Chemical profiles of particulate matter emitted from the exhaust of heavy-duty vehicles under different driving cycles

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Particulate matter (PM) represents a complex group of air pollutants with properties and impacts that vary according to its composition. Vehicle emissions constitutes one of the most important sources of PM (Karagulian *et al*., 2015). The emission rates and composition of primary PM from vehicle engines are challenging to determine since they depend on the fuel properties, technology and driving cycles. Euro emissions standards were put in place to improve air quality and health. Verification of compliance with these standards has been reported in numerous works. However, the detailed chemical speciation of the emitted PM is still very poorly understood.

In this work, different heavy-duty vehicles (HDV) were tested on a chassis dynamometer under different driving cycles (Table 1). The elemental composition of the PM emitted was analysed by ICP-MS and ICP-AES. After multi-solvent extraction and fractionation by silica gel column chromatography, a detailed organic speciation was performed by GC-MS.

Table 1. HDV tested and driving cycles.

Vehicle	Test cycle	Fuel	Standard
Heavy-duty vehicle I	VTT	Diesel 1	Euro V
	VTT	Diesel 1	Euro V
	VTT	Diesel 1	Euro V
	WHVC cold	Diesel 1	Euro V
	WHVC cold	Diesel 1	Euro V
	WHVC cold	GTL	Euro V
	WHVC cold	GTL	Euro V
Heavy-duty vehicle II	WHVC cold	Diesel 2	Euro VI
	WHVC hot	Diesel 2	Euro VI
	WHVC hot	Diesel 2	Euro VI
	WHVC hot	Diesel 2	Euro VI
	WHVC hot	Diesel 2	Euro VI
Heavy-duty vehicle III	Braunschweig hot	Diesel 2	Euro VI
	Braunschweig hot	Diesel 2	Euro VI

Major and trace elements, in their oxidised form, accounted for PM mass fractions between 6.2 and 58%. The lowest mass fractions were obtained for vehicle I fuelled with GTL and for the same vehicle when powered by diesel and following the VTT cycle. The highest element mass fractions were observed in emissions from vehicle II over the hot start WHVC cycle. In general, Na and Sr were the most abundant elements, followed by Al and Ca.

Several classes of organic compounds were identified, including alkanes, alkenes, PAHs, alcohols, various types of acids, alkyl esters of fatty acids, phenolic compounds, plasticisers, glycols, among others. Greater varieties (from C_{11} to C_{31} with no preference for odd versus even carbon numbers) and amounts of n-alkanes were detected in the exhaust (up to 6115 μg per g of PM) of the GTL fuelled vehicle (Euro V) tested by the WHVC driving cycle with cold start. When the diesel-powered Euro V vehicle followed the VTT cycle, the start-up phase mass fractions of Σ18PAHs were much higher (349 μg g^{-1}) than in the following tests (24.9-26.1 μg g^{-1}). As observed for the VTT cycle, the cold start phase of the Euro V vehicle in the WHVC test produced much higher PAH emissions (Σ_{18}PAHs = 161 μg g^{-1}) compared to the already slightly warmed-up engine (Σ_{18}PAHs = 39.0 μg g^{-1}). Σ_{18}PAHs from 32 to 125 μg g^{-1}) were recorded for Euro VI vehicles tested under the WHVC and Braunschweig hot start cycles. Retene, with mass fractions up to 9.35 μg g^{-1}, was a ubiquitous compound. Some alkylated PAHs were detected in emissions from all tests, except the Braunschweig cycle. A homologous series of n-alkanoic acids, ranging from C_8 to C_{22}, were found in the exhaust samples. The most abundant acids were C_{14}, C_{16} and C_{18}. Diacids from C_2 (oxalic) to C_{10} (sebacic) were also detected. n-Alkanols from C_8 to C_{30}, with a clear dominance of C_{18} were observed in all PM samples. Several oxygenated organic compounds were detected, as far as we know, for the first time in exhaust particulates.

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