Evolution of organics in the atmosphere: Dependence on technology of diesel vehicles and wood burning facility.

Aging of Diesel and Wood Burning Emissions in Smogchamber Experiments

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While newer European directives have introduced increasingly stringent standards for primary particulate matter (PM) emissions, gas phase organic emissions from diesel vehicles can lead to large amounts of secondary organic aerosol (SOA) in today’s atmosphere (Lipsky and Robinson 2006). Investigations of the contribution of exhaust from vehicles and wood burners to primary organic aerosol (POA) and to SOA during smog chamber photooxidation experiments will be presented. Experiments were carried out in the smog chamber of the Paul Scherrer Institute (PSI) where diesel exhaust was introduced into the chamber with an injection system developed to obtain a representative sample of the diesel exhaust into the chamber (Figure 1). An Aerosol Mass Spectrometer (AMS) was used to quantify the organic aerosol while black carbon (BC) concentrations were measured with a Multi-Angle Absorption Photometer (MAAP).

Figure 1: Setup of the diesel vehicle experiments at the PSI smogchamber (Chirico et al., 2010).

Results from several diesel vehicles with and without aftertreatment devices are compared. The smog chamber campaign showed that, for the conditions explored in this paper, primary aerosols from diesel vehicles without a particulate filter consisted mainly of black carbon (BC) with a low fraction of organic matter (OM, OM/BC<0.5), while the subsequent aging by photooxidation resulted in a consistent
production of SOA only for the vehicles without a DOC and with deactivated DOC. After 5 hours of aging ~80% of the total organic aerosol was SOA on average and the estimated emission factor for SOA was 0.23-0.56 g/kg fuel burned. In presence of both a DOC and a DPF, primary particles with a mobility diameter above 5 nm were 300±19 #/cm³, and only 0.01 g/kg fuel burned of SOA was produced after 5 hours since lights on. In summary, the combination of the diesel oxidation catalyst and the particulate filter leads to a very significant reduction of both the aerosol emissions and (!) the secondary organic aerosol production. For the wood burning experiments, much lower emissions of carbonaceous particles and secondary organic aerosol formation is found for pellet stoves during flaming phase versus log-wood ovens (Heringa et al., in preparation)

![Image of emission factors including black carbon (BC), primary organic aerosols (POA) and secondary organic aerosols (SOA) after 5 hours of aging in the smogchamber for diesel cars with no oxidation catalyst and no filter, with oxidation catalyst and no filter, and oxidation catalyst with filter (Chirico et al., 2010).](image)

**Figure 2:** Emission factors including black carbon (BC), primary organic aerosols (POA) and secondary organic aerosols (SOA) after 5 hours of aging in the smogchamber for diesel cars with no oxidation catalyst and no filter, with oxidation catalyst and no filter, and oxidation catalyst with filter (Chirico et al., 2010).

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**References**


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Burning Emissions in Smogchamber Experiments

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WOODIESEL campaign

AMS, ATOF-MS, Several BC instruments, SP-2, HTDMA,
off-line analyses, ..

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Primary and Secondary organic aerosols

**Primary Organic Aerosols**
- High temperature
- Low dilution ratio (10-100)

**Secondary Organic Aerosols**
- Ambient temperature
- High dilution ratio (1000-10000)

**Black Carbon**
(Volkamer, 2006)

**Highlights**
- Hodzic et al., ACP, 2010
- Robinson et al., Science, 2007
Experiments

- Van (Euro 2) without aftertreatment
- Passenger car (Euro 3) with oxidation catalyst operating / not operating (idle / 60 km/h)
- Passenger car (Euro 3) with oxidation catalyst and particulate filter
- Logwood burner (different burning conditions)
- Pellet burner (start phase, stable burning)
PSI smog chamber setup

Logwood oven or pellet burner or diesel car

PSI smog chamber
27 m³ Teflon bag

Highlights

- Temp., RH
- NOₓ, O₃, CO, CO₂
- DC, PAS
- CPC, SMPS
- VH-TDMA
- HR-Tof-AMS
- MAAP / Aethalometer
Characteristic aging experiment of diesel exhaust (wall loss corrected)

Primary aerosols consist mainly of BC with a low fraction of Organic Matter (OM).

Photo-oxidation of gaseous organics produces SOA.
SOA contribution to total organic mass

\[
\%\text{SOA}(t) = \left[ \frac{\text{SOA}(t)}{\text{OM}(t)} \right] \times 100
\]

DOC effect on SOA production

- No DOC
- DOC deactivated
- DOC activated
Aftertreatments effect on emissions

Chirico et al., ACPD, 2010

DOC effect

Particulate filter effect
O/C ratio of organic aerosol

Indicator of oxidation state of organic aerosol

- OA_5h
- HOA
O/C ratio of organic aerosol

Indicator of oxidation state of organic aerosol

- HOA
- SV-OOA (~ Fresh SOA)
- LV-OOA

SV = semi volatile
LV = low volatile

(Aging Time (no scale))

(Jimenez, Science 2009)
WOOD BURNING CHAMBER EXPERIMENTS

LOGWOOD

OM/BC 0.15 → 0.45

OM = \frac{OM \times BC_{10}}{BC}

PELLLET
Emissions of a pellet and an old (Weso) and new logwood burner (Attika) normalized to CO$_2$

Heringa et al., in preparation
Emissions of a pellet and two logwood burners normalized to CO

![Graph showing emissions scaled to CO](image-url)
O/C ratio as a function of time for wood burning experiments

Highly aged

Diesel
Volutility distribution of primary organics

- This redistribution needs to be assessed for various emission technologies … also including future improvements
Diesel E4 (speed ramp with speeds > 120 km/h)
CONCLUSIONS

• Aftertreatment technology in diesel cars influence strongly primary emissions and secondary particle production.
• For diesel cars at rather low loads (idle / 60 km/h), primary and secondary carbonaceous aerosols can be avoided to a large extent by oxidation catalyst and particulate filter: SUCCESS STORY
• A pellet burner during stable phase burning leads to considerably lower particulate emissions and secondary aerosol production.
• Future regulation of emissions should maybe take into account the secondary organic production potential (SOPP) analog to POCP of VOCs.
• During the first 5 hours of aging, the highest degree of oxidation of ambient air is not yet reached. Wood burning organics start from a higher degree of oxygenation.
POA concentration at the tailpipe of different vehicles

- Gasoline vehicles
- Diesel vehicles
- Mopeds

![Graph showing POA concentration over time for different vehicles](image-url)