



POLY NUCLEAR AROMATIC HYDROCARBON LEVELS IN CANADIAN UNDERGROUND MINES

J.P. Mogan and E.D. Dainty

Research Scientists, Canadian Explosive Atmospheres Laboratory, Mining Research  
Laboratories CANMET, Energy, Mines, and Resources

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c/o 555 Booth Street  
Ottawa, Ontario  
K1A 0G1

Tel: (613) 996-6285

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J.P. Mogan and E.D. Dainty\*

**SUMMARY**

Polynuclear aromatic hydrocarbons (PAH), the ubiquitous combustion generated components of urban air contamination, have been suspected as potential health threatening constituents in diesel exhaust. To determine if the PAH levels in dieselized mines were likely to be hazardous, an urban atmospheric sampling and assay protocol was adapted for underground use.

Samples were collected in nickel, salt, and uranium mines in the vicinity of diesel loaders and trucks. Vehicles with and without exhaust treatment hardware were included, to evaluate the PAH capture performance of these devices.

PAH concentrations in all of the mines tested were found to be at levels at which "the health impact, as far as lung cancer is concerned, is likely to be small".

Oxidation catalysts appeared to remove 50 to 80% of the PAH, dependent on type, while soot traps and filters collected in excess of 75%. The companion mutagen study, however, indicated that part of the PAH reduction observed when oxidation catalysts were fitted likely resulted from nitration rather than oxidation. The consequent increase in mutagen concentration may thus offset the potential benefit of PAH reduction.

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**KEYWORDS:** diesels, mining, polynuclear aromatic hydrocarbons, emission control

\* Research Scientists, Canadian Explosive Atmospheres Laboratory, Mining Research Laboratories, CANMET, Energy, Mines and Resources, Canada, Ottawa

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## INTRODUCTION

Polynuclear aromatic hydrocarbons (PAH) are fluorescent, high-boiling compounds, generally containing three to seven linked benzene rings. Many plants and animals synthesize small amounts of these substances, but the bulk of the world's inventory is a by-product of fossil fuel and biomass combustion. They are normally found associated with tars and soot, since the larger fraction of most of these compounds condenses when the combustion products are cooled. They have frequently been suspected as the causative agents in the development of occupational disease, beginning with Pott's description of chimney sweep's cancer in 1775. Indeed, as early as 1915, Yamagiwa and Itchikawa had induced skin cancer in rabbits by painting with coal tar, and Passey in 1922 produced malignancy in mice by painting with ether extracts of soot. By 1933, Cook, had isolated the potent carcinogen Benzo(a)Pyrene (BaP) from coal tar distillate.

Later, an elevated incidence of lung cancer in urban (as compared to rural) smokers led to the conjecture that urban air contamination (largely due to uncontrolled combustion of coal for domestic heating), might be a contributing factor. Accumulating evidence of excess cancer in workers exposed to coal and petroleum combustion products (roofers, coke-oven workers), additional laboratory evidence (animal) of the carcinogenic potential of extracts of these materials and pure PAHs, and an expanding inventory of PAH species in tars and soot, served to re-inforce the perception that the PAH component of urban particulate might be a contributing cause of the excess lung cancer in urban smokers. As a consequence, increasing attention was devoted to PAH assays of the particulate component of urban atmospheres, beginning with the work of Waller in 1952. Because BaP assay procedures were well established, and this compound seemed to occur in a relatively fixed proportion to other PAH species, BaP came to be regarded as an index of urban PAH contamination. In fact, it was suggested in 1972, by the US Committee on Biological Effects of Atmospheric Pollutants, that an increment of one microgram of BaP per thousand cubic metres of urban air would signal a five percent change in lung cancer incidence.\*

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\* Muir and Verma 1986, and "Polycyclic Aromatic Hydrocarbons", Health and Welfare Canada, 1979 contain complete documentation of the information summarized in the preceding section of the Introduction.

With this long standing background as a suspected (but not proven) primary carcinogen in urban particulate, it was inevitable that absorbed PAHs would be considered to represent a threat to health from one highly visible and widely distributed source - diesel soot. In fact, as late as 1982, Heinrich et al based a discussion of the likelihood of diesel-exhaust-exposed hamsters developing lung cancer solely on the PAH concentrations in the exposure chambers and their relationship to levels in four urban atmospheres. It was this perception that motivated Hakela et al (1981) to begin a survey of PAH levels in dieselized Finnish mines [in response to the discovery of an elevated incidence of lung cancer among underground workers (Standardized Mortality Ratio = 1.45), (Rantanen 1983)], and CANMET to approve funding (in 1978) of an unsolicited proposal to investigate PAH levels in nickel and uranium mines (Westaway 1980).

At the inception of the CANMET program, standardized sampling and assay procedures for the determination of PAH levels in diesel soot had not yet evolved. Bricklemeyer and Spindt (1978) had recently reported the results of the extensive study sponsored by the U.S. Environmental Protection Agency and the Co-ordinating Research Council at the Gulf Research and Development Company Laboratories. They added radiotracer labelled PAHs to dilute diesel exhaust upstream of a sampling filter, and were only able to recover a small fraction of the labelled material from the filter extract and upstream washings. Because of the uncertainty regarding sampling and assay methods, it was decided to base the CANMET program on the urban atmosphere protocol developed by Katz et al (1978). They had determined the PAH levels in "high volume" (HV) samples of urban particulate matter in four Canadian cities (including Sudbury). While it was possible that Katz's protocol might not yield the true levels of urban or underground PAH contamination, it would, at least, provide some measure of the exposure of the miner relative to the urban resident. In fact, the results could be expected to have an inherent conservative bias, since diesel soot with its "popcorn-like" structure resembling activated carbon, would likely have a greater affinity for PAH than mixed urban particulate, and in addition, no photolytic decomposition of PAHs would occur underground.

Subsequently, Schuetzle (1983), in his comprehensive analysis and overview, suggested that PAH losses of the type reported by Bricklemeyer and Spindt probably resulted from vapour phase nitration and oxidation at the 4:1 dilution which they had chosen. Williams and Chock (1980) reported that the BaP content of diesel exhaust increased to a stable maximum (i.e. reaction losses were minimized) when the dilution ratio reached 24:1. Fortunately, later, Kraft et al (1983) selected a diesel exhaust PAH assay technique (for the extensive Volkswagenwerke program) which was quite similar to Katz et al's thin layer chromatographic (TLC) procedure. They found a repeatability of 1 to 5% for the TLC method, and a 9% standard deviation when comparing TLC results to those obtained from glass capillary gas chromatography. They also

compared PAH levels in samples obtained by the total condensate (European) method and the CVS dilution (American) procedure and found a correlation co-efficient of 0.976 (Kraft et al - 1982). Thus it appeared that the mine levels of PAHs (at 50 to 100:1 dilution) which were determined with Katz's methodology would be reasonably close to the actual concentrations, and in addition would establish relationships to levels in urban air-sheds [except for the more volatile 4 ring species, and Benzo(e)Pyrene (BeP), as discussed later].

Micklethwaite (1985), working on a graduate program in tandem with the final phase of the CANMET project, studied PAH collection on 37 mm teflon-coated glass fibre filters using "personal sampler" (PS) pumps at 2 to 4 litres per minute. He reported average PAH specie concentrations from combined absorbant and filter samples of 50 to more than 900 times the levels found in simultaneous "high volume" (HV) filter samples of ambient Sudbury air. Because of this, and a desire to assess "on-board" PAH levels, it was decided to add PS 37 mm filter sampling to the final phase of the CANMET program. To determine if re-volatilization of previously captured PAH was a significant contributor to PS to HV differential, absorbant (resin) samples were collected behind both the PS and HV filters in this last phase of the underground PAH and mutagen assay program.

## METHOD

### Sample Collection

Mine particulate samples were collected on 20 by 25 cm sheets of glass fibre and later Pallflex (teflon-coated glass fibre) filters by means of a standard "high volume" (HV) sampling apparatus of the type which is normally used to collect urban atmospheric contaminants. Samples were obtained in production headings in nickel, salt, and uranium mines, and during two simulated Load-Haul-Dump (LHD) operations in nickel mines. In these simulated operations, ore was carried back-and-forth between two piles, and the normal engine lug-down (which occurs when loading from a draw point) was synthesized by pushing the bucket against the rib. The first experiment (in a non-operating mine), provided samples which were free of non-diesel contaminants (blasting fume, drill mist etc.). The second, aimed at determining the impact of several types of emission control hardware on PAH levels, yielded a number of samples collected under constantly repeated cyclic operation.

HV samplers were placed in various fixed locations downstream or adjacent to the diesel operation, dependant on the mine configuration, and generally about one metre above the floor. The HV samplers processed about 1.5 m<sup>3</sup> of mine air per minute. Sampling was continued until the flow dropped to approximately

80% of its initial value - from 0.3 to 5 hours, dependent on the ore dust level at the site.

In the final phase of the work, multiple on-board samples were collected on 37 mm teflon-coated glass fibre filters along with the fixed point HV samples. Two to four litres per minute of mine air were drawn through these 37 mm filters by means of "personal sampler" (PS) pumps. The sample flow downstream of these filters continued on through 1.2 cm diameter glass tubes containing XAD absorbing resin to trap "pass-through" PAHs which were not retained on the filters. To determine "pass-through" levels for the HV samples, aliquots (20 litres per minute) of the sample which had traversed the HV filters were drawn through a 2.5 cm diameter XAD resin bed, following a protocol for the collection of "pass-through" hydrocarbons which had been developed and validated by the US Environmental Protection Agency (Stump et al. 1982), and the Ford Motor Company (Schuetzle 1983).

#### Sample Preparation

After collection, the 20 by 25 cm filters were placed in individual polyethylene bags and stored in a freezer. They were then cut into one to two cm squares and extracted by sonication in successive washings with benzene. An intermediate methanol washing (which was discarded) helped to remove some non-PAH materials which interfered with the assay. After sonication, the filters were refluxed with benzene in a Soxhlet extractor overnight. The combined extracts and washings were then filtered and evaporated almost to dryness, re-dissolved in dichloromethane and evaporated to dryness under reduced pressure. The dry extracts were again stored in the freezer until the thin-layer-chromatographic (TLC) assay could be carried out.

The seven to fourteen PS 37 mm filters collected simultaneously with one HV filter were combined, and a similar extraction protocol followed. Since the volume of mine air sampled was 1/50 to 1/100 of that sampled with the HV unit, smaller quantities of solvents were used.

PAHs are more easily removed from XAD resin than from filtered diesel soot, so the resin samples were merely extracted with sequential washings of dichloromethane.

#### Assay Procedure

Evaporated extracts from each source (20 x 25 cm filters, 37 mm filters, and resins) were re-dissolved in a small (known) amount of toluene and spotted on 20 x 20 cm aluminum oxide TLC plates. Standards containing representative PAHs from each of the four groups which were to be separated in the first stage were spotted on the edges. The plates were developed with 5% diethylether in pentane until the standards, observed under UV light, indicated that the first

band had travelled 15 cm up the plate (i.e. the bands containing the groups had separated). The aluminum oxide containing each band was then scraped from the plate, the PAHs extracted with dichloromethane, and evaporated to dryness again under reduced pressure. Each dried extract (containing one group) was again dissolved in a small (known) amount of toluene and spotted on to an acetylated cellulose TLC plate. Standards containing at least two PAHs from the group to be assayed were spotted along the edges, and the plates developed with 25% acetone, 50% 1-propanol in aqueous solution. The separation was again monitored by following the migration of the standards with UV light.

The bands containing the individual PAH species were cut from the plate and extracted with de-oxygenated diethyl ether. The extracts were evaporated to dryness and re-dissolved in 3 ml of deoxygenated pentane. The actual quantity of PAH present in each 3 mL sample was determined by comparing emission or excitation (dependant on PAH species) spectra with standards at an appropriate wavelength on a spectrofluorometer (Westaway 1980).

Assay procedures for the PS samples and resins were similar. Not all of these samples exhibited fluorescence at all bands. When this occurred, the aluminum oxide was scraped off, or the plate sectioned in the region where the band should have appeared, and the assay continued as with the HV samples.

## RESULTS AND DISCUSSION

### Sudbury Ambient Air

Seven samples of Sudbury ambient air were collected by "High Volume" (HV) sampler in the winter of 1981-82. The average concentrations of PAH species from these samples may be compared with those of Katz et al (1978), Table 1

TABLE 1 - PAH CONCENTRATIONS IN SUDBURY AMBIENT AIR, ng/m<sup>3</sup>

PAH SPECIES	AVERAGE OF 7 SAMPLES WINTER, 1981-82	AVERAGE OF 2 SAMPLES KATZ ET AL WINTER, 1975-76
Pyrene	8.9	
Fluoranthene	1.4	
Benzo(a)Anthracene	1.2	
Benzo(e)Pyrene	4.4	0.29
Perylene	0.13	0.05
3 Methylcholanthrene	0.32	
Benzo(k)Fluoranthene	0.86	0.23
Benzo(a)Pyrene	0.36	0.39
Benzo(ghi)Perylene	0.72	2.7
Dibenzo(def,mno)Chrysene	0.08	0.03
Dibenzo(ah)Anthracene	1.0	
Naptho(1234,def)Chrysene	1.2	0.16
Benzo(rst)Pentaphene	0.15	0.03

The agreement between the two sets of data is quite reasonable, considering the five year interval, and the fact that the samples were collected at different sites. The CANMET-sponsored values are higher for all species except Benzo(ghi)Perylene (BghiP). The Benzo(e)Pyrene concentration is noticeably above the level which would be predicted from the ratios of the other species<sup>1</sup>.

#### Bare Engine

The average PAH concentrations in 12 nickel mine samples collected in the vicinity of Deutz 714 series engined LHD's which were not equipped with any type of emission control hardware are given in Table 2 (Baldisera et al. 1986, Westaway 1981). Levels measured during simulated LHD cycles in a non-operating mine (Baldisera et al. 1983) are also presented. All of the PAH concentrations measured during the simulation in the non-operating mine were within one standard deviation of the operating mine averages, suggesting that the PAH contributions from non-diesel sources in the operating mines were not large. The fact, however, that all but one of the simulation values were less than the operating mine averages suggests a small but definite non-diesel contribution.

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1. Discussion in the section on "Limitations of the Data".

TABLE 2 - PAH CONCENTRATIONS IN THE VICINITY OF DEUTZ-ENGINED LHDS  
WITHOUT EMISSION CONTROL HARDWARE, ng/m<sup>3</sup>

PAH SPECIES	AVERAGE OF 12 NICKEL MINES SAMPLES	AVERAGE OF 2 SAMPLES FROM A LHD SIMULATION IN A NON-OPERATING MINE
Pyrene	130	101
Fluoranthene	6.1	3.9
Benzo(a)Anthracene	15.1	9.2
Benzo(e)Pyrene	51.1	21.0
Perylene	1.1	0.7
3 Methylcholanthrene	5.6	---
Benzo(k)Fluoranthene	4.3	3.2
Benzo(a)Pyrene	4.3	2.7
Benzo(ghi)Perylene	13.6	5.5
Dibenzo(def,mno)Chrysene	0.8	1.1
Dibenzo(ah)Anthracene	3.6	2.9
Naptho(1234,def)Chrysene	8.5	2.7
Benzo(rst)Pentaphene	1.9	1.9

### Catalytic Purifiers

Most Canadian underground diesels have been fitted with either monolithic or pelleted catalytic purifiers. Table 3 summarizes the average PAH levels from 23 nickel mine samples from Deutz-engined LHDs equipped with monoliths, 9 salt mine samples from Caterpillar-engined loaders with monoliths, 5 uranium mine samples from Detroit-Diesel-engined trucks and LHD's with monoliths, and seven nickel mine samples from Deutz-engined LHD's with pelleted catalysts (Baldisera et al. 1983, Baldisera et al. 1986, Westaway 1980, Westaway 1981, Westaway 1982).

TABLE 3 - PAH LEVELS IN THE VICINITY OF DIESEL EQUIPMENT FITTED WITH CAPALYTIC PURIFIERS, ng/m<sup>3</sup>

PAH SPECIES	DEUTZ-ENGINE LHDs WITH MONOLITHS	CATERPILLAR- ENGINEED LOADERS WITH MONOLITHS	DADD-ENGINEED TRUCKS AND LHDS WITH MONOLITHS	DEUTZ-ENGINEED LHDs WITH PELLETED CATALYSTS	DEUTZ-ENGINEED LHDs WITH NO EMISSION CONTROL HARDWARE
Pyrene	96	248	229	50.8	130
Fluoranthene	8.1	19.3	35.9	5.2	6.1
Benzo(a)Anthracene	7.7	14.6	13.3	4.7	15.1
Benzo(e)Pyrene	24.5	55.3	35.0	6.8	51.5
Perylene	0.4	0.3	0.9	0.1	1.1
3 Methylcholanthrene	---	---	---	---	5.6
Benzo(k)Fluoranthene	2.5	5.2	3.9	0.8	4.3
Benzo(a)Pyrene	1.9	1.2	2.6	0.3	4.3
Benzo(ghi)Perylene	9.1	9.1	9.8	1.6	13.6
Dibenzo(def,mno)Chrysene	0.5	0.5	0.3	0.1	0.8
Dibenzo(ah)Anthracene	9.1	3.5	5.1	0.5	3.6
Naptho(1234,def)Chrysene	6.8	7.5	8.1	2.0	8.5
Benzo(rst)Pentaphene	0.9	1.7	0.8	0.4	1.9

The well-documented oxidation of a large fraction of exhaust carbon monoxide and hydrocarbons by catalytic purifiers suggests that there may be a similar beneficial destruction of PAHs. Comparison of the post-monolith emissions with untreated levels indicates that this does occur. The pelleted units, with their inherently longer retention of soot and exhaust gases because of their larger size, have, as would be expected, seemed to have reduced all PAH species to a greater extent.

Additional HV samples were collected along with many of the PAH assay filters for the companion mutagen study (Mogan et al. 1986). These suggested a four-fold increase in mutagenic activity (to 70,000 revertants per m<sup>3</sup>) with the monoliths, and a five-hundred fold increase with the pelleted units. The decrease in PAH concentration with catalytic purifiers may thus be partly due to nitration and partial oxidation to more mutagenic species, and may be less beneficial than a consideration of the PAH inventory alone suggests.

#### Catalytic Trap Oxidizer

Table 4 presents the average of four samples obtained in a nickel mine experiment (Baldisera et al. 1986) with a Deutz-engined LHD equipped with a catalyzed metal-mesh trap (CTO). Comparison with untreated levels again suggests a considerable reduction in all PAH species. This time, the companion study (Mogan et al. 1986) indicates a reduction in mutagen concentration to 4700 rev./m<sup>3</sup>, suggesting that the PAHs were retained on the trap for a sufficient time for a more complete oxidation, which offset any potential negative impact of nitration.

TABLE 4 - PAH CONCENTRATIONS LEAVING THE STOPE DURING SIMULATED CYCLES  
WITH A CTO EQUIPPED LHD IN A NICKEL MINE, ng/m<sup>3</sup>

PAH SPECIES	AVERAGE OF 4 SAMPLES WITH A CTO EQUIPPED LHD	AVERAGE OF 5 SAMPLES WITH NO EXHAUST TREATMENT
Pyrene	43.8	211
Fluoranthene	3.1	7.7
Benzo(a)Anthracene	1.1	19.5
Benzo(e)Pyrene	22.5	73
Perylene	0.1	0.9
3 Methylcholanthrene	1.1	1.6
Benzo(k)Fluoranthene	0.4	3.2
Benzo(a)Pyrene	0.3	4.6
Benzo(ghi)Perylene	0.9	11.7
Dibenzo(def,mno)Chrysene	0.02	0.9
Dibenzo(ah)Anthracene	---	---
Naptho(1234,def)Chrysene	3.1	8.4
Benzo(rst)Pentaphene	0.2	1.2

### Ceramic Filters

Two samples were obtained in the vicinity of a Deutz-engined LHD equipped with a ceramic filter, loading nickel ore in a production stope (Baldisera et al. 1986). Comparison with levels measured when the same vehicle operated without emission control indicated a significant reduction in PAH content, Table 5. Although the mutagen results (Mogan et al. 1986) spanned a much greater range (2400 to 34,000 rev/m<sup>3</sup>) than those with the CTO (as might be expected when sampling in an operating mine), the average, 15,000 rev/m<sup>3</sup>, again suggested that post-capture nitration did not unduly augment the mutagen inventory, in contrast to the effect observed when catalytic purifiers were fitted.

TABLE 5 - PAH CONCENTRATIONS NEAR A CERAMIC FILTER EQUIPPED LHD IN A PRODUCTION STOPE IN A NICKEL MINE, ng/m<sup>3</sup>

PAH SPECIES	AVERAGE OF 2 SAMPLES WITH A CERAMIC FILTER EQUIPPED LHD	AVERAGE OF 2 SAMPLES WITH NO EXHAUST TREATMENT
Pyrene	30.9	146
Fluoranthene	3.7	14.2
Benzo(a)Anthracene	3.5	30.9
Benzo(e)Pyrene	22.4	100
Perylene	0.4	4.1
3 Methylcholanthrene	---	1.6
Benzo(k)Fluoranthene	2.9	13.9
Benzo(a)Pyrene	1.8	11.7
Benzo(ghi)Perylene	5.4	44.6
Dibenzo(def,mno)Chrysene	0.4	1.0
Dibenzo(ah)Anthracene	1.1	2.5
Naptho(1234,def)Chrysene	6.0	23.5
Benzo(rst)Pentaphene	1.7	7.0

### Resin Samples

Both sets of resins (downstream from the PS and from the HV filters) yielded a number of values below the threshold of detection, as might be expected with these small samples. Only 6% of the nine least volatile PAH species were non-zero, however, in comparison to 40% of the four more volatile species. Thus, the four-ring more volatile PAHs [Pyrene (Py), Fluoranthrene (Fl), Benzo(a)Anthracene (BaA) and "BeP"<sup>1</sup>] contribute most of the (pass-through) material that is not retained on the glass-fibre filters.

### Personal Sampler Filters

There were large discrepancies between the PS assay values and the corresponding HV results. Individual PS PAH specie levels ranged from a high of 350 times the HV value, to a low of less than 45% of the HV.

The four-ring (more volatile) PAHs (Py, Fl, BaA, and "BeP"<sup>1</sup>) were always found in larger quantities on the PS filters. This is consistent with the resin results and many of the recent studies of vapour-phase/particulate-phase PAH partitioning for ambient air and combustion engine exhaust (Barton et al. 1981, Brockhaus 1974, Galasyn et al. 1984, Handa et al. 1980, Pederson and Ingwersen 1980, Thrane and Mikalsen 1981, Yamasaki et al. 1978).

Some insights into the probable origin of the PS/HV differential for the other nine PAH species (which encompass all of the moderate and strong carcinogens monitored in this work) may be gained from an examination of all of the LHD simulation samples collected (Baldisera et al. 1986, Micklethwaite 1985) when no exhaust treatment hardware was fitted - a set of 6 HV and 13 PS samples collected from a reasonably uniform mine atmosphere. Since the larger PS assay values appeared to be confined to the samples with the smallest total volume, the PS samples were divided into two groups - 6 with a sample volume greater than 3.5 m<sup>3</sup>, and 7 with volumes less than 3.5 m<sup>3</sup>. (The average HV sample was about 250 m<sup>3</sup>). Comparison of the average PAH specie concentrations of the six larger PS samples with the averages of the six HVs disclosed no significant difference at  $\alpha = 0.01$  (Natrella 1963). Four of the nine specie averages of the smaller sample volume PS group were significantly larger ( $\alpha = 0.01$ ) than the HV averages, however.

PS to HV discrepancies for the nine less volatile species thus likely result from difficulties in analyzing minute quantities of PAH in the smaller samples. Since proportionally larger quantities of mine air would be required for reliable PS assay when PAH modifying or trapping hardware is fitted, the on-board PS samples did not provide a great deal of significant information on emission control performance. [The post-CTO PS samples averaged 2.6 times baseline for example, while the ceramic filter samples indicated a 30% PAH

reduction, in contrast to the 80 to 90% of the laboratory studies (Manicom and Vergeer 1985, Manicom et al. 1986, Vergeer and Szabo 1984) and the HV results].

#### LIMITATIONS OF THE DATA

Schuetzle and Frazier (1986), summarized the variation in Fl to Py, BeP to BaP, and Py to BaP ratios from seven recent diesel exhaust assays reported in the literature. They noted that Fl to Py varied from 0.8 to 1.1:1 (average 1.0:1), BeP to BaP ranged from 1.1 to 4.3:1 (average 2.3:1), and the Py to BaP ratio spanned values from 12 to 44:1 (average 32:1). The average underground Fl to Py ratio for the bare engine, Table 2, equalled 0.046:1, and the BeP to BaP ratio, 12:1. The Py to BaP ratio, however, at 32:1 was in close agreement with the ratios reported by Schuetzle and Frazier. This normal level, coupled with the atypical Fl to Py and BeP to BaP ratios, suggests a Fl deficit and a BeP excess, which could have resulted from a systematic error in the analysis. The disproportionately higher BeP content of Sudbury air relative to that reported by Katz, Table 1, is also consistent with an assay related difficulty for Fl and BeP. This shortcoming, fortuitously, has relatively little significance, as Fl and BeP are non-carcinogens.

#### CONCLUSIONS

Since most diesels operating in Canadian underground mines have been equipped with catalytic purifiers, exposure of underground workers to PAHs may be best approximated by the levels in Table 3. The reasonable agreement between Sudbury ambient air levels and those measured by Katz et al, Table 1, suggests that some assessment of the likely health impact of underground PAHs may be derived from a comparison of these values with ambient PAH levels in urban centres. On a species-by-species basis, winter exposures of residents of Hamilton, Ontario vary from 0.4 to 5.5 times the levels underground. If the "BaP index" has some validity, underground exposure is actually less than that of the worst exposure in Katz et al's four cities survey i.e. winter levels in Hamilton, Ontario (2.7 vs 1.9 ng/m<sup>3</sup>).

The reasonable agreement between the levels of the five-ring and larger PAH's found on the larger PS and the HV filters indicates quantitative absorption on and recovery from diesel soot, a finding that is supported in the literature, (Draper et al. 1988, Kraft et al. 1982). The very much greater quantities of pyrene on the PS filters, on the other hand, suggests a significant vapour phase fraction of this non-toxic material. The levels of nitrogen dioxide customarily found underground, however, (0.8 to 1.2 ppm,

Dainty et al. 1986) are insufficient to induce much vapour-phase nitration of pyrene to its highly mutagenic nitro-derivatives.

Comparison of operating and non-operating mine levels, Table 2, suggests that relatively little of the underground PAH contamination comes from non-diesel sources.

Monolithic catalysts in current use in nickel mines appear to reduce the 13 PAH's assayed by around fifty percent. An increase in the mutagen content of the mine air, however, suggests that this reduction may have resulted from nitration to more mutagenic species, and thus may have an overall negative impact. The new emission control hardware tested - traps and filters - brought about an eighty to ninety percent reduction in PAH content. Simultaneous mutagen assay demonstrated that these devices did not likely release an undue excess of nitrated PAHs.

Although the BaP exposure levels from Table 3 are higher (nickel 1.9, salt 1.2, and uranium 2.6 ng/m<sup>3</sup>) than the overall averages calculated by Muir and Verma (1986), (nickel 1.1, salt 0.6, and uranium 2.4 ng/m<sup>3</sup>), they are still in the "very low" workplace category proposed by Lindstedt and Sollenberg (1982). Inclusion of the 1986 (Baldisera et al.) studies in the averages, thus does not affect the validity of Muir and Verma's assessment: "The evidence thus suggests that underground PAH's are undesirable, that efforts should be made to reduce them, but that the health impact as far as lung cancer is concerned is likely to be small".

What, however, of the recent multiplicity of evidence that exposure to dilute diesel exhaust (at levels only slightly above those measured underground) has induced excess lung tumours in animals (Brightwell et al. 1986, Inshinishi et al. 1986, Iwai et al. 1986, Mauderly et al. 1986, Stöber 1986, Takemoto et al. 1986). A large number of post-1982 studies of mutagenic potential have shown that tiny quantities of nitro-substituted compounds are more likely causative agents than the parent PAHs. Some authorities also suggest (Stöber 1987, Wolff et al. 1987, Vostal 1986) that the physical rather than the chemical attributes of diesel soot could be significant (an epigenetic mechanism akin to the tumour induction observed with massive exposure to titanium dioxide).

This work has shown, given the previous widespread acceptance of the PAH fraction's role as a threat to health, that sufficient ventilating air had been provided underground to reduce possible hazards from this source.

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TABLE 3 - PAH LEVELS IN THE VICINITY OF DIESEL EQUIPMENT FITTED WITH CAPALYTIC PURIFIERS, ng/m<sup>3</sup>

PAH SPECIES	DEUTZ-ENGINE LHDs WITH MONOLITHS	CATERPILLAR- ENGINEED LOADERS WITH MONOLITHS	DADD-ENGINEED TRUCKS AND LHDs WITH MONOLITHS	DEUTZ-ENGINEED LHDs WITH PELLETED CATALYSTS	DEUTZ-ENGINEED LHDs WITH NO EMMISSION CONTROL HARDWARE
Pyrene	96	248	229	50.8	130
Fluoranthene	8.1	19.3	35.9	5.2	6.1
Benzo(a)Anthracene	7.7	14.6	13.3	4.7	15.1
Benzo(e)Pyrene	24.5	55.3	35.0	6.8	51.5
Perylene	0.4	0.3	0.9	0.1	1.1
3 Methylcholanthrene	---	---	---	---	5.6
Benzo(k)Fluoranthene	2.5	5.2	3.9	0.8	4.3
Benzo(a)Pyrene	1.9	1.2	2.6	0.3	4.3
Benzo(ghi)Perylene	9.1	9.1	9.8	1.6	13.6
Dibenzo(def,mno)Chrysene	0.5	0.5	0.3	0.1	0.8
Dibenzo(ah)Anthracene	9.1	3.5	5.1	0.5	3.6
Naptho(1234,def)Chrysene	6.8	7.5	8.1	2.0	8.5
Benzo(rst)Pentaphene	0.9	1.7	0.8	0.4	1.9