Semivolatile fraction's characteristics from engine and car exhaust

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Introduction

Semivolatile compounds (SVC) in the exhaust from cars and vehicles are not well-known and they are not directly limited by emission standards. Furthermore, SVCs partly pass the filters for collecting the particulate matter (PM). Phase partitioning of SVC compounds varies depending on their concentration and saturation pressure, the other constituents of exhaust gas, and the sampling parameters.

Methodology

We studied polyaromatic hydrocarbons (PAHs) from PM and SVC fractions collected from the exhaust from heavy-duty (HD) diesel engine, Euro 2 car and Euro 6a cars. A high-speed HD non-road common-rail diesel engine without exhaust aftertreatment system was operated with ISO 8178 RMC-C1 test cycle. Euro 6a passenger cars using diesel, gasoline, ethanol and natural gas, and Euro 2 diesel car, were tested with the European chassis dynamometer driving cycle (NEDC) at -7 °C. SVCs were collected with membrane disks (HLB). For SVC from diesel engine, simulated distillation clarified its distillation range and thermal-optical analysis (TOA) its carbon content. GC-MS indicated type of compounds present in the SVC fraction.

Results

SVC fraction from HD engine contained largely diesel-type C9-C19 compounds distilling at 160-375 °C, which was supported also by TOA (Figure 1a-c). PAHs were found in higher concentrations from the SVC than from the PM, however, the PAH profiles were different (Figure 2a). Lighter PAHs were found especially in the SVC fraction. For cars, sum of 24 PAHs was especially high in the SVC fraction from Euro 2 diesel, Euro 6a gasoline and FFV/E85 cars, while low for the Euro 6a diesel with diesel particulate filter (DPF) and for the NGV/CNG car. For these cars, priority PAHs classified as carcinogenic were reported by Aakko-Saksa et al. (2020), while here also lighter PAHs are included.

Incomplete combustion of fuel and lubricating oil leads to SVC emissions containing PAHs and other compounds. These are not necessarily detected by flame ionisation detector (FID) that is used for analysis of total hydrocarbons (THC). FID detects alkanes up to C12 and aromatics up to C10-C11, approximately, while heavier compounds may not reach FID. Additionally, part of the SVC emissions originating from unburned fuel and lubricating oil may not be sufficiently heavy to be collected with the PM filter in the typical sampling conditions. The SVC fraction carry light PAHs and may contribute to formation of secondary aerosols.

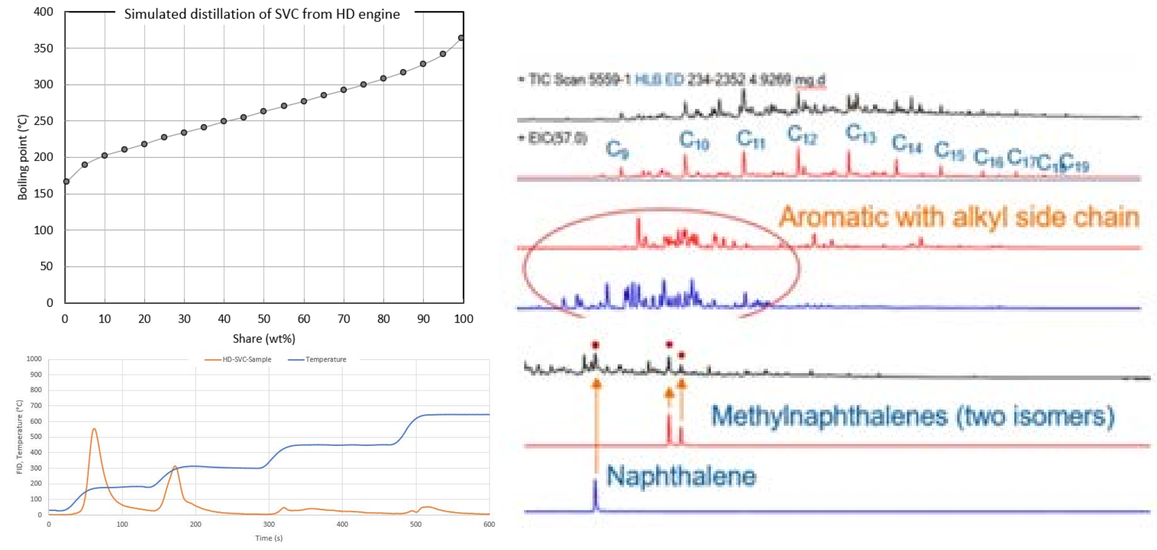

Figure 1. SVC sample from HD engine analysed by a) simulated distillation b) thermal-optical analysis c) GC/MS.

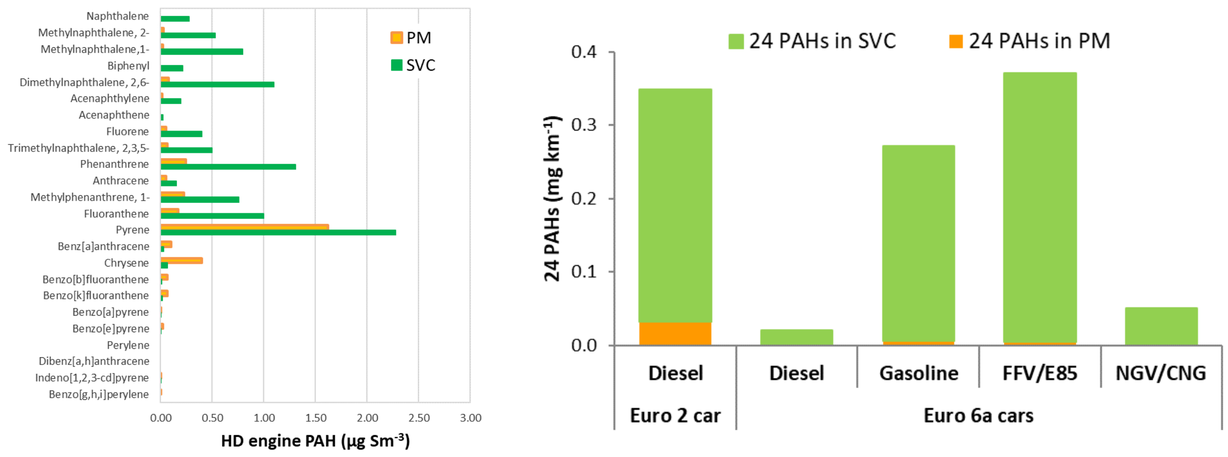

Figure 2. a) PAHs in PM and SVC for HD engine b) 24 PAHs for cars. FFV = flexible fuel vehicle; E85 = 85% ethanol and 15% gasoline; NGV/CNG = natural gas vehicle

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Conclusion

- **SVC fraction from HD engine contained diesel-type C9-C19 compounds distilling at 160-375 °C.**
- **Light PAHs, e.g. naphthalene, were found in higher concentrations from the SVC than from the PM.**
- **The SVC bound PAH emissions varied between car technologies.**
- **Incomplete combustion of fuel and lubricating oil leads to SVCs carrying light PAHs and other potentially harmful compounds.**

References

Aakko-Saksa et al. *Atmos. Environ.*, 236, 117643, 2020. doi.org/10.1016/j.atmosenv.2020.117643
Lu et al. *Atmos. Chem. Phys.*, 18, 17637–17654, 2018. doi.org/10.5194/acp-18-17637-2018.

Note: SVCs are often classified using n-alkane series, however, volatility depends on the structure of each compound.*
**For example, IVOCs C12-22, SVOCs C23-C32, LVOCs C33-C36 in Lu et al. (2018).*

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