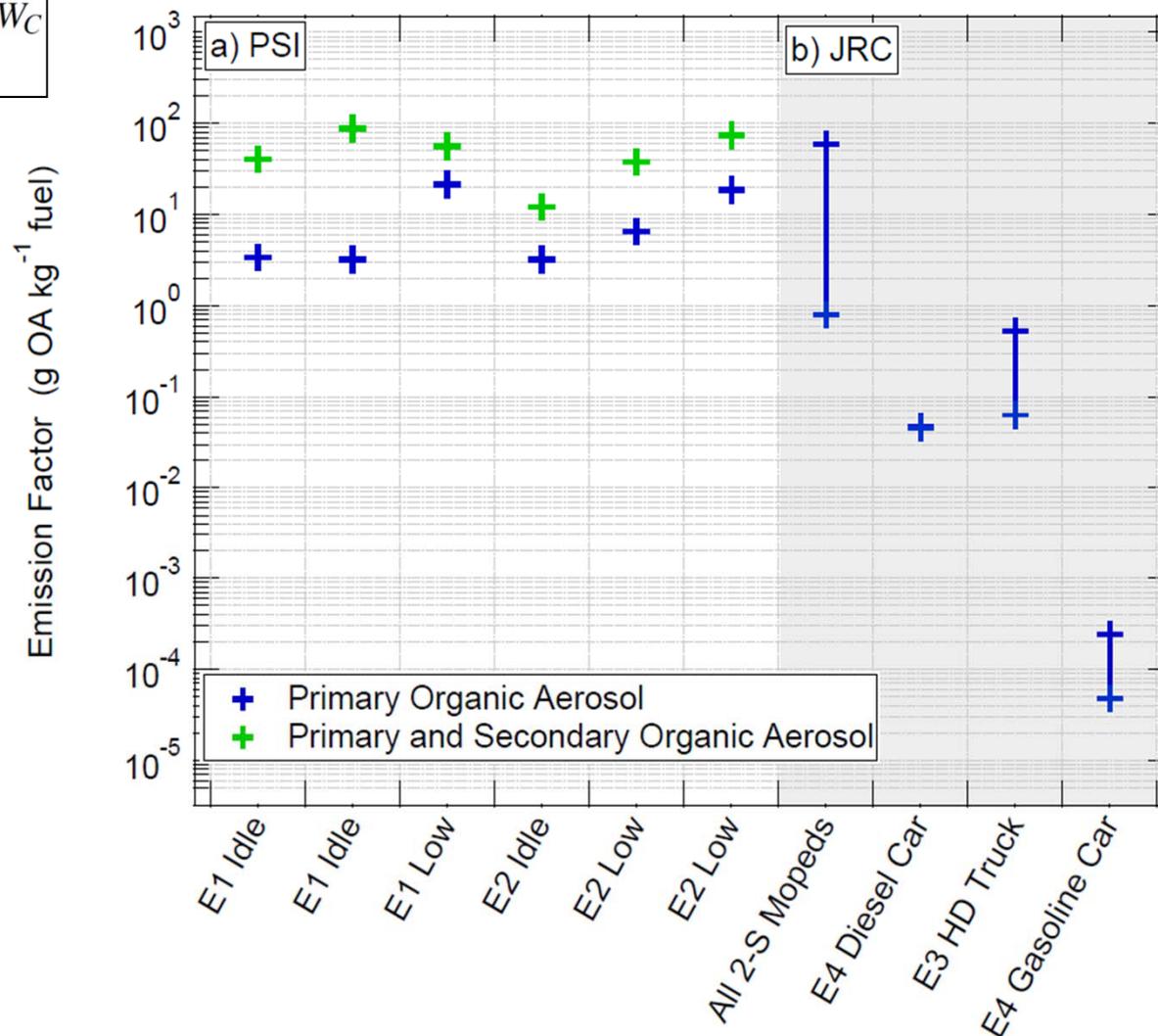
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$$EF = \left( \frac{OA}{C_{CO_2} + C_{CO} + C_{HC} + C_{POA}} \right) W_C$$

C=Carbon, OA=Organic Aerosol

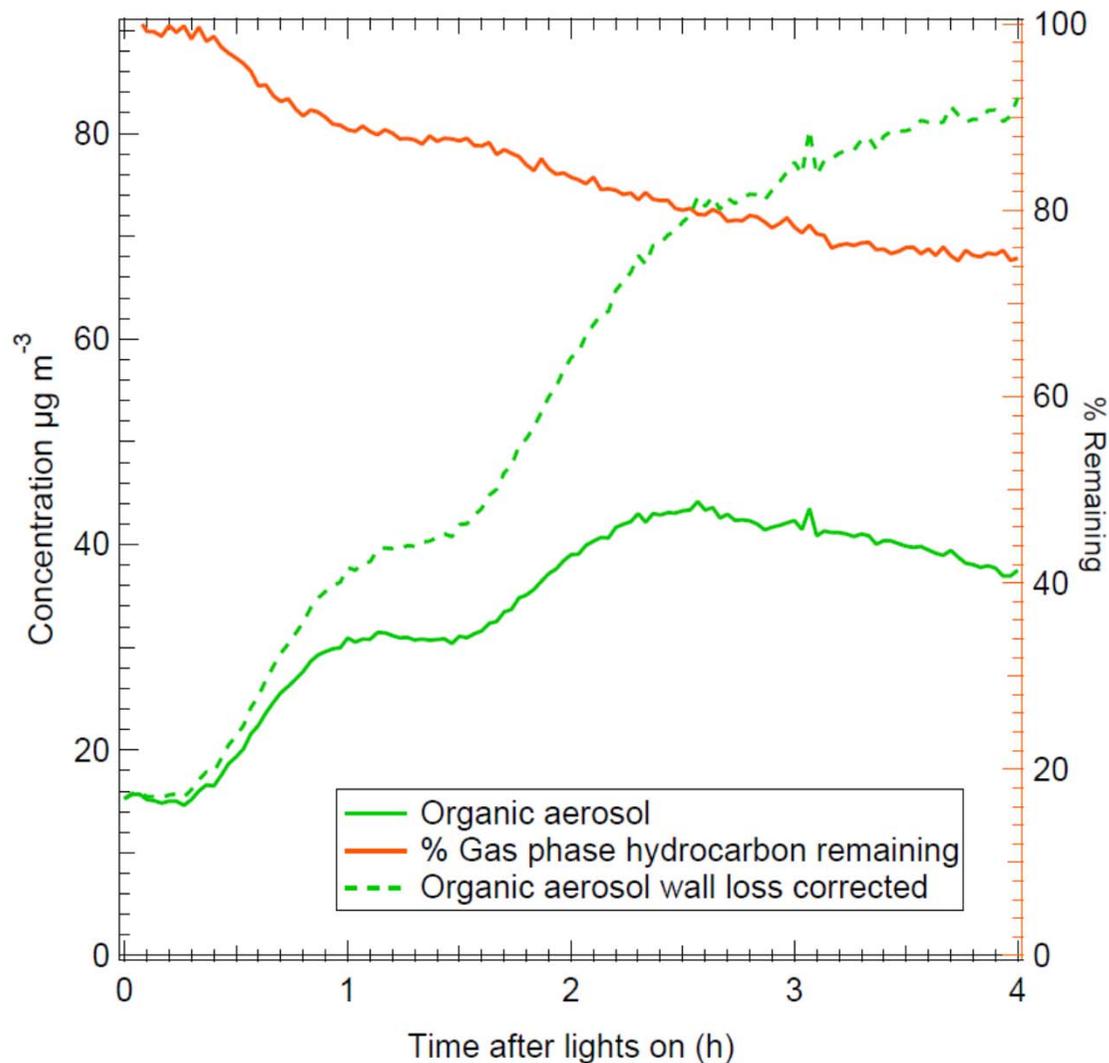
$W_C$ =Fuel Carbon Content

- Logarithmic scale
- High POA
- Even higher SOA
- OA 1,200,000 higher than Euro4 gasoline
- 1000 higher than Euro4 diesel

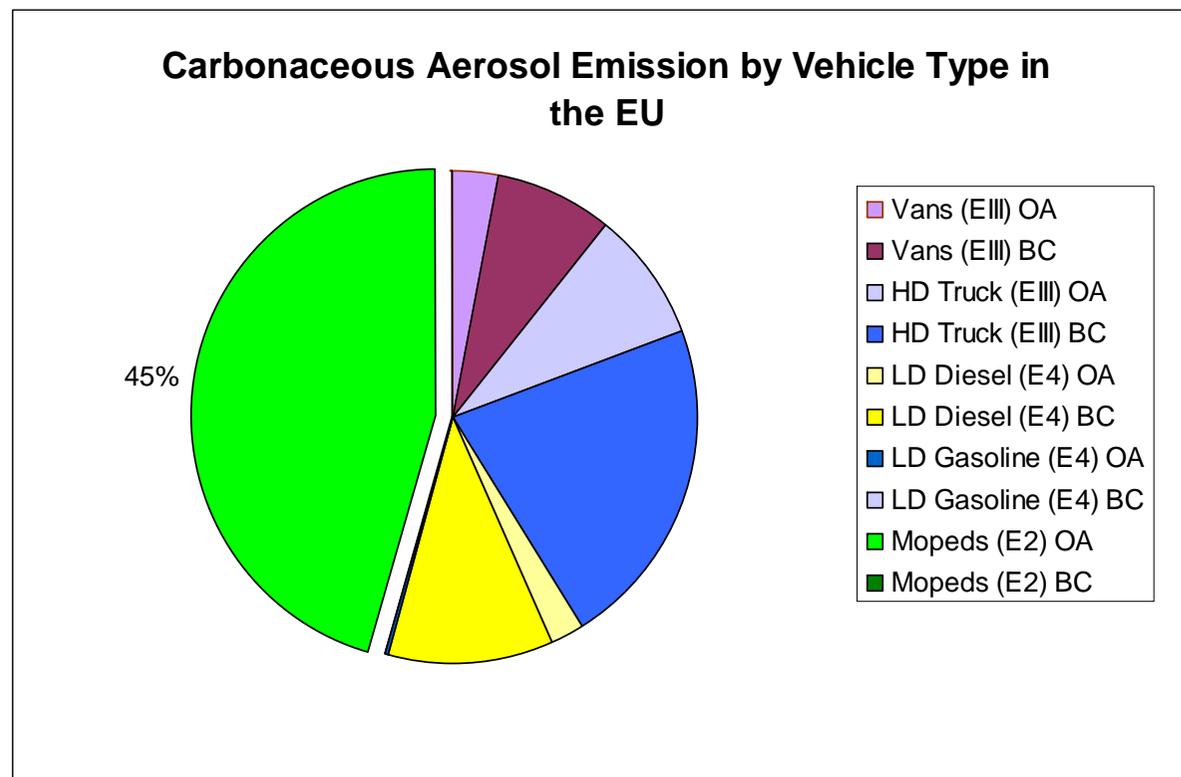


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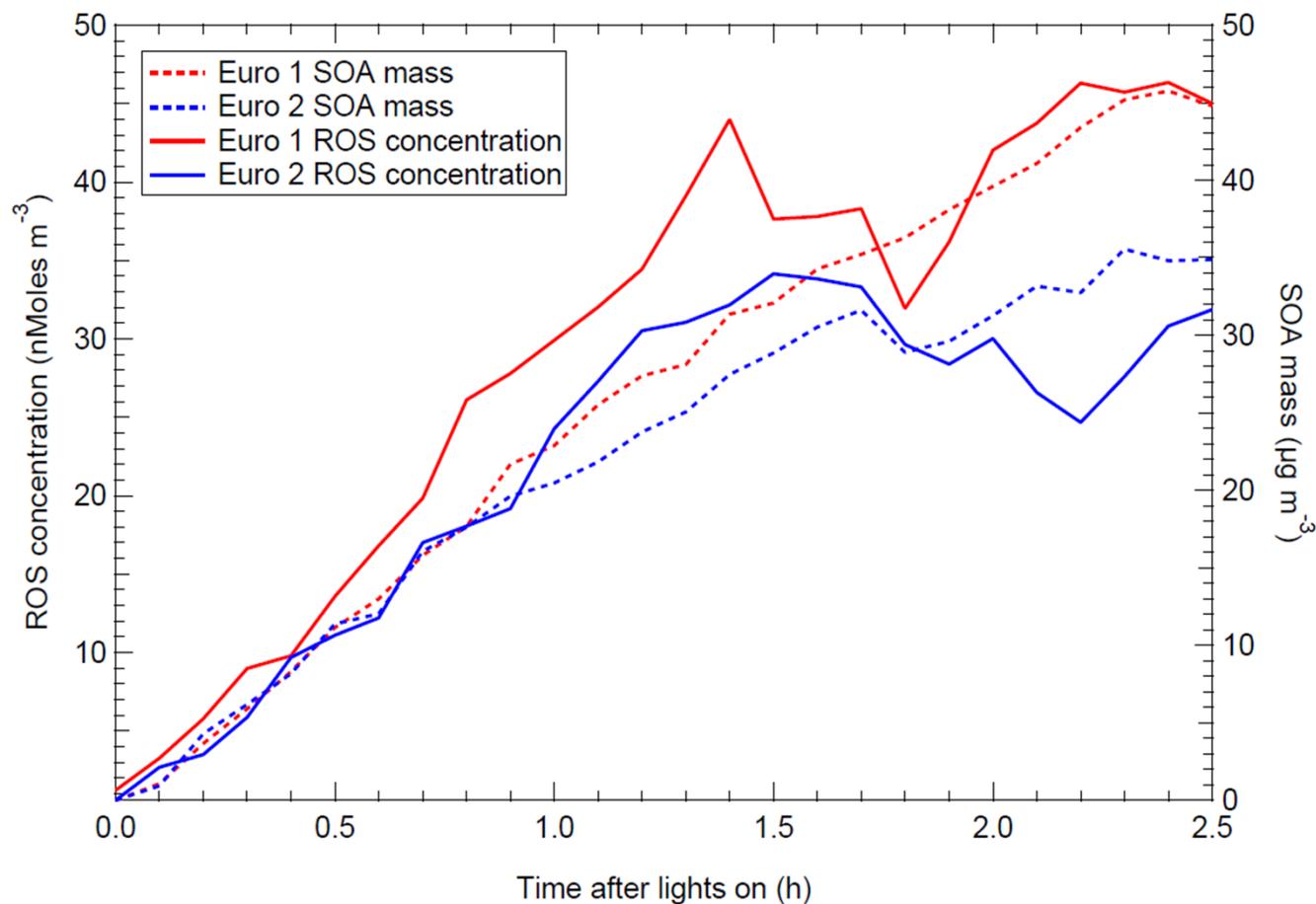
- Total hydrocarbon instrument (only gas phase)
- Most gas phase hydrocarbon remains at experiment end
- Higher SOA may be possible



- Combined model data with emission factors
- OA includes SOA
- mopeds the major player in EU

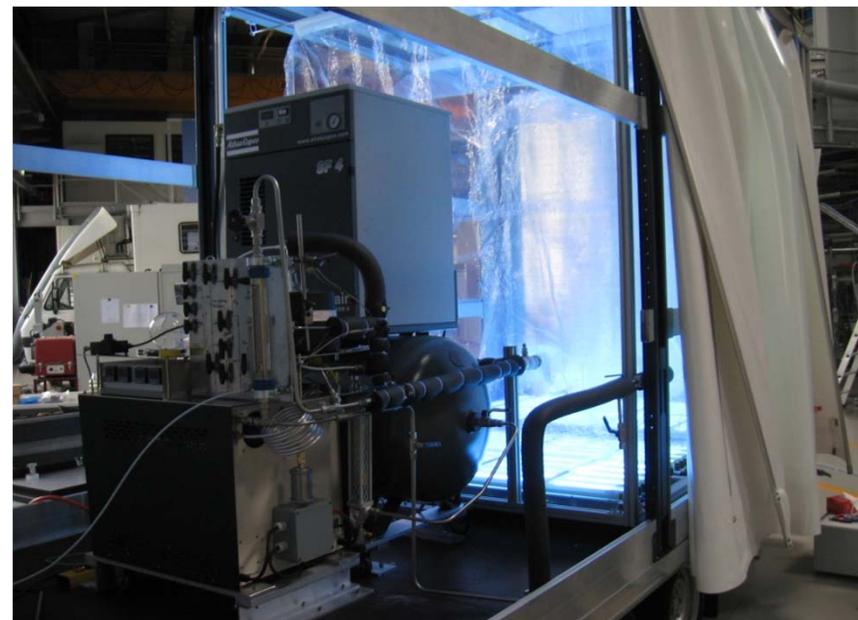


- Reactive oxygen species 'ROS'
- Health effect proxy
- Here associated with SOA formation



New mobile chamber, smog chamber/ test bench measurements combined:

- Vehicle emissions under cold start conditions
- Emissions at high speeds ( ~120 km/ hour)
- Fuel blends
- Hand held tools, ships etc. ...ideas/ proposals welcome!



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- 2-stroke moped primary organic aerosol emissions orders of magnitude higher than other vehicles, up to over one million
- Significant SOA production, though we may not have observed full SOA formation potential
- 2-stroke mopeds may be the largest single vehicle pollution source in the EU today
- Evidence of health impacts via online quantification of proxy compounds

- PSI: J. Slowik, P. Barmet, L. Pfaffenberger, M. Heringa, A. S. Prévôt, J. Dommen, U. Baltensperger
- JRC: M. Clairotte and C. Astorga
- R. Chirico, now at Italian National Agency for New Technologies, for test bench measurements
- S. Fuller and M. Kalberer of Cambridge University for ROS work



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Thank you for your attention!