1-7990255

MRL 87-181(OP,J)C.2

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MRL 87-181 (OP,J) MARCH, 1987.

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MUTAGEN LEVELS IN THE TREATED AND UNTREATED EXHAUST OF DIESEL ENGINES IN COMMON USE IN UNDERGROUND MINING

By

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ABSTRACT

The concentrations of mutagens (mutagen densities) produced by heavy-duty diesel engines in use in underground mines were measured. The aim was to establish the relationship of these power units to the light-duty engines used in recent animal exposure studies. Samples were collected in an emission lab at approximately 16:1 dilution, and underground during actual and simulated mining operations at 50 to 235:1 dilution. There was quite good agreement between the mutagen densities measured in these two divergent sampling regimens. The second part of this research program compared lab and underground levels of mutagens for a variety of current and proposed emission control hardware. Again, there was good agreement between mutagen densities underground and in the lab. Oxidation catalysts in widespread use underground were found to increase densities from 8 (monoliths) to 150 (pelletted units) times untreated levels. There was a wide variation, however, in the laboratory results for the pelletted catalysts, with only one sample reaching the consistently high underground levels (due apparently to storage/release of mutagens that readily occurred in underground operating cycles, but could rarely be duplicated in the lab). Both of the new emissions control options tested - a metal-mesh catalyzed trap and a ceramic wall-flow filter - yielded concentrations of mutagens significantly below the best treatment devices in current use. The 1200-hr mine trial of the ceramic filter (sampled at 200 hr intervals), however, produced specific activities covering a very wide range - 0.013 to 1.51 revertants/μg - suggesting that a storage/release phenomenon may also have occurred here.

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KEYWORDS: diesel, emission control, catalyst, filter, mutagen.

INTRODUCTION

The exhaust products of diesel engines used in underground mining and tunnelling are typically diluted about 50 to 100 fold with fresh air to reduce their impact on the health of underground workers. This results in exposure levels (Dainty, Gangal et al, 1986) several orders of magnitude above those predicted for the urban environment at even the worst case scenario of a 25% penetration of the diesel into the car and light truck market. Thus, the indirect-injection (IDI) diesel with its inherently low levels of exhaust soot, CO_2, hydrocarbons, and NO_x has been the predominant engine type chosen for underground service. Since the favourable IDI emission characteristics result from a two-stage combustion process (initiation in the fuel-rich pre-chamber, followed by the highly turbulent combustion of the remaining fuel charge in the main chamber above the piston), production of minor exhaust constituents is quite time dependant. Thus the concentration and character of these materials in the exhaust of the heavy-duty IDI diesels can be expected to be somewhat different from their higher revving light-duty cousins used in cars and light trucks. Further, the direct-injection (DI) heavy-duty diesels favoured in heavy truck applications because of their inherent fuel efficiency, utilize single-stage combustion of the atomized fuel sprayed directly into the main chamber above the piston. Since the minor constituents in this case are largely produced by combustion quenching in proximity to the piston and cylinder walls, in contrast to the soot-stripping reactions of the second-stage of the IDI system, they are also likely to be of considerably different character.

Because the recent surge in diesel health effects research was stimulated by an anticipated worsening of urban diesel contamination (currently largely from heavy trucks and buses) by the entry of a significant light-duty component, it was considered unlikely that many studies would involve the heavy-duty IDI engine. In fact, only one of the nine recent diesel animal exposure studies (Lewis et al, 1986) utilized an IDI heavy-duty engine, and was directed to mining concerns. Even that one has limited relevance to most hard-rock mining operations, since the exhaust was water-scrubbed before the exposure chambers (mandatory for coal mines, but used infrequently elsewhere).

Most underground diesels have been equipped with catalytic purifiers (larger versions of the platinum impregnated pellets or monoliths used for automotive emission control since the mid-70s) to reduce CO, hydrocarbons, and odours. When soot and the substances absorbed there-on were identified as the major health impacting constituents of diesel exhaust, a three-government collaborative research program (Dainty, Mitchell, et al 1986) was initiated to develop soot-capturing replacements for the catalytic purifiers. The work summarized here represents the mutagenic component of this research, undertaken to permit screening comparisons of new and existing hardware, as suggested by the "Consensus Report" of the Stockholm Conference (Holmberg and Ahlborg, 1983). The baseline (no exhaust treatment) portions of this collaborative program also provided data on the mutagenic potential of the heavy-duty IDI engines, which permits risk comparisons with the light-duty IDI and heavy-duty DI engines of the animal studies, as endorsed by McClellan (1986).

METHODS

Dilute laboratory samples were collected in a 10 cm diameter tube, using exhaust back-pressure to feed a raw exhaust aliquot to the open mouth of the tube, Figure 1. Fresh air suction and sample collection were provided by a standard High-Volume sampler at the opposite end of the tube. The dilution ratio was maintained at about 16:1 by continuous analysis of raw (exhaust) and dilute CO_2 (a value which was previously established, Lawson et al, 1981, to yield consistent mutagenic response). The tube was maintained at 48 to 51°C by means of electric heating tapes.

Since the Load-Haul-Dump (LHD) mining vehicle (a low-profile diesel-powered bucket loader) contributes the major portion of diesel fume contamination in hard rock mines, underground sampling was confined to real or simulated (ore carried back-and-forth between two piles) LHD operations. Samples were obtained with standard High-Volume samplers placed on empty drums. Undiluted CO_2 (or particulate soluble fraction) measured during dynamometer simulations of mine operating cycles, were divided by mine CO_2 (or soluble fraction) levels to establish underground dilution ratios. These varied from 50:1 to 235:1, depending on the amount of fresh air which was supplied to the mine sections.

The High-Volume filters obtained in the laboratory and underground were Soxhlet extracted with dichloromethane, evaporated to dryness under nitrogen, re-dissolved in dimethylsulphoxide, and assayed for mutagenic activity according to the plate incorporation assay procedures recommended by Ames et al (1975). Early samples were tested "with" and "without" S9. The "with S9" results were invariably slightly less active than "without", so "with S9" tests were not continued. All of the results reported are "without S9". In addition, there was often insufficient material available for multistrain assays. It was impossible to estimate the quantity of diesel soot solubles (SOF) which had been obtained in advance of the extraction, because of varying quantities of ore dust, drill oil, lubricating oil, etc. which were also collected on the filters. Other details of the mutagen test procedures are summarized in Appendix I.

RESULTS AND DISCUSSIONS

UNTREATED EXHAUST

Laboratory and underground specific activities (SAs) of the extracts of samples from the exhaust of (or collected in the vicinity of) six and eight cylinder Deutz 714 series air-cooled heavy-duty IDI engines without exhaust treatment hardware are presented in Figure 2. The fourth TA98 value at 2200 rpm, 7/8 load, illustrates a condition (under controlled laboratory operations) which was normal for the underground samples. During this test, excess lubricating oil appeared in the exhaust due to partial piston-ring failure in the engine. This diluted the mutagenically active fraction, resulting in a specific activity which was less than one-third of the other laboratory values. Underground, other non-mutagenic solubles such as drill-oil mist (from the pneumatic rock-drills), vaporized oil from external engine leaks, etc., are always present in unpredictable quantities. As a result, the SAs of laboratory and underground samples are not readily compared. The increased quantity of SOF, however, directly compensates for the reduction in SA, so mutagen densities, revertants per cubic meter, adjusted to an undiluted exhaust basis (SA x SOF x dilution ratio) provide a direct basis of comparison of laboratory with underground values, Figure 3.

Stewart et al's (1976) study of underground LHD cycles suggests that the average emissions of a cycle may be approximated by 2/3 the 2200 rpm, 7/8 load value plus 1/3 the 1600 rpm, full load level. This yields the calculated LHD cycle averages of Figure 2, which are quite close to the mine cycle averages for all three salmonella species.

MONOLITHIC PURIFIERS

Figure 4 compares laboratory and underground mutagen densities for Deutz 714 series engines (lab and mine) and Caterpillar engines (mine) equipped with monolithic catalytic exhaust purifiers. (SAs for the monoliths, and the other hardware tested are listed in the Tables of Appendix II.) Lab and mine densities are quite close, with the TA98 densities averaging at least 3½ times those with no exhaust treatment. The fact that the densities of TA98/1,8 DNP_6 and TA98NR/1,8DNP_6 remained relatively close to untreated levels, plus the presence of significant quantities of NO_x (and an oxygen deficit) in diesel exhaust suggests that the increase results from nitration of the SOF as it passes through the parallel channels in the catalyst substrate.

PELLETTED PURIFIERS

Underground samples collected in the vicinity of Deutz 714 series diesels equipped with pelletted purifiers (containing platinum impregnated alumina spheres) invariably yielded very high TA98 mutagen densities, Figure 5. The limited data with the nitroreductase deficient strains suggests mutagen generating reactions which are similar in character but much more extensive than with the monolith. This is entirely consistent with the pelletted unit's larger volume and the resultant longer residence time of the exhaust constituents in the catalyst container.

The third laboratory sample of exhaust solubles from a pelletted purifier equipped Deutz F6L714 yielded a mutagen density (424,000 rev/m^3) similar to those measured underground, thus providing solid evidence that treated diesel exhaust was the source of the 370,000 to 1,800,000 rev/m^3 in the mine. The other nine lab samples exhibited widely varying mutagen densities in spite of attempts to favour regular generation and release of mutagens by modifying the operating cycle and sampling conditions.

A subsequent attempt to collect additional underground samples with high activity only produced levels which were close to the baseline values. The mine layout for this trial, however, included a 20% gradient in the haulage way which resulted in a considerably heavier average engine load. This work, and the laboratory findings, suggest mutagen generation and storage at lighter engine loadings, with periodic random release when higher loads are reached.

SOOT TRAPS

A catalyst impregnated metal-mesh soot-trap was the first of the new soot-reduction options tested. The underground trial of this device utilized a simulated LHD operation, with ore carried back-and-forth between piles by an F8L714 engined machine. Figure 6 illustrates the excellent agreement between underground and laboratory trials achieved when the normal variations of operating cycle in a producing mine are absent. Although the SAs were quite close to baseline, suggesting that there was minimal production of additional mutagenic material, the reduction in the quantity of SOF yielded mutagen densities which were one-third of untreated levels.

FILTERS

Figure 7 presents the variation in mutagen density for six samples collected at 200 hour intervals downstream from a production diesel equipped with a wall-flow ceramic soot filter. The three lowest values are consistent with laboratory trials of catalyzed ceramic filters, while the larger values could have come from other sources of mutagenic material in the mine. The possibility that larger quantities of mutagens are periodically released from the filter, however, cannot be discounted. The proportional response of the nitroreductase-deficient strains, sample 1, reinforces the suspicion that these transient increases are primarily diesel in origin.

CONCLUSIONS

The laboratory to underground comparisons have shown that appropriate concentrations of "real-world" mutagens can be produced in laboratory simulations, and can be retrieved from samples obtained at 16:1 dilution.

Most of the heavy-duty IDI diesel samples without exhaust treatment suggest a mutagen concentration of less than 15,000 rev/m^3 on an undiluted exhaust basis, in contrast to the 40,000 to 150,000 rev/m^3 for the light-duty engines of the animal exposure studies. (A fairly wide spectrum of levels may be derived from the data in the literature - one set yields 13,000 rev/m^3 for the 5.7 litre Oldsmobile FTP - but most are in the quoted range.) Since TA98 activity has been shown to overpredict the health impact from diesel exposure (Albert and Chen, 1986), this work suggests that the heavy-duty IDI diesels used underground likely present a slightly reduced impact relative to the light-duty diesels of the animal exposure studies (at similar exposure levels).

Add-on emission control hardware has been shown to sometimes substantially increase the mutagenic activity of the effluent diesel exhaust. The unchanging response of the 1,8DNP$_6$ strains (treated to untreated) suggests that this may be due to increased nitration during transient storage on a substrate, trap, or filter.

Collection of laboratory samples for ranking alternate add-on emission control hardware by biological end-point evidently requires careful selection of engine and sampling parameters to avoid missing transient release of highly active materials.

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APPENDIX I

Salmonella tester strain TA98 was obtained from Dr. B.N. Ames, University of California, Berkely, CA. The nitroreductase deficient strains were obtained from Dr. H.S. Rosenkranz, Case Western Reserve University, Cleveland, Ohio. Spontaneous revertant levels from the four salmonella strains (± S.D.) were: TA98, 32(± 10); TA98NR, 25(± 11); TA98/1,8DNP$_6$, 18(± 9); TA98NR/1,8DNP$_6$, 22(± 13). Twelve to fifteen doses per sample were used in the early work, and for trials (such as the pelletted purifier) where toxicity and response levels were unpredictable, (60% of the total overall). Seven to ten doses were used in 30% of the work, and the remaining 10% was restricted to six doses by sample availability. Sixty percent of the assays were triplicates, and thirty-one percent duplicates, with the remaining 9%, single assays for rechecks and samples with insufficient material. Specific activities (revertants/μg) were calculated as the slopes of a least squares fit to the linear portion of the dose-response curve. In order to be considered positive, a response was required to be at least 2½ times the spontaneous level, with at least three well defined points on the linear portion of the curve.

APPENDIX II

As noted, specific activities of the laboratory and underground samples are not readily compared because variable quantities of non-diesel solubles are included underground. The laboratory samples do not generally contain non-diesel material, so the specific activities recorded in Table 1 may be compared to others published in the literature. The underground specific activities are presented in Table 2 as an indication of the level of variation in the underground results.

Table 1: Specific Activities, Revertants/μg, of Diesel Soot Extract - Laboratory Samples at 16:1 Dilution.

ENGINE	EMISSION CONTROL	SPEED (RPM) /LOAD OR CYCLE	Specific Activity Revertants/μg			
			TA98	TA98NR	TA98/1,8DNP$_6$	TA98NR/1,8DNP$_6$
DEUTZ F6L714	NONE	2200/ 7/8	1.60	0.48	0.10	0.10
			0.98	0.58	0.22	0.06
			0.89			
			0.30			
		1600/FULL	0.43			
			0.41			
			0.27			
DEUTZ F6L912W	NONE	2200/ 7/8	0.72	0.33		
			0.51	NEG.		
		LHD	0.41	NEG.		
			0.36	NEG.		
CATERPILLAR 3304NA	NONE	2200/ 7/8	1.35	0.81		
			1.24	0.60		
DETROIT DIESEL	NONE	2100/ 7/8	NEG.			
			NEG.			
DEUTZ F6L714	MONOLITHIC CATALYST	2200/ 7/8	4.01			
			7.81			
			0.93			
			2.28			
DEUTZ F6L714	PELLETTED CATALYST	2200/ 7/8	0.75	0.18	0.08	0.01
			0.41			
			50.8	39.1		
			13.5	9.2		
			0.54			
			3.20		0.12	0.10
			11.1	1.17		
			1.85	5.6		
			1.14			
			8.8	0.49		
				4.8		
DEUTZ F6L714	METAL-MESH SOOT-TRAP	LIGHT LHD	1.3*	NEG.	NEG.	
		HEAVY LHD	0.75	0.40	0.04	

* CALCULATED TIME WEIGHTED AVERAGE

Table 2: Specific Activities, Revertants/μg, of High Volume Filter Extracts, Collected in the Vicinity of Underground Diesel LHD Operations

Engine	Emission Control	Mine Type	Dilution Ratio	Specific Activity, Revertants/μg			
				TA98	TA98NR	TA98/ 1,8DNP$_6$	TA98NR/ 1,8DNP$_6$
DEUTZ F8L714	NONE	NICKEL, EXPERIMENT	55:1	0.29	0.09	0.08	NEG.
			97:1	0.19	0.10	NEG.	NEG.
			80:1	0.20	NEG.	NEG.	NEG.
			60:1	0.19		NEG.	NEG.
		NICKEL, PRODUCTION	97:1	0.25			
			55:1	0.18			
			75:1	0.15	0.11	NEG.	
			75:1	0.11	NEG.	NEG.	
DEUTZ F6L714	NONE	NICKEL, EXPERIMENT	97:1	0.20	0.07	NEG.	
			93:1	0.10	NEG.	NEG.	
			74:1	0.20			
			69:1	0.13			
DETROIT DIESEL	NONE	URANIUM PRODUCTION	-	NEG.			
				NEG.			
DEUTZ F8L714	MONOLITHIC CATALYST	NICKEL PRODUCTION	212:1	2.6			
				3.8			
CATERPILLAR 3304NA	MONOLITHIC CATALYST	SALT, PRODUCTION	-	NEG.			
				NEG.			
DEUTZ F8L714	MONOLITHIC CATALYST	NICKEL, PRODUCTION	100:1*	0.41	0.19	NEG.	
				0.40	0.20	NEG.	
DEUTZ F8L714	PELLETTED CATALYST	NICKEL, PRODUCTION	134:1	66.			
			233:1	210.			
		NICKEL, PRODUCTION	97:1	57.			
				39.			
		NICKEL, PRODUCTION	68:1	79.			
			55:1	88.	15.5	0.30	0.10
DEUTZ F8L714	METAL-MESH SOOT TRAP	NICKEL, PRODUCTION	80:1	0.22	NEG.	NEG.	
			80:1	0.17	NEG.	NEG.	
			58:1	0.21	0.09	NEG.	
			62:1	0.20	0.04	NEG.	
DEUTZ F10L714	CERAMIC FILTER	NICKEL, PRODUCTION	84:1	0.64	0.41	0.04	
			51:1	0.13	0.06	NEG.	
			100:1*	0.013			
			100:1*	0.26			
			100:1*	0.17			
			100:1*	1.51			

* ESTIMATED VALUE

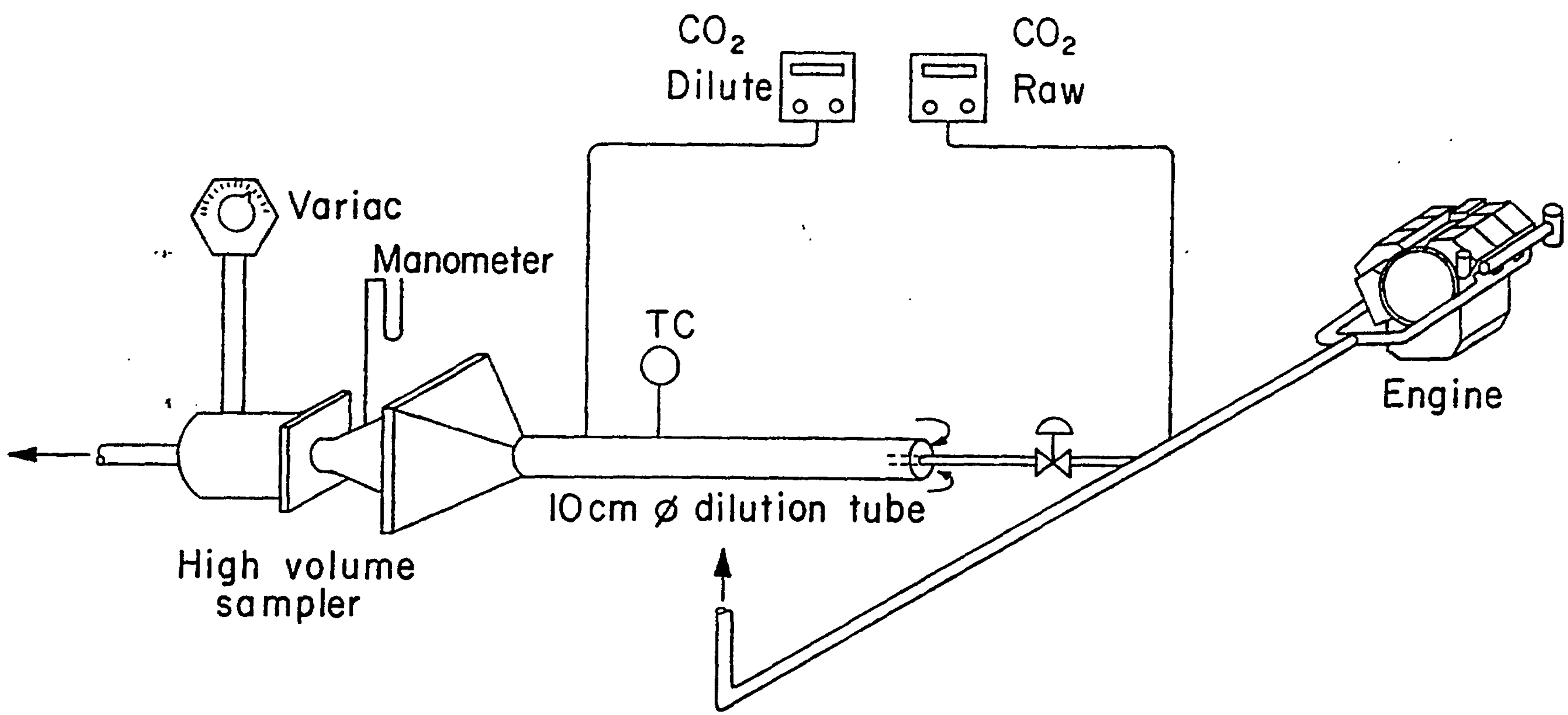

Fig 1 Dilution Tube for Laboratory Sampling

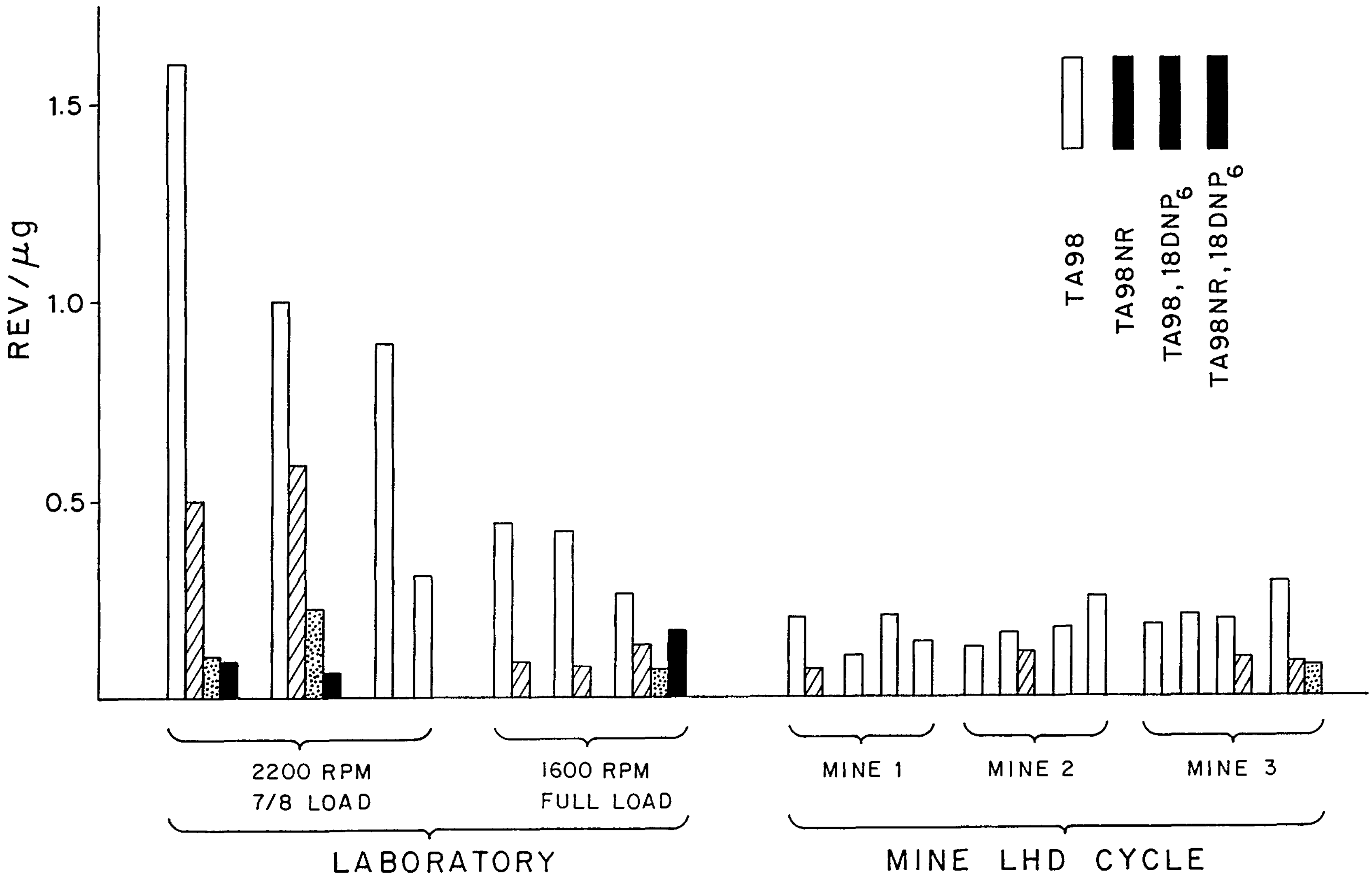

Fig. 2 Specific Activities, Revertants/μg, Deutz 714 Series Engines Without Exhaust Treatment

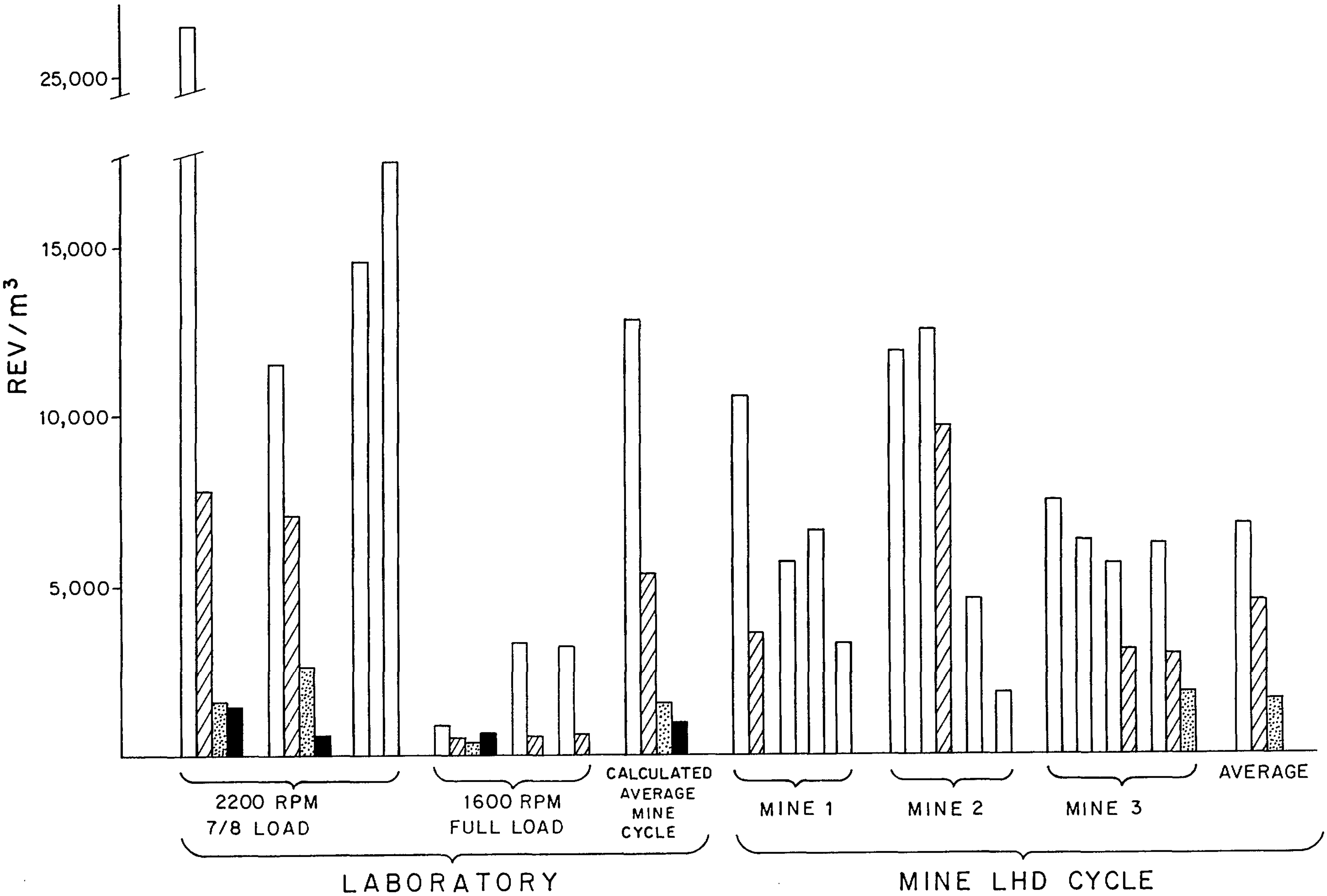

Fig. 3 Mutagen Densities, Revertants/m^3, Undiluted Exhaust Basis, Deutz 714 Series Engines without Exhaust Treatment

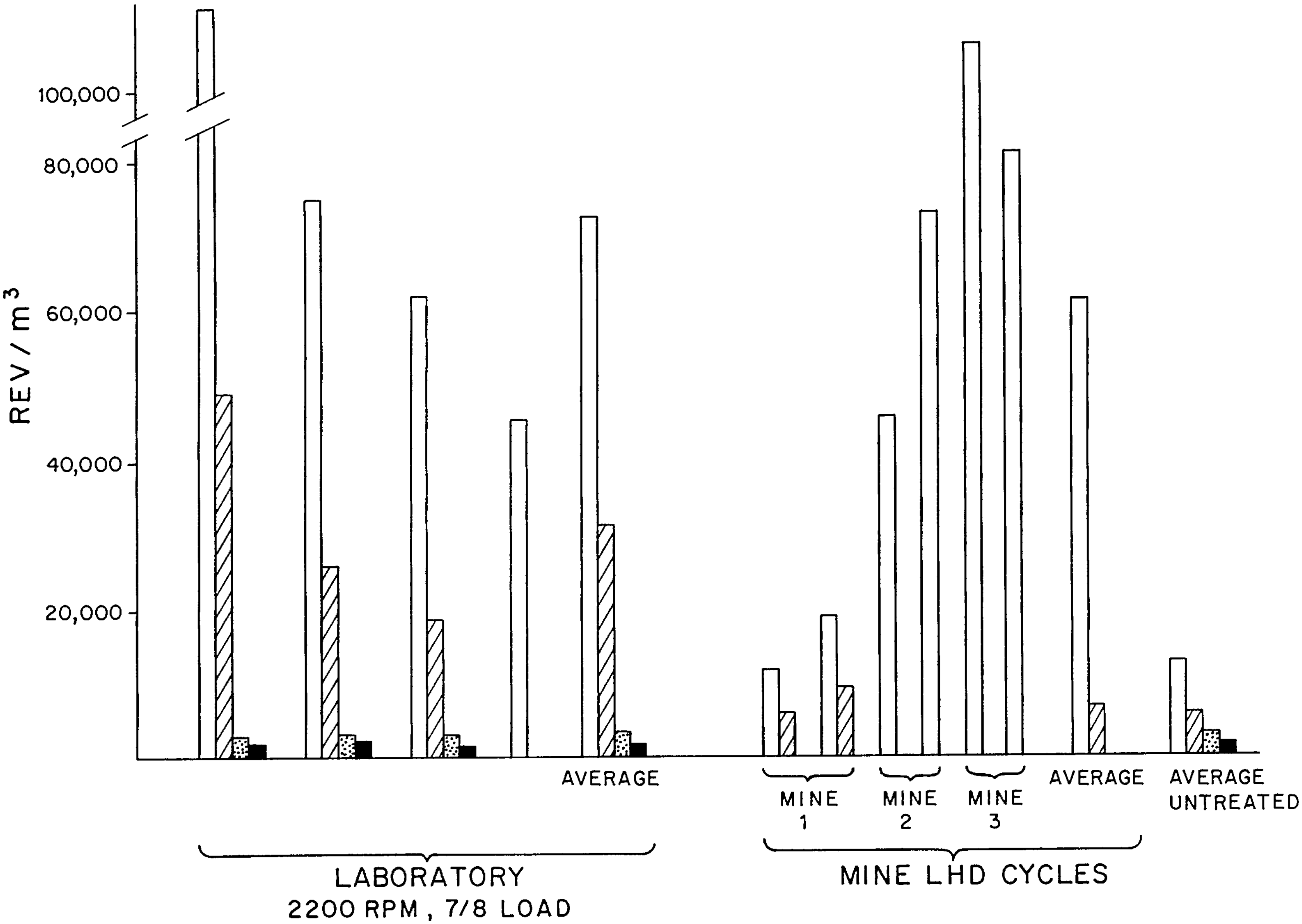

Fig. 4 Mutagen Densities, Revertants/m³, Undiluted Exhaust Basis, Deutz and Caterpillar Engines with Monolithic Catalytic Exhaust Purifiers

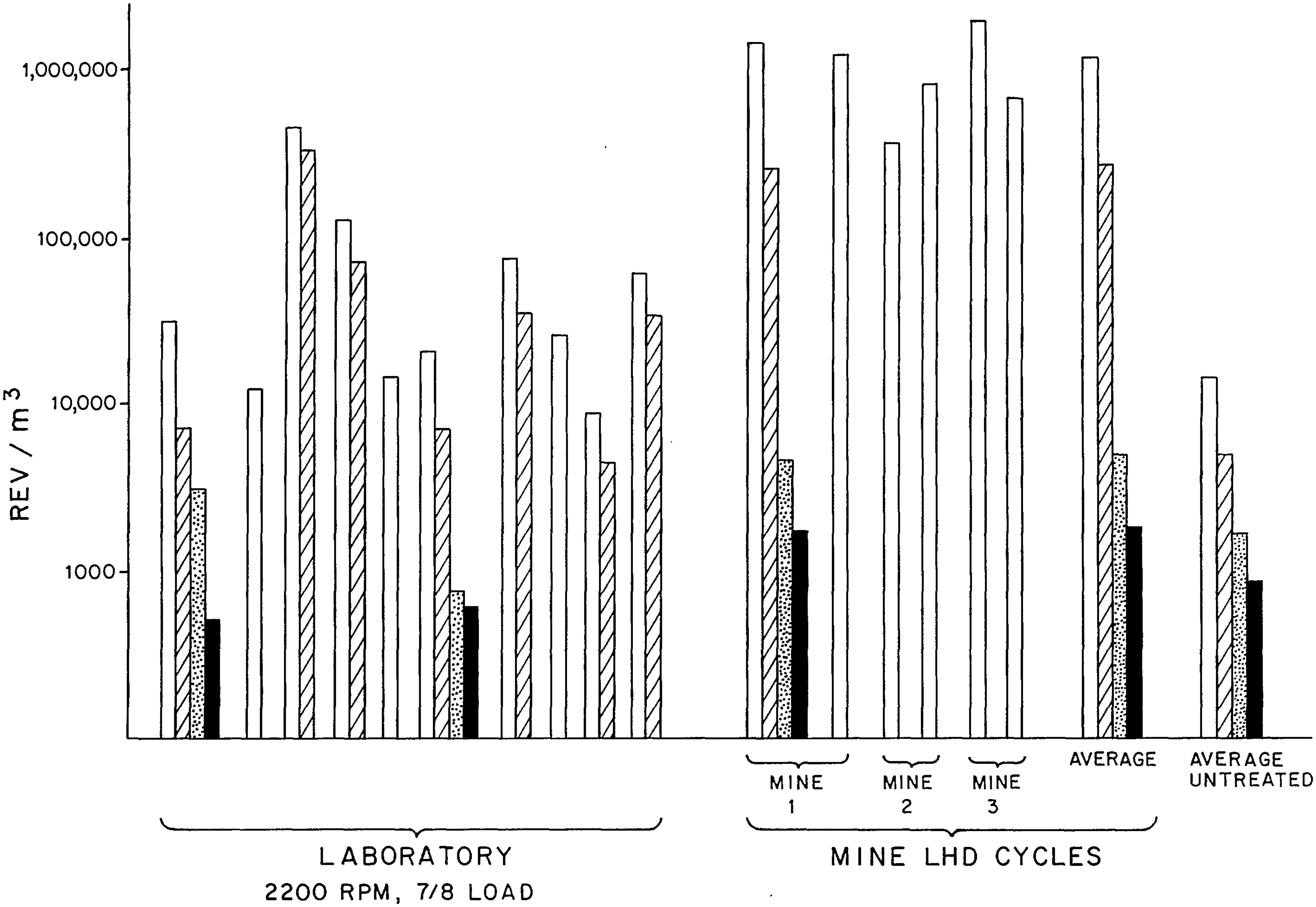

Fig. 5 Mutagen Densities, Revertants m/^{3}, Undiluted Exhaust Basis, Deutz 714 Series Engines with Pelletted Catalytic Exhaust Purifiers

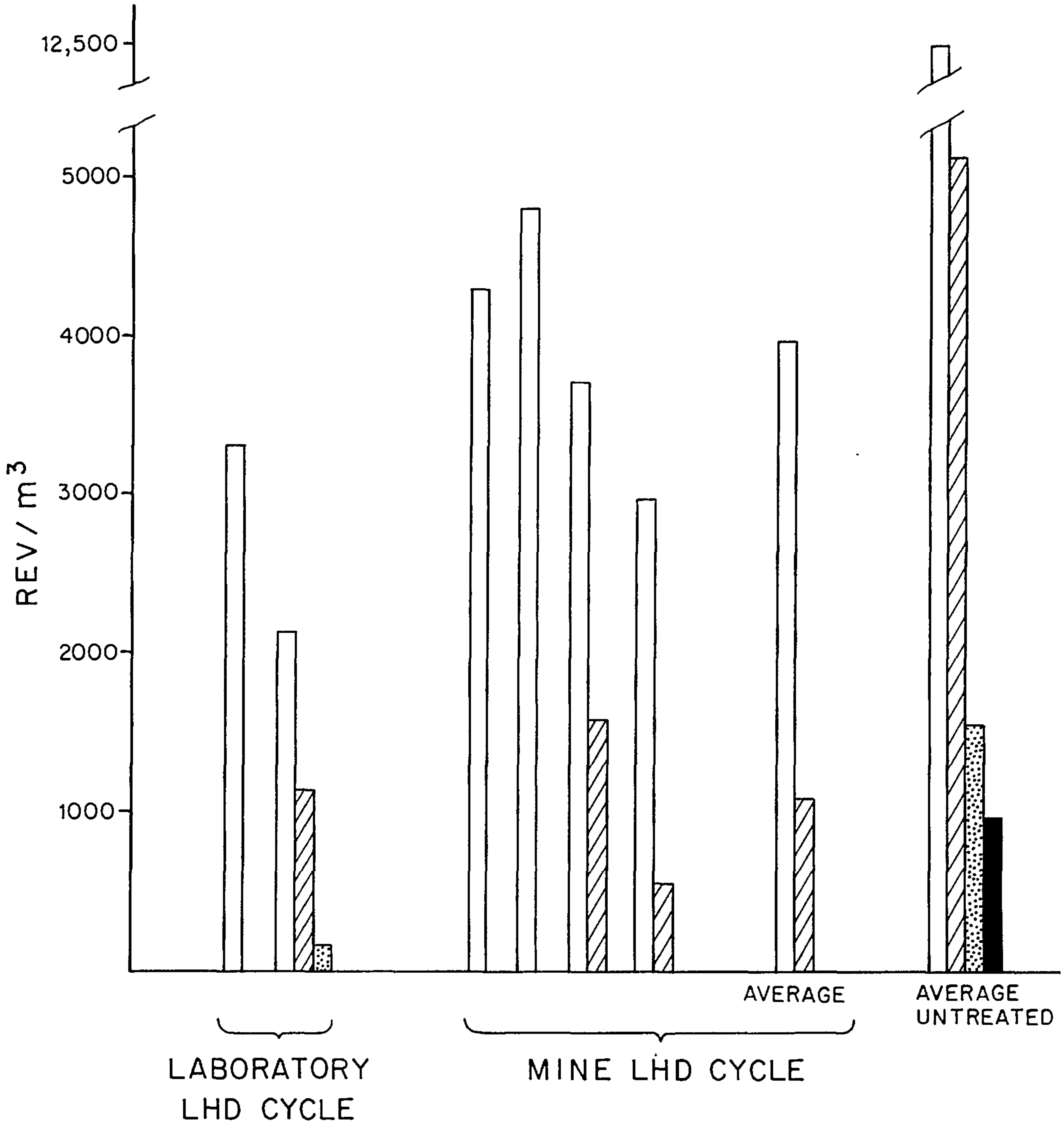

Fig. 6 Mutagen Densities, Revertants/m^3, Undiluted Exhaust Basis, Deutz 714 Series Engines with a Catalytic-Trap-Oxidizer