

Analysis of Particle and Vapour Phase PAHs from the Personal Air Samples of Bus Garage Workers Exposed to Diesel Exhaust

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The levels of particle and vapour phase polycyclic aromatic hydrocarbons (PAHs) derived from the diesel exhaust compounds in bus garage work were measured in winter and in summer. Five personal air samples were collected from the breathing zones of 22 garage workers every other day of consecutive weeks. Control samples ($n = 22$) were collected from office workers in Helsinki. Fifteen PAHs in the air samples were analysed by HPLC using a fluorescence detector. Statistically significant differences were observed between total PAH levels of the exposed workers (2241 and 1245 ng/m³) and the control group (254 and 275 ng/m³) in both winter ($P < 0.001$) and summer ($P < 0.001$). Phenanthrene, pyrene, benzo[ghi]perylene and fluoranthene were the major compounds in the particle phase, and naphthalene, phenanthrene and fluorene in the vapour phase. About 98% of PAHs measured were related to the vapour phase compounds, whereas the high molecular weight PAH compounds were detected only in the particle phase. The PAH levels in the garages were twice as high ($P < 0.001$) in winter as in summer. Even though the exposure levels were low in the bus garages, the low level does not allow conclusions to be drawn about the possible adverse health effects due to exposure to diesel exhaust.

Keywords: air sampling; diesel exhaust; occupational exposure; polycyclic aromatic hydrocarbons

INTRODUCTION

The diesel exhaust emitted from heavy and light duty engines is a mixture of gases, vapours, semivolatile compounds and particles. In the 1980s, animal experiments demonstrated that exposure to diesel emissions impaired respiratory function and was suspected of causing pulmonary carcinoma (Heinrich *et al.*, 1986). Since then several studies have shown that exposure to diesel engine emissions can provoke asthma, cardiovascular diseases and an increased lung cancer risk in several occupations (Boffetta *et al.*, 1988; Bröske-Hohlfeld *et al.*, 1999; Hong *et al.*, 2002). On the other hand, some contradictory results have also been reported (Muscat and Wynder, 1995; Valberg and Watson, 2000). It has recently been proposed that the fine and ultrafine particles may

cause the most harmful effects to the lungs (MacNee and Donaldson, 2000).

About 90% by mass of diesel exhaust particles are $<1 \mu\text{m}$ in diameter. They are formed in the combustion chamber of the engine exhaust system and are released as respirable emissions into the atmosphere after agglomeration and condensation (Kleeman *et al.*, 2000). The particles, which contain elemental carbon and organic compounds, represent a good adsorption surface for the hundreds of compounds produced after incomplete combustion in diesel engines. Well-known groups of compounds released within the emissions are polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (Pederson and Siak, 1981; Miguel *et al.*, 1998). Polyaromatics may also originate from unburned diesel fuel, lubricating oil and the pyrosynthesis of low molecular weight polyaromatics. PAHs with two or three aromatic rings are mostly detected in the vapour phase, whereas those with between four and seven fused rings are found mostly in the particle phase. In addition to

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PAHs, there is also a mixture of several compounds such as nitrogen, carbon and sulphur oxides, formaldehyde and butadiene in the gas phase of diesel exhaust (IPCS, 1998).

A recent report by Gerde *et al.* (2001) focused on the release of benzo[a]pyrene (B[a]P) from the surface coating of diesel particle soot. They reported a rapidly released pulse of B[a]P, which was quickly adsorbed through the alveolar epithelium after inhalation. B[a]P appeared mostly unmetabolized in the circulation, but after 1 h B[a]P was systemically metabolized. The data indicate that absorption through the alveolar epithelium is an important route of entry to the circulation of unmetabolized B[a]P.

Several occupational studies have reported B[a]P levels in various job categories due to its major carcinogenic potential. Exposure to B[a]P levels of 1.5–184 ng/m³ have been measured among truck drivers and bus garage workers (Guillemin *et al.*, 1992; Hemminki *et al.*, 1994; Schoket *et al.*, 1999). Estimates of the occupational exposure to diesel exhaust in Finland showed that during 1990–1993, ~39 000 workers were exposed via land transport. In 1997, exposure to PAHs alone was notified as having affected 1545 machine and engine repair workers and foundry workers (Kauppinen, 2001). Reformulated fuels with aromatic hydrocarbon contents <20% by vol and sulphur content <0.005% by mass are used in Finland by virtually all heavy and light duty diesel engines in trucks, buses and other vehicles. Two types of reformulated diesel fuels are used due to the seasonal changes in the climatic conditions. The main differences in the reformulated summer and winter grade diesel fuels are the density and cetane number (Mikkonen *et al.*, 1997).

This study reports the analysis of PAHs derived from diesel engine emissions in the personal air samples of bus garage workers. The distributions of 15 vapour and particle phase PAHs in summer and winter were measured and the levels of PAHs in garages were estimated.

SUBJECTS AND METHODS

Study population

A group of 20 male and two female non-smoking bus garage workers participated in this study. Personal data, job type and daily working hours were obtained from questionnaires completed by every participant. The average age and employment of garage workers were 48 yr (range 30–59) and 26 yr (range 9–41), respectively. The control group consisted of 48 non-smoking office workers and research scientists, who had no occupational exposure to PAHs. The average age was 49 yr (range 25–61) and duration of employment 16 yr (range 1–43). The working time in the garages was 7.5 h. The garage workers consisted of mechanics, electricians, welders,

painters, foremen and workers who cleaned, washed and refuelled the buses. The work was done completely inside in both the study and the control groups. The bus fleet was no older than 5–6 yr, and 200 buses were serviced daily in three garages. Typically, buses were driven from outdoors into a large hall, where engine repair, washing, cleaning and refuelling were carried out. Inside the halls, the engines were started and stopped several times and the diesel exhaust occasionally became elevated. Especially in the winter, diesel exhaust drifted into the repair halls when the engines were cold-started outdoors close to the garages.

Description of the bus garages

Garage number 1 was built in 1962 and partially remodelled in 1988. The size of the hall is 2000 m² and 70 buses are kept in this hall. About 400 buses are fixed or cleaned there every month. Detailed information on ventilation is not available, but the ventilation operates in summer and in winter. The exhaust pipes of the buses were connected to a pipeline to carry the exhaust of running engines out of the hall. The ventilation removes heat, but the air is not circulated. The incoming air is filtered.

Garage number 2 was built in 1952 and remodelled in 1992. No buses are kept in this 1800 m² hall. About 140 buses visit this repair and cleaning hall per month. No detailed information on the ventilation is available, but the ventilation system is very similar to garage number 1.

Garage number 3 was built in 1966 and the total size of the hall is 3750 m². The hall is divided into a repair shop and a washing line, which process about 200 buses per month. The air is circulated in the hall and some fresh outdoor air is conducted into the hall. This garage will be remodelled in 2004.

Air sampling

Outdoor temperature during the sampling period varied from –24 to 0°C in winter and from 9 to 17°C in summer. Five air samples were collected from the breathing zone of each garage worker by sampling every other day of consecutive weeks. Each person carried around the waist a pump connected via a silicon tube to the air sampling device, which was attached to the clothing on the right shoulder ~10 cm away from the mouth. The sampling strategy was similar in summer and winter. Small battery powered pumps (SKC Models 222 and 224 and DuPont model S2500) were used to pump air through the sampling device containing a filter and an adsorbent tube. Particles were collected on a polytetrafluoroethylene (PTFE) filter (Zefluor™, 37 mm diameter, 2.0 µm pore size; SKC Inc.), providing a very low background in the analysis and an efficient retention of agglomerated particles and PAHs bound to carbon due to the matrix of randomly oriented fibres, which

are wound or bonded together in several layers (depth filter) and retain particles on the surface and throughout the matrix (ASTM, 1999). The PTFE filter was placed in a closed face aerosol analysis monitor (field monitor MAWP 037 AO; Millipore), which was connected to the XAD-2 adsorbent (226-30; SKC Inc.) collecting vapour phase compounds. Air samples were collected during a full working day with a flow rate of 1.4 l/min for 5–8 h (400–700 l/sample). Sampling devices were protected against light during and after sampling by wrapping them in aluminium foil. The samples were stored at -20°C before the analyses. Using the personal air sampling devices, the control samples were collected as stationary air samples from the offices in which the control persons worked 8 h/day.

Analytical methods

The air samples collected on filters and XAD-2 adsorbents were extracted with 5 ml of cyclohexane and 1 ml of acetonitrile, respectively. Extraction was carried out by sonication for 30 min at room temperature (Yrjänheikki *et al.*, 1995). After cyclohexane extraction, the solvent was concentrated under nitrogen and changed to acetonitrile at 40°C . Acetonitrile was added dropwise while evaporating cyclohexane in order to prevent the samples drying out. Cyclohexane as the upper layer easily evaporated and the final volume was adjusted to 1 ml with acetonitrile. Before the analyses all samples were filtered through a GHP filter ($0.45\text{ }\mu\text{m}$ Bulk Acrodisc Syringe Filter; Gelman). A standard mixture containing 16 PAHs in acetonitrile was obtained from Ehrenstorfer (Augsburg, Germany). Fifteen PAHs were quantified; only acenaphthylene was not detected, due to its weak fluorescence. Standards were prepared by spiking known amounts of PAH mixture onto the filter and XAD-2 adsorbent. As background impurities, naphthalene (1.2–11 ng/sample), acenaphthene (7–20 ng/sample), fluorene (5–23 ng/sample) and phenanthrene (0.5–18 ng/sample) were analysed in the XAD-2 adsorbent. These background values were subtracted from the corresponding compounds measured in the air samples. PAH analyses were carried out according to the methods of the National Institute of Safety and Health (NIOSH methods 5506 and 5800) (NIOSH, 1998). The HPLC apparatus (HP1100; Agilent Technologies, Waldbronn, Germany) was equipped with a fluorescence detector with two programmable emission channels (FLD1A and FLD1B). A guard column ($10 \times 3\text{ mm}$; ChromPack) and an analytical PAH column ($100 \times 3\text{ mm}$, $5\text{ }\mu\text{m}$ particle size; ChromPack) separated the samples at a flow rate of 0.3 ml/min. Typically, $15\text{ }\mu\text{l}$ in acetonitrile was injected into the HPLC. A gradient of water (solvent A) with an increasing acetonitrile content from 40 to 100% (solvent B) over 16 min was used, followed by 100% B for 13 min. Between

the injections, the column was washed with 100% acetonitrile for 2–3 min at a flow rate of 0.6 ml/min (Mäkelä and Pyy, 1995).

Statistical evaluation

The results are presented as arithmetic means of PAH concentrations; when calculating the means, observations below the limit of quantification (LOQ) were given a value of 0. A repeated measurement method was applied for statistical comparisons between the exposure and control groups with respect to PAH concentrations (Diggle *et al.*, 1994; Littell *et al.*, 1996). In this method, the correlation of five measurements from the same person was taken into account. A logarithmic transformation was performed to obtain a normal distribution of the data (values below the LOQs were replaced with values of half the LOQs). The Spearman rank correlation coefficient was used in correlation analysis.

RESULTS

Recovery and limit of quantification (LOQ)

Recoveries for 15 PAHs in the particle and vapour phases with the relative standard deviations ($\pm\text{RSD}$) were determined using six parallel samples spiked with two concentrations (4.0 and 20 ng/ml) of the PAH standards (Table 1). The recovery of each PAH obtained from the filters spiked with 20 ng/ml ranged from 72 to 122% (± 2 –12%), being clearly dependent on the individual PAH. The recovery varied from 82 to 108% (± 5 –20%) at the low concentration of 4.0 ng/ml (data not shown). Seven PAHs with between two and four fused aromatic rings were analysed from the XAD-2 adsorbent. The recoveries for naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene at a concentration level of 200 ng/ml were between 57 and 84% (± 5 –26%). The LOQ values calculated for 700 l of air varied from 0.9 to 3.7 ng/m^3 for particulate PAH and from 3.3 to 50 ng/m^3 for vapour phase PAHs (Table 1). The limit of detection (LOD) for PAHs varied from 0.02 to 1.1 ng/sample and the day-to-day variation at a concentration level of 5.0 ng/ml was 7–17%. Figure 1 shows an example of the HPLC chromatograms analysed for PAHs in the standard mixture (Fig. 1a), an air sample of the vapour phase (Fig. 1b) and the particle phase (Fig. 1c) obtained from an exposed worker.

Garage workers were mainly exposed to naphthalene, fluorene and phenanthrene in winter and summer, although other low molecular weight PAHs in the vapour phase were also detected (Fig. 2a). The concentrations of naphthalene, fluorene and phenanthrene were about 2-fold higher in winter when compared with those in summer. In winter, mean levels of 1285, 167 and 730 ng/m^3 were determined for naphthalene, fluorene and phenanthrene, respect-

Table 1. The recovery and the limit of quantification (LOQ^a) of the measured PAH compounds

Compound	Excitation wavelength (nm)	Emission wavelength (nm) 1/2 ^b	PFTE filter		XAD-2	
			Recovery (RSD, <i>n</i> = 6)	LOQ (ng/m ³)	Recovery (RSD, <i>n</i> = 6)	LOQ (ng/m ³)
1 Naphthalene	230	350/360	92 ± 7	3.7	84 ± 19	50
2 Acenaphthene	245	350/450	78 ± 12	2.7	60 ± 26	25
3 Fluorene	245	350/450	88 ± 7	1.6	73 ± 5	41
4 Phenanthrene	245	350/450	101 ± 12	3.5	69 ± 15	23
5 Anthracene	245	413/450	72 ± 9	0.9	67 ± 6	11
6 Fluoranthene	245	450/413	95 ± 6	1.8	70 ± 7	5.1
7 Pyrene	245	413/450	87 ± 7	1.3	57 ± 10	5.3
8 Benzo[<i>a</i>]anthracene	270	413/450	77 ± 3	1.1	ND	3.3
9 Chrysene	270	413/450	85 ± 3	0.9	ND	3.3
10 Benzo[<i>b</i>]fluoranthene	270	450/413	103 ± 2	0.6	ND	2.8
11 Benzo[<i>k</i>]fluoranthene	270	413/450	122 ± 2	1.3	ND	3.9
12 Benzo[<i>a</i>]pyrene	270	413/450	75 ± 5	0.9	ND	4.5
13 Dibenzo[<i>ah</i>]anthracene	305	413/487	94 ± 9	2.3	ND	3.3
14 Benzo[<i>ghi</i>]perylene	305	413/487	76 ± 7	2.0	ND	4.5
15 Indeno[1,2,3- <i>cd</i>]pyrene	305	487	87 ± 3	1.0	ND	6.2

^aLOQ, 10 times standard deviation + the smallest calibration standard 0.2–0.4 ng/ml.

^b1, wavelength used for quantification; 2, wavelength used for qualification.

ND, not determined.

ively, in the vapour phase (Table 2). In the summer samples, the corresponding values were 760, 64 and 405 ng/m³. The means of four other PAH compounds detected in the vapour phase were invariably below 6.6 ng/m³ in both winter and summer. Naphthalene was only detected in the vapour phase, accounting in winter for 58% and in summer for 62% of all vapour phase PAHs. The level of anthracene was low in both phases and fluoranthene and pyrene were slightly higher in the particle phase. Fluorene and phenanthrene were determined in winter and summer at concentrations from 50 to 200 times lower in the particle than in the vapour phase.

Thirteen PAH compounds were determined in the particle air samples (Fig. 2b). The mean value of the exposure to particle phase PAHs was 25 ng/m³ (range ND–494 ng/m³, *n* = 106) in winter and 8.5 ng/m³ (range ND–46 ng/m³, *n* = 111) in summer. A statistically significant exposure difference between the exposed and controls in winter (*P* < 0.001) and in summer (*P* < 0.005) was observed as far as PAHs present in the particle phase were concerned. The most abundant PAHs in particle phase samples in winter were phenanthrene, fluoranthene, pyrene, B[a]P and benzo[*ghi*]perylene. In summer, the PAH profile in particles was slightly different, with the most abundant compounds being fluorene, phenanthrene and fluoranthene. The highest concentration in the particle phase, in both winter and summer, was analysed for the non-carcinogenic phenanthrene. The total PAH concentrations of weak (benzo[*a*]anthracene, benzo[*ghi*]perylene and chrysene) and strong carcinogens (benzo[*b*]fluoranthene, benzo[*k*]fluoranthene,

B[a]P, dibenzo[*ah*]anthracene and indeno[1,2,3-*cd*]pyrene) in all air samples analysed were less than 2%.

The average levels of B[a]P and pyrene were 2.9 and 3.6 ng/m³ in winter and 0.6 and 0.8 ng/m³ in summer. In winter, the exposure to B[a]P and pyrene was about four times higher than in summer. A significant correlation (*r* = 0.78, *P* < 0.001, *n* = 44) between B[a]P and pyrene concentration in the personal air samples was observed (Fig. 3).

The levels of PAHs in the three bus garages are shown in Fig. 4a. The mean level of PAHs was about the same (1000 ng/m³) in garages numbers 1 and 2 in summer, but garage number 3 had a significantly higher (*P* < 0.001, *df* = 80) mean level (1700 ng/m³). Elevated levels were observed in all garages in winter time (1500–2400 ng/m³). However, garage number 2 had a slightly lower level of PAHs in winter than garages 1 (*P* < 0.001, *df* = 70) and 3 (*P* < 0.001, *df* = 64).

The mean total PAH concentrations of 2241 and 1245 ng/m³ in the exposed workers' air samples in winter and summer, respectively, were significantly higher (*P* < 0.001, *df* = 38.3 and *df* = 35.7) than the 254 and 275 ng/m³ of the control group (Fig. 4b). Large differences in levels of PAHs were observed between the air samples (890–5960 ng/m³ in winter and 247–3260 ng/m³ in summer). The concentrations of PAHs measured in the bus garages were significantly higher in winter than in summer (*P* < 0.001, *df* = 43.7), however, no seasonal variation in the control group (*P* = 0.93, *df* = 2, 12) was observed.

Table 2

Compo

Volatil

Nap

Ac

Flu

Phe

Ant

Flt

P

Sum o

PAH o

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Phe

Ant

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P

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Table 2. Exposure of bus garage workers and control persons to PAHs in winter and summer (corrected for recovery)

Compound ^a	Bus garages				Controls			
	Winter (n = 104 or 106 ^b)		Summer (n = 106 or 111 ^c)		Winter (n = 5)		Summer (n = 17)	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Volatile PAH (ng/m ³)								
Napht	1285	640–3362	760	204–2450	226	160–303	230	100–510
Ac	6.6	ND–232	ND		ND		ND	
Flu	167	53–936	64	ND–460	ND		ND	
Phe	730	63–2664	405	43–1180	33	25–53	40	ND–215
Ant	0.4	ND–29	ND		ND		ND	
Flt	0.4	ND–20	1.3	ND–40	ND		ND	
P	2.6	ND–40	0.3	ND–10	ND		ND	
Sum of 7 PAH	2198 ^{d,f}	875–5465	1230 ^d	247–3230	254	190–355	275	100–720
PAH on particles (ng/m ³)								
Flu	1.6	ND–24	1.4	ND–28	ND		ND	
Phe	4.1	ND–50	1.9	ND–15	ND		ND	
Ant	0.2	ND–10	0.01	ND–1.1	ND		ND	
Flt	3.1	ND–79	1.4	ND–8.9	ND		ND	
P	3.2	ND–105	0.8	ND–12	ND		ND	
BaA	1.0	ND–29	0.3	ND–3.3	ND		ND	
Chr	1.7	ND–24	0.2	ND–2.5	ND		ND	
BbF	1.5	ND–17	0.5	ND–2.6	ND		ND	
BkF	0.4	ND–11	0.06	ND–1.4	ND		ND	
B[a]P	2.9	ND–60	0.6	ND–8.9	ND		ND	
DBA	ND		ND		ND		ND	
BPe	3.1	ND–58	0.6	ND–6.3	ND		ND	
IP	2.3	ND–34	0.2	ND–2.8	ND		ND	
Sum of particle PAH	25 ^{d,f}	ND–494	8.5 ^e	ND–46	ND		ND	
Σ(particles+volatile)	2241 ^{d,f}	890–5960	1245 ^d	247–3260	254	190–355	275	100–720

^aNapht, naphthalene; Ac, acenaphthene; Flu, fluorene; Phe, phenanthrene; Ant, anthracene; Flt, fluoranthene; P, pyrene; BaA, benzo[a]anthracene; Chr, chrysene; BbF, benzo[b]fluoranthene; BkF, benzo[k]fluoranthene; B[a]P, benzo[a]pyrene; DBA, dibenzo[a,h]anthracene; BPe, benzo[ghi]perylene; IP, indeno[1,2,3-cd]pyrene.

^bDifferent number of particle (106) and volatile (104) samples due to losses in sample preparation.

^cDifferent number of particle (111) and volatile (106) samples due to losses in sample preparation.

^d $P < 0.001$ when result is compared with controls.

^e $P < 0.005$ when result is compared with controls.

^f $P < 0.001$ when winter and summer samples are compared.

ND, not detected, < LOQ.

The exposure as a function of the job title is shown in Fig. 4c. In general, exposure was lower in all groups in summer than in winter, but as far as the exposure was concerned there was only an insignificant difference between the groups in any season. The workers were divided into three groups according to high (>2500 ng/m³), medium (1000–2500 ng/m³) and low (<1000 ng/m³) exposure to PAHs. In the winter and summer, the high exposure group consisted of mechanics (winter 43%, summer 0%), welders (winter 29%, summer 0%), refuelling persons (winter 14%, summer 0%) and foremen and electricians (winter 14%, summer 0%). There were mechanics (winter 60%, summer 47%), welders (winter 7%, summer 20%), refuelling persons (winter 7%, summer 15%) and foremen and electricians

(winter 27%, summer 20%) in the medium exposure group. None of the workers were in the low exposure group in winter and only mechanics (67%), foremen and electricians (33%) were in this particular group in summer.

DISCUSSION

There are a few occupational studies evaluating the distribution of vapour and particle phase PAHs originating from diesel exhausts. The complex mixture of diesel exhaust has been assessed in earlier studies using diesel particulate matter, carbon and gaseous components as surrogates (Heinrich *et al.*, 1986; Muscat and Wynder, 1995; Brüske-Hohlfeld *et al.*, 1999; MacNee and Donaldson, 2000; Valberg and

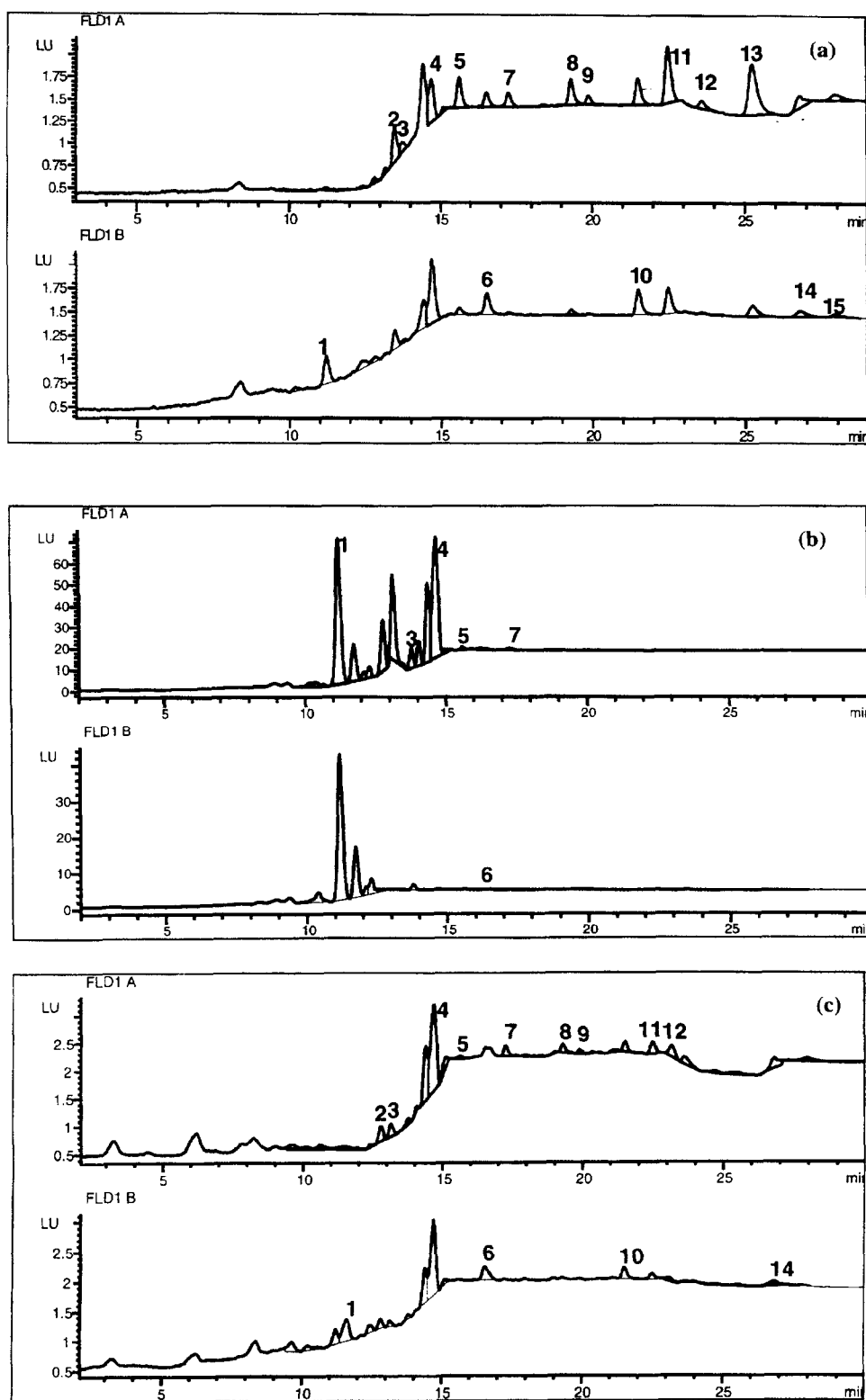


Fig.

Pyrene (ng/m³)Fig.
ex

Fig. 1. An example of HPLC chromatograms of the PAH standard mixture at a concentration level of 1 ng/ml (a) and of the vapour phase (b) and particle phase (c) air samples of an exposed worker. FLD1A and FLD1B refer to the two emission channels used. PAH compounds analysed were: 1, naphthalene; 2, acenaphthene; 3, fluorene; 4, phenanthrene; 5, anthracene; 6, fluoranthene; 7, pyrene; 8, benzo[*a*]anthracene; 9, chrysene; 10, benzo[*b*]fluoranthene; 11, benzo[*k*]fluoranthene; 12, benzo[*a*]pyrene; 13, dibenzo[*ah*]anthracene; 14, benzo[*ghi*]perylene; 15, indeno[1,2,3-*cd*]pyrene.

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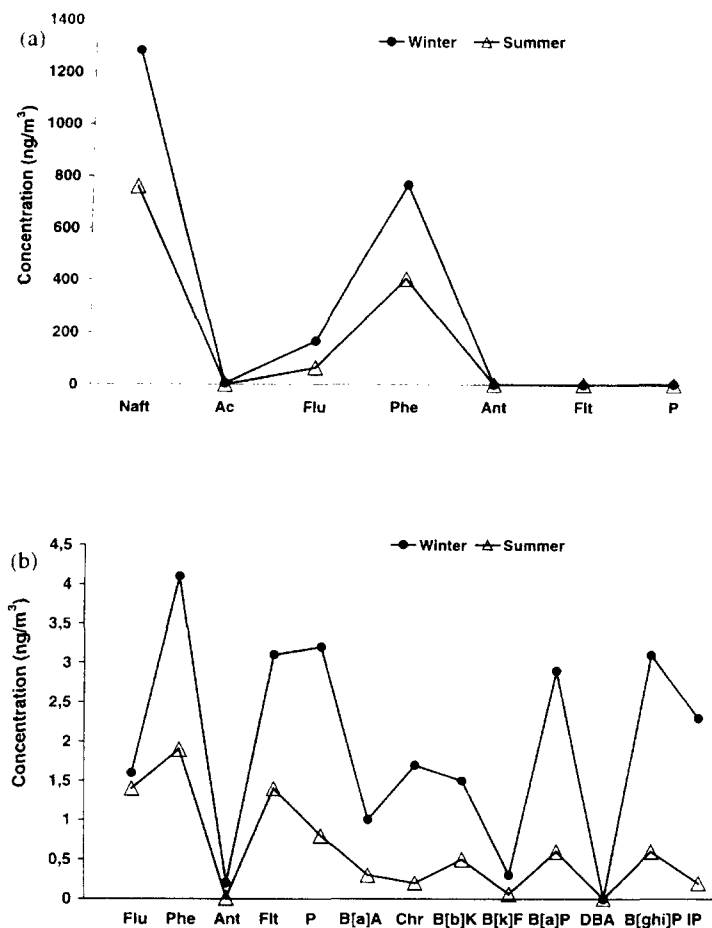


Fig. 2. The average concentration (ng/m³) of vapour (a) and particle (b) phase air samples of the exposed garage workers analysed for single PAH compounds in winter (filled circles) and in summer (open triangles).

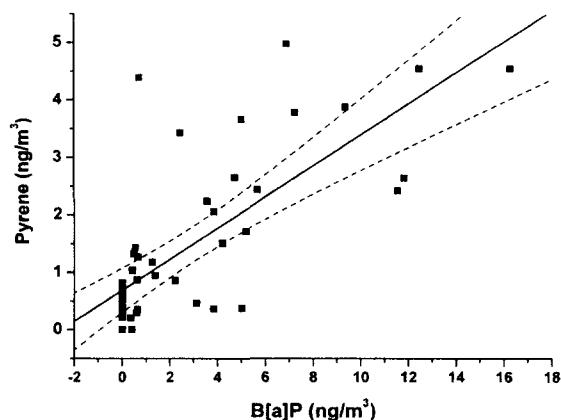


Fig. 3. The correlation ($r = 0.784$, $P < 0.0001$, $n = 44$) between the average pyrene and B[a]P air concentrations among exposed garage workers. The dashed lines display the 95% confidence limits.

Watson, 2000; Hong *et al.*, 2002). This study evaluated the seasonal exposure of 22 bus garage workers to 15 PAH compounds in personal air samples. The measurements confirmed that ~98% of PAHs measured were related to the vapour phase compounds.

Our data are in line with other reports, which have indicated that if a back-up adsorbent is not used, three to five ring PAH compounds are lost during sampling (Davis *et al.*, 1987; Hansen *et al.*, 1994; Kleeman *et al.*, 2000). High molecular weight PAHs (between four and seven rings) were only detected in the particle phase. Other factors that influence the distribution of PAHs between the two phases are temperature, air sampler, filter type, particulate matrix and equilibrium concentrations (Davis *et al.*, 1987). Most of the vapour phase PAH compounds are not carcinogens, but their measurement is justified by the fact that some of them are important precursors of highly mutagenic nitro-PAHs (Arey *et al.*, 1986; Atkinson and Arey, 1994). Naphthalene accounted for ~85% of the total PAH load in an iron foundry study (Hansen *et al.*, 1994), whereas in our study the naphthalene concentrations (0.6–3.3 $\mu\text{g}/\text{m}^3$) in the bus garages ranged from 60 to 80% of total PAHs. Naphthalene, fluorene and phenanthrene were significant constituents of total PAHs analysed in a new Finnish coking plant (Yrjänheikki *et al.*, 1995). This observation is similar to our data, in which they were also the major

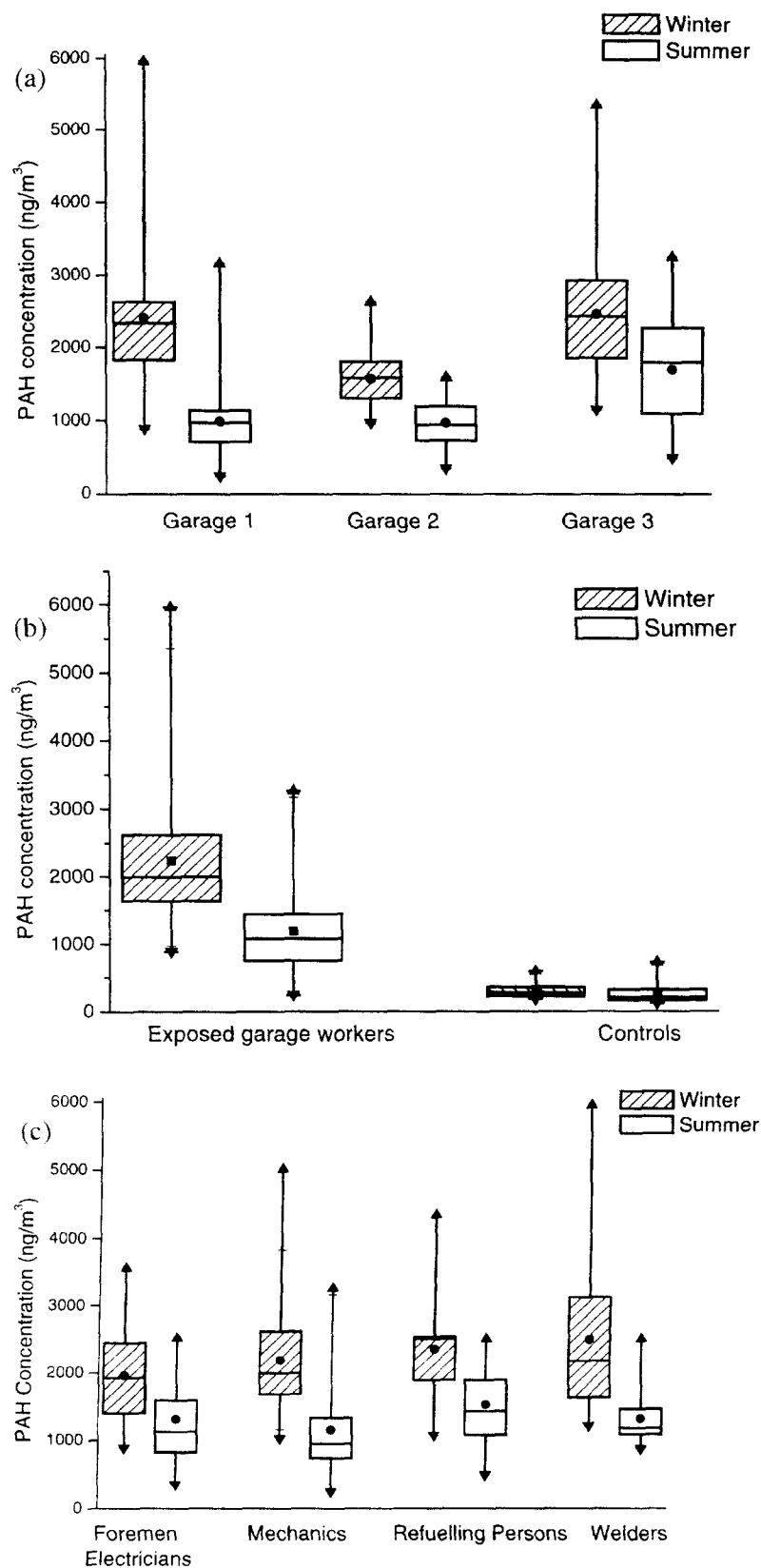


Fig. 4. A box plot presentation of PAHs in garage work. The levels of PAHs in three different garages (a), the difference between the exposed group and the control group (b) and the difference in exposure between the job groups (c). The arithmetic mean (filled circles), minimum (filled inverted triangles) and maximum (filled triangles) values are shown and three horizontal lines from the top of the box indicate the number of data points that are below 75, 50 and 25% of all measurements.

constituents, but present at much lower concentrations.

We noticed only minor variations in the mean total PAH concentrations between the three garages. In the largest garage, the average PAH level in both seasons (1698 ng/m³) was at the same level as that of the smallest garage (1245 ng/m³). The highest PAH exposure (2140 ng/m³) was detected in the mid-size garage, apparently being attributable to its old ventilation system. The exposure to PAHs among the control subjects was lower or at the same level as that reported in other studies (Guillemin *et al.*, 1992; Schoket *et al.*, 1999). We analysed 12 PAHs in the particles, five being non-carcinogenic and seven carcinogenic compounds; dibenzo[ah]anthracene was not detected. The concentrations of these PAHs in the particle phase were about 140-fold lower in summer and 90-fold lower in winter than the concentration of total PAHs in the vapour phase.

Biomonitoring studies conducted in the garages have shown higher (15–184 ng/m³) levels of B[a]P compared with our results (Hemminki *et al.*, 1994; Schoket *et al.*, 1999). The low B[a]P exposure detected in our study is in better agreement with data obtained from truck drivers, a bus station (0.77–3.45 ng/m³) and ambient air measurements (mean 0.62–0.85 ng/m³) (Guillemin *et al.*, 1992; Schoket *et al.*, 1999; Zmirou *et al.*, 2000; de Pereira *et al.*, 2002).

Ratios between PAHs such as B[a]P and pyrene and B[a]P and benzo[ghi]perylene measured in the air samples have been used to characterize the origin of PAHs (Masclet *et al.*, 1986; Chiang *et al.*, 1996; Zmirou *et al.*, 2000). In general, a ratio >1 between high and low molecular weight PAHs corresponds to gasoline and a ratio <1 to diesel vehicles. In our study, the ratio 0.01 indicates that the PAHs were attributable to diesel-driven vehicles. The B[a]P:benzo[ghi]perylene ratio has been used as indicative of exposure to vehicle or heating sources. Our data show ratios of 1.12 (in winter) and 1.02 (in summer), values that are in agreement with the study of Masclet *et al.* (1986), emphasizing the origin of exposure to vehicle emissions.

The seasonal variation in total PAH exposure in the garages was 2-fold higher in winter than in summer. The concentrations of vapour phase PAHs were 2–10 times higher in winter than in summer. In the particles, a 1- to 20-fold difference was observed. Although not the case for all individual PAHs, the difference in total PAHs concentration between winter and summer was statistically significant.

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