

Metals from Heavy-duty Diesel Vehicles Equipped with Advanced PM and NOx Emission Controls¹

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Introduction

US EPA and California Air Resources Board (CARB) promulgated new stringent emissions standards for heavy-duty diesel engines, which limit the PM and NOx emissions to 0.01 g/bhp-hr (as of 2007) and 0.2 g/bhp-hr (as of 2010), respectively. In order to achieve such ultra low PM and NOx emissions, a preferred approach is to combine diesel particulate filter (DPF) and selective catalytic reduction (SCR) technologies.

Bioavailable soluble and particle bound metals can do harm to human health. Metal based catalysts have been used in the after-treatment devices to reduce the emissions. Recent studies suggest elevated ambient levels of platinum group elements (PGE) since introduction of three-way catalytic converters for gasoline vehicles. There is a parallel concern metals will be released from the after-treatment devices from heavy-duty (HD) vehicles. In the current work we present a comprehensive profile of metals emissions from several vehicles and after-treatment devices evaluated at the California Air Resources Board's Heavy-duty Diesel Emissions Test Laboratory located in Los Angeles, CA.

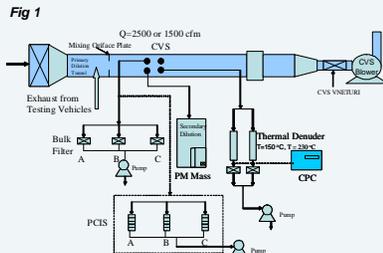


Figure 1. Experimental Setup. PM Samples collected by bulk filter A, B and C were analyzed for total trace elements, ions and EC/OC, respectively. PCIS A was analyzed for size-resolved total and water-soluble elements. Samples collected by PCIS B and C were archived for further analysis.

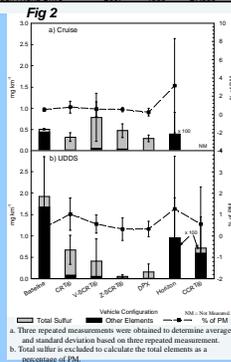
Experimental

Four heavy duty diesel vehicles in seven configurations include various types of diesel particulate filters (DPF): catalyzed and un-catalyzed, passive and active DPFs; prototype vanadium- or zeolite-based selective catalytic reduction (SCR) systems, and a hybrid diesel electric drive vehicle fitted with a catalyzed DPF. Three cycles were tested, 50mph Cruise, UDDS, and Idic. Not all vehicles were tested on all three cycles. ULSD was used. Fuel and engine oil were collected for chemical analysis.



Vehicle				Engine				Aftertreatment (AT)						
Vehicle Number	Make	Model	Year	Miles	GVWR (lb)	Tested Wt (lb)	Model	Year	Size (L)	Rebuild / Recover	Make and type	Description	Miles on AT	
Veh#1, Baseline	Kenworth	T800B	1998	374000	28,640	80,000	53,320	Cummins M11, refashed	1998	11	no	JM CRT®	DOC + DPF	64,000
Veh#1, CRT®	Kenworth	T800B	1998	374000	28,640	80,000	53,320	Cummins M11, refashed	1998	11	no	JM CRT®	CRT + Vanadium SCR	50,000
Veh#1, V-SCRT®	Kenworth	T800B	1998	360000	28,640	80,000	53,320	Cummins M11, refashed	1998	11	no	JM SCRT®	CRT + Zeolite SCR	0 on SCR, 80,000 on CRT
Veh#1, Z-SCRT®	Kenworth	T800B	1998	360000	28,640	80,000	53,320	Cummins M11, refashed	1998	11	no	Engelhard DPX	Catalyzed DPF	30,000
Veh#2, DPX	International	4900	1999	40,000	15,300	27,500	20,920	International DT466E	1999	7.6	no	Clearaire Horizon, EGR	Uncatalyzed DPF	31,000
Veh#3, Horizon	Thompson	SafetyLiner	1988	325000	22,200	36,200	20,720	Cummins	2003	5.9	RPW at 275,000mi	JM CCRT®	Catalyzed DPF	1000
Veh#4, CCRT®	Clearaire	DPX with Allison Hybrid Drive	2007	1000	27,500	39,400	30,400	Cummins	2006	5.9	no	Clearaire DPX	Catalyzed DPF	1000

Figure 2. Emission Rates of Total Trace Elements. The baseline vehicle emitted overall total trace elements (excluding sulfur) of 0.44 ± 0.02 mg km⁻¹ and 1.68 ± 0.87 mg km⁻¹ at cruise and UDDS cycle, respectively. The overall emission rates of total trace elements from retrofit vehicles (excluding CCRT and Horizon) varied from 0.01 ± 0.01 mg km⁻¹ (DPX at UDDS cycle) to 0.09 ± 0.06 mg km⁻¹ (CRT at UDDS cycle). Trace elements as a percentage of PM



for the retrofit vehicles are comparable to the baseline vehicle (less than 1%), which could be due to the similar trend of reductions of PM and trace elements. The retrofit vehicles significantly reduce the emissions of the overall total trace elements (>85% and 95% for cruise and UDDS, respectively) when compared to the baseline.

Figure 3 - Emissions Rates of Selected Elements.

The vehicles with only a DPF (i.e. CRT®, DPX, Horizon and CCRT®) were efficient at reducing almost all the metals except for Pt emissions during both the cruise and UDDS cycles. The DPF+SCR (SCRT®s) also showed substantial reduction of most metals. V was statistically significant for the V-SCRT® during both cruise (561.6 ± 265.4 ng km⁻¹) and UDDS (209.4 ± 120.0 ng km⁻¹) cycles. The presence of Ti and V emissions from the V-SCRT® indicates the possible release of catalyst washcoat from the SCR system during high temperature event (cruise cycle and UDDS at high engine load). We also observed elevated platinum emission rates for the catalyzed retrofit vehicles (1.1 ± 0.6 ng km⁻¹ to 4.2 ± 3.6 ng km⁻¹) as compared to the baseline (0.3 ± 0.1 ng km⁻¹) during the cruise cycles. However, those values are still much lower than the emission rates by three-way catalytic converter (TWCs) equipped gasoline vehicles (10-100 ng km⁻¹)

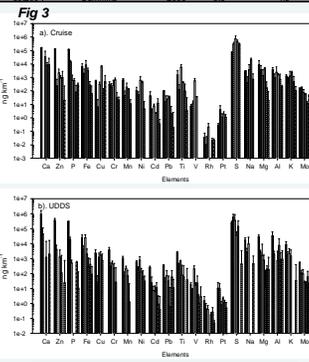
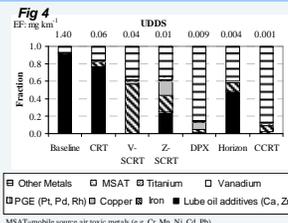
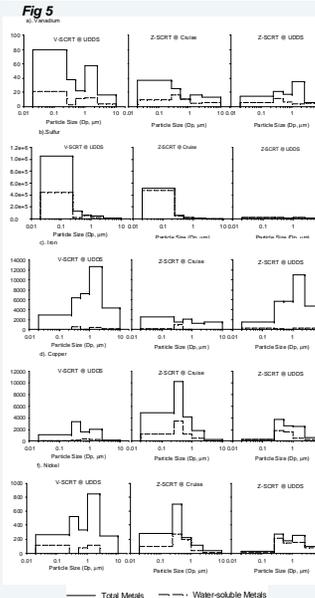


Figure 4 - Fraction of Metal Compounds. The baseline vehicle showed consistent and similar fractions of metals at both cruise and the UDDS cycle with Ca and Zn dominating. The distribution of the fraction of metals is substantially different for all retrofit technologies, when the cruise and UDDS results are compared. While not shown here the cycle type plays a significant role in the profile of metals emitted by a diesel technology.



MSAT-mobile source air toxic metals (e.g. Cr, Mn, Ni, Cd, Pb)

Figure 5 - Size-resolved Total and Water-soluble Metals. The vanadium results clearly show a bimodal distribution, one maxima in the smaller size range (Dp<0.25µm) and the other peak is around 1.0 to 2.5 µm. Fe was present mainly in the fine particle range (1-2.5 µm). Copper predominates at the particle ranges of 0.25-0.50 µm, suggesting that Cu was real lease from the system. Ni showed a bi-modal distribution for both SCRTs at UDDS cycle.



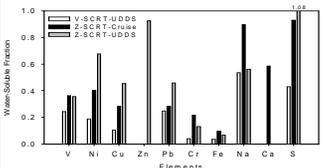
See also at AAAR

9A.1 Thursday 9:20 am: Chemical Speciation of PM Emissions from Heavy-Duty Diesel Vehicles Equipped with DPF and SCR Retrofits.

10A.3 Thursday 11:15 am: Toxicity of Particulate Matter from Heavy-Duty Vehicles Retrofitted with Emission Control Technologies.

10A.5 Thursday 10:45 am: Ionic and Organic Species in PM Emissions from Advanced Technology Heavy-Duty Diesel Vehicles

Figure 6 - Water-soluble Fraction of Metals. The inter-element trends in the water-soluble fraction are generally consistent, even across different elemental groups such as the alkaline-earth and transition metals. In general most of the metals emitted from the Z-SCRT® are more soluble than those emitted from the V-SCRT®.



Summary

All the DPFs significantly reduced emissions of total trace elements (>85%). Catalyst metals were seen released from the after-treatment devices at low levels. For example, the vanadium-based DPF+SCR vehicle during cruise operation exhibited higher emission rates of vanadium (562 ± 265 ng km⁻¹) and titanium (5841 ± 3050 ng km⁻¹), suggesting the possible release of SCR washcoat (V₂O₅/TiO₂) from the catalyst under high temperature conditions. During cruise cycle, vehicles with catalyzed aftertreatment emitted higher levels of platinum (1.1 ± 0.6 ng km⁻¹ to 4.2 ± 3.6 ng km⁻¹) when compared to the baseline (0.3 ± 0.1 ng km⁻¹). For the DPF+SCR systems, Fe-zeolite-based system showed a higher water-soluble fraction of the emissions of most metals than vanadium based system.

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Reference

1. Hu, S., Herner, J. D., Shafer, M., Robertson, W., Dwyer, H., Collins, J., Huai, T., Schauer, J. J., and Ayala, A. (2008). Metals emitted from heavy-duty diesel vehicles equipped with advanced PM and NOx emission controls. Atmospheric Environment Submitted.

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