Environmental Health Perspectives
Vol. 47, pp. 53-63, 1983

Emission of Carcinogenic Components with Automobile Exhausts

by Ulf Stenberg,* Tomas Alsberg* and Roger Westerholm*

Different sampling methods for mutagenic polynuclear aromatic hydrocarbons (PAH) are described. These methods involve either direct sampling of raw exhausts which prior to filtering are cooled in a condenser, or filter sampling of exhausts diluted in a tunnel. The relevance of gas-phase PAHs of samples from diluted exhausts is discussed; methods used are either adsorbents (XAD-2) or cryogenic condensation.

The emission of benzo(a)pyrene and certain other PAHs is reported from vehicles using different fuels (gasoline, diesel, LPG, alcohols) or different emission control systems. The emission of some volatiles, such as benzene, ethylene and alkylnitrites, is also presented from different types of fuels used.

Introduction

During the past 30 years, an increasing interest has been focused on automobile exhausts and their potential in causing cancer. The first work within this research field directed the interest on polynuclear aromatic hydrocarbons, a component class which contains known carcinogens, proved by skin painting tests on rodents (*1*). However, by the development of short-term tests *in vitro*, the information on biologically active components has increased substantially, and today a significant portion of research has been assigned to components other than these hydrocarbons. It is now generally accepted that PAHs alone contribute only a minor part of the mutagenicity/carcinogenicity of automobile exhausts.

Internal combustion engines emit a very complex mixture of unburnt fuel and newly formed products, and this emission is gaseous as well as associated to particles. Generally, the composition of the exhausts is dependent on several factors such as: engine concept, fuel and oil composition, operating conditions, etc. Due to legislative regulations during the 1960s and 1970s, on-line measurements have been developed for components such as NO/NO_2, CO and unspecified gaseous hydrocarbons (HC), but in order to analyze what we nowadays denote as "unregulated" pollutants, other techniques have to be used.

The objective of this paper is to summarize different sampling methods and reported emission values of known or suspected mutagens/carcinogens. However, it is necessary to emphasize that still most of these data include only PAH (mostly represented by one component, e.g., benzo(a)pyrene). Less information is available on the emission of derivatives of PAH or other component classes, but some of these findings are discussed elsewhere in this issue (*2*).

Preconditioning

Prior to a test it is necessary to bring all vehicles to the same status, i.e., they must be conditioned. For routine measurements on gaseous emissions like HC and CO there are standardized methods. However, for the measurement of PAH no such procedure exists. The PAH are associated to particles, which makes it probable for deposits on valves, manifold, exhaust system etc., thus delaying their emission. To circumvent this "carry-over" effect between tests, it has been suggested that the

*Department of Analytical Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden.

vehicle must be driven under heavy load for a certain amount of time before testing. This can either be accomplished on the road or on a chassis dynamometer. Due to heat formation it is preferable to perform the conditioning on the road. In one investigation (*3*), attempts were made to compare the emission, with the deposits of PAH (including what was found in the lubricating oil), and the conclusion was that only a minor part (1%) is deposited in the engine, compared to what is found in the emission and the lubricating oil.

However, the authors emphasized the need for the vehicle to achieve a steady state after changing the fuel, i.e., to have a substantial driving period with the new fuel before sampling.

Direct Sampling of Raw Exhausts

The early works published from the mid-50s to the early 70s often involved very bulky sample equipment which as a consequence necessitated voluminous extraction and clean up procedures. Two reasons can be seen for this: large sample amounts were required for the analytical procedures used and biological tests were performed with skin painting on whole animals.

In 1954, Kotin et al. (*4*) published their results concerning cancer caused by skin painting on mice with extracts from particulate gasoline engine emissions, and the samples were recovered by filtering at the actual exhaust temperature. Later, Mittler and Nicholson (*5*) enriched some of the gaseous PAH by condensation of exhausts from both gasoline and diesel engines, however, no particulate emission was recovered.

A general approach was given by Stenburg et al. (*6*) when they used condensation before filtering and applied this technique to different suspected PAH emission sources, among these being the automobile. The principle of this method was later utilized by several investigators and has proven to be very useful. In 1962, Begeman and Colucci (*7*) described a sampling system which enabled them to collect both gaseous PAH and particle-associated PAH. They concluded that a large water condenser prior to the filter package should be sufficient to collect PAH quantitatively. This trapping system was dimensioned to enrich the total exhaust volume from a 364 in.^{3} (6 L) V-8 engine operated in a chassis dynamometer.

About 10 years later, Gross used a similar system, and the chemical analysis of the exhausts involved benzo(a)anthracene (BaA) and BaP as well as phenols (*8*). The investigation included the impact of parameters such as engine deposits, PAH content of the fuel and emission control devices on the emissions. The two latter factors will be further commented later. The emission of BaP and BaA are given in Table 1.

A mobile sampling system, in which the equipment was built-in the vehicle and the driving was performed on ordinary roads, was presented 1966 by Hangebrauck et al. (*9*). However, the system had the same disadvantages as those described earlier, with its cumbersome extraction procedures. The condensed water increased the back-pressure in the system, and approximately 5-8% of the engine power was lost. In which way this may affect the emission of PAH was not reported. However, the possibility of obtaining samples from real conditions should be emphasized. The average emission from four selected PAHs from vehicles from the late 50s and the early 60s is given in Table 2.

It is noteworthy that for these previously described sampling systems very little or no information is at hand concerning optimization arrangements or recovery data. At that time, almost no consideration had

Table 1. PAH emissions.[a]

	PAH emission, μg/km[b]					
	Vehicle A[c]		Vehicle B[c]		Vehicle C[c]	
	Low PAH fuel[d]	High PAH fuel[e]	Low PAH fuel[d]	High PAH fuel[e]	Low PAH fuel[d]	High PAH fuel[e]
BaP	2.4	5.8	0.7	1.3	0.4	1.0
BaA	4.4	9.0	1.5	2.8	1.0	2.5

[a]Data of Gross (*8*) condensation before filter.
[b]Gross' data originate from different fuel types and deposit levels in the engine and are originally reported as μg/gallon fuel used. Values above represent mean values from several fuels, and the recalculations in μg/km were made by the authors on an estimated mileage of 21 miles/gallon from a 7 mode cycle.
[c]A = vehicle without emission control, 1966; B = vehicle with engine modification, 1968; C = vehicle with engine modification, 1978.
[d]Low PAH fuel: BaP ≤ 0.1 ppm.
[e]High PAH fuel: BaP = 3 ppm.

Table 2. Emissions obtained from real conditions.[a,b]

	Emissions, μg/km	
	Vehicle A	Vehicle B
Phenanthrene	6.4	33
Pyrene	43	97
BaP	5.3	8.7
Benzo(ghi)perylene	24	37
Coronene	9.3	16

[a]Data of Hangebrauck et al. (*9*); condensation before filter.
[b]Average speed 35 km/hr, maximum speed 51 km/hr; 19 km route. "A realistic composite of business, arterial and rapid transit driving." Mean value of four vehicles.

been paid to the possibility for losses of volatile species from filter, artifact formation or degradation during sampling.

Grimmer et al. presented in 1972 (*10*) a construction for the collection of the total exhaust volume. They choose a vertical glass condenser with a cooling area of 0.25 m^2. The reason for having a glass device was the ease of controlling the washing procedure, and that catalytic effects on the condensed material should be lower. An evaluation of the collecting arrangement was performed and some general conclusions could be drawn. The entrance temperature on the filter should not exceed 35°C if quantitative trapping of three-ring PAHs was intended. Prolonged sampling, in this case sampling during repetitive ECE tests, involves losses of certain species, either due to volatilization or degradation.

Compared to earlier enrichment methods, this equipment has been "scaled down" and requires less laborious procedures. It has been used in large series of analyses for the assessment of the total PAH emission from gasoline vehicles. However, the dimensions of the condenser made it difficult to handle the emission from a vehicle operated in another driving cycle, e.g., FTP 1 972, since the cooling capacity is too low. The Grimmer method has been extensively used in the Federal Republic of Germany, especially by car manufacturers such as Volkswagen (*3*) and Daimler Benz (*11*). Grimmer and co-workers presented in 1975 (*12*) an investigation of the emission of PAHs in 100 vehicles. The vehicles were the 20 most sold in the Federal Republic of Germany. CO at idling was controlled and set to 2–3%. No oil was changed prior to sampling, and the same fuel was used for all vehicles, which were driven according to the European test procedure.

In summary, Grimmer and Hildebrandt concluded that 100 μg BaP is emitted per kilogram of fuel used. This corresponds to approximately 10 μg/km. However, it must be emphasized that there was a wide variation within this population of vehicles, from 1.2 μg/km up to 66 μg/km (See also Table 3).

These results were obtained in a cold start procedure according to certification rules, +20°C. One vehicle was also tested with cold start at -15°C. In this test, the emissions increased 10-fold. On the other hand, tests performed with hot start with the engine temperature at approximately +80°C, the PAH emission was decreased by a factor of 2.

These findings are also consistent with results published by VW (*3*). The ECE-test consists of four consecutive cycles of 195 sec. The first cycle containing the cold start comprised 36% of the total PAH emitted, while the remaining amount was emitted during cycles two, three and four.

An improved vertical glass condenser has recently been presented by VW (*13*) for the trapping of the total exhaust volume. The system has been used for both gasoline and diesel vehicles, and the precision over four determinations is reported to be approximately 10% for most of the analyzed PAH (Table 4).

A report from Fiat (*14*) presents data from vehicles with comparatively small engines, such as

Table 3. Emissions in ECE test cycle.[a,b]

	Emissions, μg/km
Phenanthrene	288
Pyrene	184
Chrysene	48
BaP	10
BghiP	32
Coronene	20

[a]Data of Grimmer and Hildebrandt (*12*); condensation before filter.
[b]Average of 100 vehicles driven in ECE test cycle with cold start. Recalculations made by the authors based on an estimated mileage of 10 km/L and a BaP emission of 10 μg/km.

Table 4. Emissions of some selected PAH in 1975 Federal Test Procedure.[a,b]

	Emissions, μg/km	
	Rabbit D (1978), diesel fuel	Golf (1979), gasoline
Pyrene	70	60
BeP	6	7
BaP	5	6
BghiP	6	4
Coronene	1	1

[a]Data of Kraft and Lies (*13*); condensation before filter.
[b]The data include both gas and particulate phase PAH. Data given here are taken from logarithmic histograms on a μg/mi basis, reporting the emissions of ten PAH in three different test procedures.

Fiat 126 and Fiat 128. The sampling procedure is not fully described but involves cooling prior to filtering of the raw exhausts, and the vehicles were driven in the ECE-test, cold start. The emission values are summarized in Table 5. This investigation also concludes that the emission control standards initiated by ECE in 1971 and 1979 resulted in a decrease of the PAH emission.

Investigations in Japan using another type of cooling device before filtering of undiluted exhausts has been conducted by Handa et al. (*15,16*). Different evaluation experiments are described, and oil consumption was found to be one of the major factors to influence the PAH emission. All these tests were performed in the Japanese 10-mode driving cycle which simulates city driving. Handa and co-workers concluded that a very small portion (1-2%) of the PAH in the gasoline survived the combustion, and that the emitted PAH mainly originated from pyrolyzed oil. Table 6 summarizes some of the results.

Proportional Sampling

The collection of the total exhaust volume is a method which is time-consuming for subsequent work and expensive. One way to circumvent the large sampling equipment is by using proportional sampling. This technique allows the handling of a small sample, and has become an interesting alternative with the development of more sensitive analytical methods and biological tests *in vitro*. A proportional sampling system has been described by Chipman and Massey for the sampling of gaseous pollutants like HC, CO and NO_x (*17*). However, the same type of equipment can be used for the collection of PAH, thus decreasing the needed condensing area etc. Most proportional sampling systems use a reference signal which reflects the amount of emitted exhaust. This is most easily obtained by measuring the air passing through the carburetor of the engine. This flow can be determined by a laminar flow element, thus creating a reference signal which is compared to a signal obtained from a similar element in the sample stream (*18*).

Stenberg et al. (*19*) used a proportional system connected to a glass condenser followed by a glass fiber filter. The resulting filter temperature was approximately 50°C. Typically about 10% of the total exhaust volume was sampled, and the PAH emission was determined from both FTP-7 2 and ECE-15 driving cycles. This sampling equipment was also used in an extensive investigation of 34 vehicles, three makes of the most sold in Sweden (*20*). In all, 15 different PAHs were determined from both particulates and gas phase. Tests were performed in different driving cycles with both cold and hot start. One vehicle was also tested at temperatures below 0°C and the result was in line with Grimmers', reported previously. The emission of five selected PAHs is summarized in Table 7, where also the difference in hot and cold start procedure can be noticed.

The significant difference (Table 7), in the emission between makes A and B and C was also reflected in the CO emission, which was approximately 50% higher for A. However, it is not possible, from the results obtained in this investigation, to distinguish a high PAH-emitting vehicle only from the CO emission pattern. This has also been concluded from other investigations (*8,12*), but a high CO emission value could be used for the selection for further measurements of the PAH emission.

All vehicles in this investigation (*20*) used the same fuel which was analyzed for PAH content. These results are given in Table 8. When comparing these values with the emission of PAH, it is seen that some of these substances are destroyed during the combustion, while others seem to be synthesized. Cyclopenteno(cd)pyrene (CPcdP) could not be detected in the gasoline (≤0.01 ppm). Assum-

Table 5. Fiat data on emissions in ECE test.[a,b]

	Emissions, μg/km	
	Fiat 126	FIat 128
Pyrene	90	758
Baa	25	50
BaP	10	5
Coronene	ND[c]	4

[a]Data from Fiat (*14*); condensation before filter.
[b]Mean value of three tests from vehicles driven in ECE test cycle with cold start.
[c]ND = not determined.

Table 6. Emissions obtained from Japanese 10 mode city driving cycle.[a,b]

	Emissions, μg/km		
	Vehicle A[c]		Vehicle
	New oil	Used oil[d]	B[c]
Pyrene	—	—	54
BaA	11	19	9
BaP	3.6	6.2	2.5

[a]Data of Handa et al. (*15*); condensation before filter.
[b]Includes both cold and hot start.
[c]Vehicle A = vehicle with 1.6 liter engine; vehicle B = mean value of five tested vehicles.
[d]Oil used for 3000 km.

Table 7. Emission obtained from FTP, cold start and hot start.[a]

	Emissions, μg/km					
	Vehicle A[b]		Vehicle B[b]		Vehicle C[b]	
	Cold	Hot	Cold	Hot	Cold	Hot
CpcdP	51	10	29	11	2	0.5
BaA	25	15	9	8	8	3
BaP	38	7	7	2	4	2
BghiP	44	8	13	6	13	5
Coronene	21	2	16	4	6	3

[a]Data of Stenberg (*20*); condensation before filter.
[b]A = mean value of 12 vehicles; B = mean value of 13 vehicles; C = mean value of 12 vehicles.

ing this amount as input, 1 μg should be emitted during 1 km driving. However, 50 μg/km is emitted by make A. Even make B seems to produce CPcdP in significant amounts during the combustion while make C emits one order of magnitude less. The same pattern can be recognized for coronene, while BaA and BaP substantially are degraded. Approximately 2-8% of the latter components will survive the combustion. However, if the combustion occurs at richer air:fuel ratio these values will increase, as can be seen for vehicle make A. Table 7 also shows that the emission decreases overall if the measurements are carried out during hot tests; approximately 50% less can be expected. As mentioned previously, the PAH emission will increase substantially if the vehicles have a start temperature below 0°C. Temperature-dependent emission—and this involves not only PAH and derivatives of these—has been sparcely investigated and ought to be further elucidated. This is also of concern regarding emission control devices such as catalytic converters, since these have to reach a high temperature before they are effective.

Sampling in a Dilution Tunnel

The previously described sampling methods utilized raw gases for the determination of PAH, i.e., the emission has not been mixed with ambient air where possible instant reactions with the atmosphere might occur. Consequently, one crucial question is whether measurements of undiluted (raw) exhausts reflect the actual composition which continuously exposes the environment.

However, a technique has been developed in order to simulate reactions of gases and particles when mixed with ambient air, i.e., a dilution tunnel. Originally the construction of such an equipment was devoted to the measurement of lead emissions from gasoline vehicles (*21,22*). However, the utility of the dilution tunnel has been extended, and it is now used in almost all measurements of automotive emissions, especially for unregulated pollutants. A figure of a dilution tunnel and a brief description is given elsewhere in this issue (*2*).

Another approach to the sampling of PAH was published by Newhall et al. (*23*). After dilution of the exhaust, not in a dilution tunnel, but rather in a small tube (0.1 × 5 m), approximately 10% of the exhaust/air mixture was taken through two condensers in series, followed by a scrubbing tower and reaching finally an absolute filter. Recovery studies of radioactive BaP added to the exhausts showed a yield better than 90%, and the authors emphasized that the trapping at subambient temperatures should minimize degradation processes. Analytical data refer to BaP and BaA, and the findings indicated that the PAH emission was influenced by fuel aromaticity as well as of PAH content of the fuel and lube oil. The emissions reported are summarized in Table 9.

As mentioned previously, the dilution technique has now become ubiquitous at measurements of unregulated pollutants. Although the technique has been used for a number of years, only limited data are available on measurements of PAH and related components. We have only found a few papers which report PAH emission from transients cycles, especially from gasoline fueled vehicles. Some of the results are summarized in Tables 10 and 11.

Table 8. PAH in test fuel.[a]

	PAH concn, ppm	Fuel input, μg/km
CpcdP	≤ 0.01	1
BaA	5.2	520
BaP	0.9	90
BghiP	3.7	370
Coronene	≤ 0.01	1

[a]Data of Stenberg (*20*).

Table 9. Emissions obtained from FTP (includes both cold and hot start).

Vehicle	Emissions, μg/km		
	Vehicle A[b]	Vehicle B[b]	Vehicle C[b]
BaA	38	20	5
BaP	12	7.5	3.3

[a]Data of Newhall et al. (*23*); condensation before filter.
[b]A = vehicle 1969; B = vehicle 1970; C = vehicle 1972, equipped with air pump and exhaust reactor.

These values are somewhat lower, compared to results obtained from undiluted exhausts. However, they are definitely within the expected range. In a study from Ford (*26*) the BaP emission from a stratified charged engine is reported to be 0.9 μg/km. This emission was obtained from hot tests at constant speed of 50 km/hr.

Gas phase trapping is by definition trapping of components which are not retained by a Teflon membrane filter at a temperature not higher than 125°F. The enrichment methods employed have been either adsorbent trapping (*18,26*) or a cryo technique (*27,28*). Lee et al. (*26*) used XAD-2 traps on gasoline emissions, and found that a large portion of three-ring and four-ring PAH were present in the gas phase. They also reported problems with background from the adsorbent, probably due to degradation. A cryo technique has been briefly described (*27*) consisting of two washing flasks immersed in liquid nitrogen, and the authors concluded that five-ring PAH and larger molecules were adsorbed to 100% on particles from gasoline emissions. The other analyzed species (anthracene, fluoranthene, and pyrene) predominated in the gas phase. A cryo technique has also been used by Handa et al. (*15*), but no information is given of the relative distribution of gas phase and particle-associated PAH.

A gas-phase trapping system which can be used both on diluted and undiluted exhausts is described elsewhere in this issue (*28*). The system contains three condensers (ice/water, CO_2/ethanol and liquid nitrogen), and it has been shown that compounds like phenanthrene and pyrene are present to more than 50% in the gas phase after dilution of gasoline exhausts. The significance of PAH in the gas phase will be discussed later, and some comparison with ambient air concentrations will be presented.

Parameters Which Influence the Emission

Accumulation of PAH in Oil

PAH from the gasoline and from the combustion will be enriched in the oil (*8,16,29*). Experiments have shown that fresh oil with "virtually no" PAH at start will increase its content of BaP by three orders of magnitude during normal use for 10,000 km (*29*). Handa and co-workers (*30*) showed a correlation between PAH emission and oil consumption, and the emissions increased with mileage of the oil.

PAH Content of Fuel

The origin of the PAH found in automobile exhausts has been investigated by several authors (*8,27,31,32*). All results are not consistent, but some conclusions can be drawn.

The input of PAH with the fuel exceeds by far the emission with the exhausts. Addition of C_8–Cl_{10} aromatics in the form of catalytic reformate leads to increased PAH emissions. Whether this is a func-

Table 10. Emission obtained from FTP.[a,b]

	Emissions, μg/km					
	Diesel		Gasoline		Gasoline, catalyst	
	A[c]	B[d]	A[c]	B[d]	A[c]	B[d]
Pyrene	15	ND[e]	8	ND[e]	0.7	ND[e]
BaP	0.5	3.9	3	3.2	0.1	< 0.1
6 NO_2-B(a)p	< 0.1	ND[e]	0.9	ND[e]	< 0.1	ND[e]
1 NO_2-Pyrene	2	ND[e]	0.1	ND[e]	< 0.1	ND[e]

[a]Data of Williams and Swarin (*25*) and Gibson (*24*).
[b]Only particulate emission from dilution tunnel.
[c]A = Gibson, one vehicle, hot start.
[d]B = Williams and Swarin. Diesel: mean value of two vehicles; gasoline: mean value of seven vehicles, Gasoline catalyst: mean value of four vehicles, cold start.
[e]ND = not determined.

tion of aromaticity as such, or of high levels of PAH in the reformate is not clear.

Addition of a certain PAH to a test fuel will give an increased emission of this component. High levels of PAH in the fuel will create larger deposits of these in the combustion chamber and exhaust system. This must be taken into account if measurements of different fuels are considered. "Carry-over" effects can make it impossible to distinguish any difference in the emission between low and high PAH level fuels.

Comparison between Differently Fueled Vehicles

Due to an increasing interest of alternative fuels in Sweden, this laboratory in co-operation with the Swedish Motor Fuel Technology Co and Air Pollution Research Laboratory at Studsvik, Motor Vehicle Section has conducted an investigation on the PAH emission from different vehicles and fuel combinations (*33*). The samples were taken in a dilution tunnel and consisted of both particulates and gas phase. The particulate emission was also screened for mutagenicity according to Ames (*34*). These results are in part described elsewhere in this issue (*35*).

The investigated fuels were as follows: diesel fuel, standard gasoline, leaded and unleaded, alcohol-blended fuels (15% methanol or 23% methanol) and finally LPG liquefied petroleum gas) and 95% methanol (5% isopentane). In addition some engine modifications, such as different compression ratios and "lean burn combustion" were tested with emission control devices, e.g., different catalyst systems. We will here briefly summarize some of the PAH emission data. The comprehensive results from this investigation will be published elsewhere (*36*).

The fuels can roughly be divided into three groups regarding the mean emission level (filter sampling only, diluted exhausts). (1) diesel Σ PAH_{15} 500–1000 μg/km, BaP $\simeq$ 10 μg/km; (2) gasoline, M15, E23 Σ PAH_{15} 35–170 μg/km, BaP = 0.5–5.5 μg/km; (3) M95, LPG Σ PAH_{15} 2–9 μg/km, BaP $\leq$0.1 μg/km. The "total PAH" represents 15 components as given in Table 11 and includes particle-associated PAH only.

For vehicles fueled with LPG and neat methanol, the emission of PAH is drastically reduced compared to standard gasoline vehicles. The emission when using these fuels is in the same order of magnitude as for catalyst equipped vehicles.

The difference in the "total" PAH emission between gasoline and diesel emission is mainly due to a larger portion of lower molecular weight PAH from the diesels. These substances are substantially more particle associated in the diesel emission as compared to gasoline exhausts. For compounds such as phenanthrene and pyrene it is not sufficient to use only a particulate sample from gasoline emissions. Phenanthrene is to more than 90% in the gas phase after dilution, and the corresponding value for pyrene is approximately 50%. For diesel emissions approximately 50% of phenanthrene and 10% of pyrene will be in the gas phase.

Table 11. Emissions from FTP, cold start.[a,b]

	Emissions, μg/km			
	Gasoline	Gasoline, catalyst	Gasoline M15[c]	Diesel
Phenanthrene	1.7	0.06	2.3	223
Fluoranthene	12.0	0.07	3.3	210
Pyrene	20.0	0.2	6.3	263
BghiF[d]	6.9	0.07	4.7	48
CPcdP	4.5	0.06	3.2	3.4
BaA	6.2	0.06	2.0	34
Chrysene	6.9	0.2	2.5	46
BbkF[e]	6.8	0.4	3.0	37
BeP[f]	5.5	0.3	3.2	33
BaP	1.7	0.1	1.1	11
IndP[g]	1.3	0.3	1.7	14
BghiP	3.9	0.7	5.2	22
Coronene	1.7	0.8	4.4	12

[a]Data of Egebäck (*36*).
[b]Only particulate sample from dilution tunnel. Mean value from three tests; diesel two tests.
[c]Gasoline blended with 15% methanol.
[d]BghiF = Benzo(ghi)fluoranthene.
[e]BbkF = Benzo(b and k)fluoranthene.
[f]BeP value includes also benzo(cd)pyrenone.
[g]Ind P = Indeno (1,2,3-cd)pyrene.

Possible Reactions of Gaseous PAH

The occurrence of pyrene in the gas phase after dilution opens some aspects of its fate when it is emitted into the atmosphere. It is well documented that some nitroderivatives of pyrene are extremely potent mutagens, as described elsewhere in this issue (*37*). Sampling in a dilution tunnel (according to the *Federal Register*) does not reflect real outdoor conditions, however. The temperature in the tunnel is approximately 30–40°C, which during most conditions will prevent the dew point of water from being reached. Consequently, the particles will not adsorb as much water as they would with a lower temperature and the formation of water droplets will also be lower. The condensed water from automobile exhausts is acidic (pH 2-4), most likely due to nitric and nitrous acids. Pitts has shown that vehicle exhausts contain both HNO_2 and HNO_3 (*37*). This acid precipitation could contribute to the anticipated formation of nitrated species and this aspect should be considered if the temperature is lowered below the dew point of water.

Condensation techniques for the enrichment of gaseous components in automobile exhausts will produce acidic solutions, and most likely this will also occur in the atmosphere when condensation takes place on the ambient particles. Nitration of polycyclics in water solutions can rather easily be performed during experimental conditions (*37,38*). However, very little is known about whether there is a corresponding nitration process in ambient air. The detected amount of nitrated polycyclics in ambient air is low (*24,39*), and it may be questioned whether these are formed during the sampling procedure. Doubt has also been raised in the case of sampling automobile exhausts, especially for condensation processes (*2,40*): i.e., the mutagenicity found downstream of filter samples taken from a dilution tunnel could be attributed to compounds formed in the condensate and actually not occurring in the emission.

Work is under progress in our laboratory in collaboration with the Division of Toxicology Genetics at Wallenberg Laboratory to identify mutagenic species found in the gas-phase condensates. The question whether these compounds are sampling artifacts must be considered in view of that standard sampling in a dilution tunnel prevents precipitation of acids and only reflects what will be adsorbed on the particles during favourable conditions. Research in this field with different dilution temperatures and ratios is strongly needed, especially in conjunction with biological tests and analytical chemistry with fingerprint capability.

Gaseous Emissions of Some Selected Components

All previously mentioned data of the emission from vehicles involved only polycyclics of which the major part is associated to the particle emission. However, a vast amount of the emission from vehicles belong to a lower molecular range MW $\leq$ 150, and are either combustion products or unburnt fuel. These substances are gaseous under normal ambient conditions. They are mostly hydrocarbons, i.e., olefins, aromatics or aliphatics but minor parts are oxidized compounds such as aldehydes, phenols, and carboxylic acids. It is beyond the scope of this paper to list all components, but some of these gaseous components might be of significant interest due to their health effects. In Table 12 some components are listed with their expected emission ranges.

Regarding specially fueled vehicles such as methanol or ethanol, especially oxidized species should be expected, but also products from reaction with nitrogen oxides. Methyl nitrite, however, has also been determined in the emissions from vehicles using ordinary gasoline. This is not the case for ethyl nitrite, which was found only in the emissions from the ethanol blended fuel. Vehicles using a 95% methanol/5% isopentane blend have a substantial emission of MeONO (5 mg/km) and MeOH, (3-4 mg/km). The emission of formaldehyde from alcoholic fuels is also increased compared to ordinary gasoline (*41*).

Fingerprint Analysis of Source and Recipient

Recent development of capillary gas chromatography has facilitated the separation of PAH and PAH derivatives with an improved resolution, and with this technique it is possible to obtain a "finger-

Table 12. Emissions obtained from FTP, cold start.[a]

	Gaseous emissions, mg/km	
Vehicle	Gasoline	Gasoline, catalyst
Benzene	50–100	1–10
Toluene	100–200	2–20
Ethylene	100	10
Propylene	50	5
Me-ONO[b]	100–150	30–50
Et-ONO[c]	400–600	ND

[a]Data of Egebäck (*36*).
[b]Me-ONO = Methyl nitrite, μg/km.
[c]Et-ONO = Ethyl nitrite, μg/km. Note: emission only found from vehicle using gasoline blended with 23% ethanol.

print" of the emission of interest. Figures 1 and 2 give examples of typical gas chromatograms from gasoline exhausts and ambient particulate matter. Elsewhere (*42*), PAH emission profiles from other sources are illustrated. A large number of components can be separated, and the relative concentrations of specific components are used to trace the emission source. As previously concluded, a predominant part of the PAH with molecular weights ≥ 226 are associated with the particle phase.

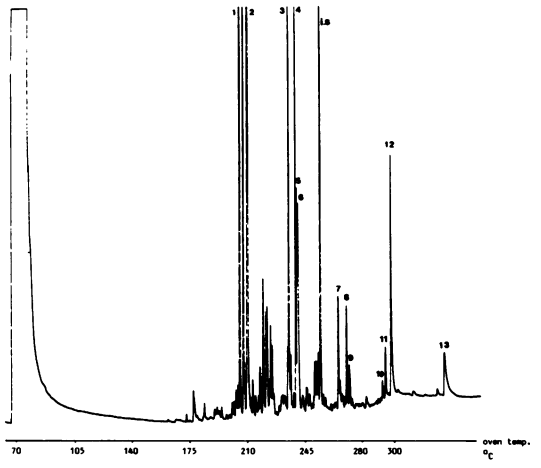

FIGURE 1. Capillary gas chromatogram of PAH fraction (MW ≥ 202) from gasoline automobile exhausts. Gas and particulate phase, condensation before filter. Sample clean-up: liquid/liquid extraction with dimethylformamide-water (9:1) and cyclohexane, silica gel chromatography, solid phase deactivated with 10% water, eluted with cyclohexane, finally Sephadex LH-20 gel chromatography, elution with isopropanol. Peak assignments: (1) fluoranthene; (2) pyrene; (3) benzo(ghi)fluoranthene; (4) cyclopenteno(cd)pyrene; (5) benzo(a)anthracene; (6) chrysene; (7) benzo(b,k)fluoranthene; (8) benzo(e)pyrene; (9)benzo(a)pyrene; (10) indeno(1,2,3-cd)-fluoranthene; (11) ideno (1,2,3-cd)pyrene; (12) benzo(ghi)-perylene; (13) coronene; IS = internal standard (β, β-binaphthyl).

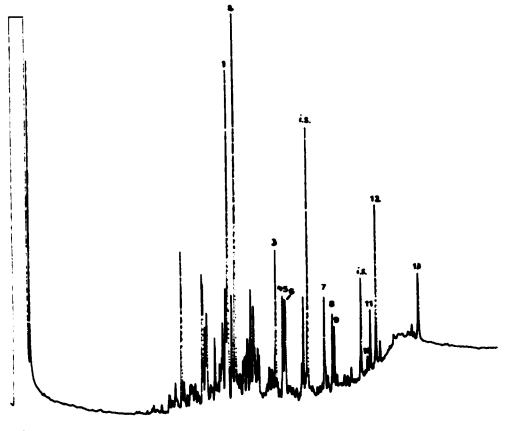

FIGURE 2. Capillary gas chromatogram of PAH fraction from airborne particulate matter from downtown Stockholm. Sample clean-up as in Figure 1, but without Sephadex LH-20 gel chromatography. Peak assignments as in Fig. 1. IS = internal standard (β, β-binaphthyl and *p*-quarterphenyl).

Although PAH will undergo atmospheric reactions, as has been demonstrated elsewhere in this issue (*38,43*), it is still possible to recognize typical emission patterns. The approach to use gas chromatographic profiles is exemplified in Figure 3. The amounts are given on a relative basis [benzo(e)pyrene = 1], in order to obtain comparative figures. The amount of three- and four-ring PAH found in the gaseous state in the atmosphere has been investigated (*44–46*), and a conclusion is that phenanthrene, anthracene, fluoranthene and pyrene are more than 50% in the gas phase. For other four-ring PAHs, such as benzo(a)anthracene and chrysene, the amount found in the gas phase is lower; 10-15% is reported. Handa et al. (*44*) found experimentally that the amount of these "volatile" PAH in the gas phase was dependent of the flow rate of the sampling system. This was pronounced for four-ring PAHs and the phenomenon might be due to evaporation from the retained particles in front of the gas trapping system. Figure 3 demonstrates that the

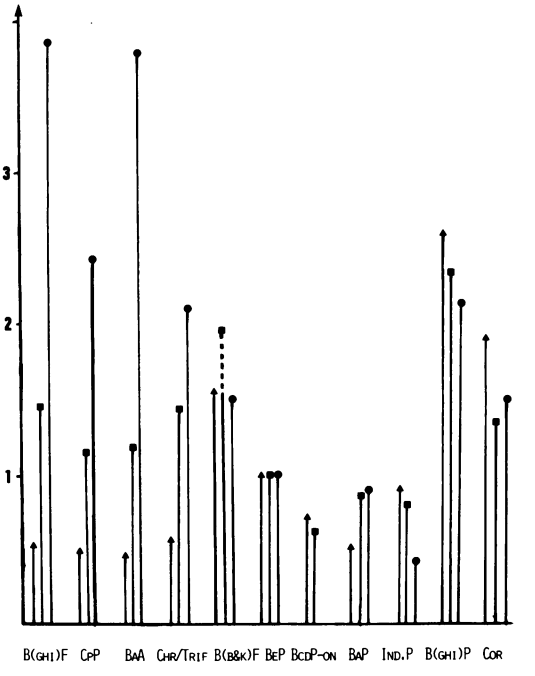

FIGURE 3. PAH profile from airborne particles and automobile exhausts: (▲) S:t Eriksgatan, temperature 20°C, LIB sampler, 250 m^3, 16 hr, n = 12; (■) Norra Stationsgatan, temperature 0°C, hi-vol sampler, 200-400 m^3, 3-6 hr, n = 7; (●) automobile exhausts from gasoline vehicles, gas and particulate phase, condensation before filter, n = 31.

pattern of PAH with MW ≥ 252 is similar for particles from automobile exhausts and ambient air. However, since the automobile exhausts sample also contains gas phase, there is a poor correlation between more volatile PAH which are not exclusively associated to the ambient air particles.

Conclusions

Emission rates of PAH have been determined by several investigators during the past 30 years. These substances are associated with both particulate and gaseous emissions, and they are considered to be partly responsible for the carcinogenic/mutagenic properties of vehicle emissions. Many of these early investigators focused the interest on one or a few specific components; and benzo(a)pyrene (BaP) is the most frequently analyzed.

The emission of PAH is dependent on several factors. Among these are: air/fuel ratio (a fuel-rich combustion increases the emission), starting temperature of the engine which affects the A/F ratio and emission control devices. Driving conditions seem to have little effect, while mileage of the engine is of importance, essentially due to an increased oil consumption.

Some emission factors can be given. These values refer only to light duty vehicles equipped with standard engines. For gasoline vehicles, 1-10 μg BaP/km; for gasoline vehicles with a catalyst, 0.1-1 μg BaP/km; for diesel vehicles, 1-10 μg BaP/km. During cold periods (<0°C), an increased emission should be expected, more pronounced for gasoline vehicles, by a factor of approximately five times. This effect occurs during the first 3-4 km.

Alcohol blended fuels do not seem to have a significant influence on the PAH emission, while high aromaticity of the fuel may lead to an increased emis sion of PAH, probably due to a corresponding increase of the PAH content of the fuel.

For gaseous components, which may either be directly harmful for the health, such as benzene, or via atmospheric reactions produce biologically active components, such as olefins, the following emission factors for gasoline vehicles could be estimated: benzene, 50-150 mg/km; benzene (catalyst), 1-10 mg/km; ethylene, 50-100 mg/km; ethylene (catalyst), 5-10 mg/km. Here "catalyst" refers to new catalyst, three-way/closed loop.

Derivatives of PAH and heterocyclics is of special importance with reference to diesel vehicles. Among these are oxidized components such as ketones, quinones, anhydrides, acids and aldehydes, as well as sulfur- and nitrogen-containing polycyclics. The emission of these constituents are not determined as completely as PAH, but some preliminary data can be given. These values are based on weight measurements from HPLC separation of a particulate extract. Data are reported for the aromatic fraction which contains three rings or more (*47*): PAH, 10%; oxy-PAH, 19%; heterocyclics + acids, 71%.

REFERENCES

1. Clar, E. Polycyclic Hydrocarbons, Vol. 1, Academic Press, New York-London, 1968.
2. Schuetzle, D. Sampling of vehicle emissions for chemical analysis and biological testing. Environ. Health Perspect. 47: 65-80 (1983).
3. Anonymous. Ermittlung polyzyklischer aromatischer Kohlenwasserstoffe im Automobileabgas in Abhängigkeit von Motorkoncept und Fahrzustand, VW-report UB-II, 2-334, 62-10/75, Wolfsburg 1975.
4. Kotin, P., Falk, H. L., and Thomas, M. Aromatic hydrocarbon II. Presence in the particulate phase of gasoline engine exhausts. Arch. Ind. Hyg. Occup. Hyg. 9: 164-177 (1954).
5. Mittler, S., and Nicholson, S. Carcinogenicity of atmospheric pollutants, Ind. Med. Surg. 26: 135-138 (1957).
6. Stenburg, R. L., von Lehmden, D. J., and Hangebrauck, R. P. Sample collection techniques for combustion sources—benzopyrene determination. Am. Ind. Hyg. Assoc. J. 22: 271-275 (1961).
7. Begeman, C. R., and Colucci, J. M. Apparatus for determining the contribution of the automobile to the benzene-soluble organics in air. National Cancer Inst. Monograph, 9: 17-57 (1962).
8. Gross, G. P. Gasoline composition and vehicle gas polynuclear aromatic content. CRC-APRAC project CAPE-6-68, July 30, 1972.
9. Hangebrauck, R. P., Lauch, R. P., and Meeker, J. E. Emissions of polynuclear hydrocarbons from automobiles and trucks. Am. Ind. Hyg. Assoc. J. 1: 47-56 (1966).
10. Grimmer, G., Hildebrandt, A., and Böhnke, H. Sampling and analytics of polycyclic aromatic hydrocarbons in automobile exhaust gas: 1. Optimization of the collecting arrangements. Zbl. Bakt. Hyg., I. Abt. B158: 22-34 (1973).
11. Anonymous. Daimler Benz Report no EB 740366, Stuttgart, Sept. 1974.
12. Grimmer, G., and Hildebrandt, A. Assessment of the contribution of passenger cars to air pollution by carcinogenic polycyclic hydrocarbons, Zbl. Bakt. Hyg., I. Abt. B161: 104-124 (1975).
13. Kraft, J., and Lies, K. H. Polycyclic aromatic hydrocarbons in the exhausts of gasoline and diesel vehicles. Society of Automotive Engineers, Warrendale, PA, 1981, paper no. 810082.
14. Anonymous. Emission of PAH, reactive and non-reactive hydrocarbons and aldehydes from current production cars, Fiat 1980, Accordo di Ricerca Feemas 13/80.
15. Handa, T., Yamamura, T., Kato, Y., Saito, S., and Ishii, T. Determination of predominant factors of PAH emissions from gasoline engine vehicles in ordinary city service. J. Japan. Soc. Air Pollut. 14: 464-473 (1979).
16. Handa, T., Yamamura, T., Kato, Y., Saito, S., and Ishii, T. The effect of automotive operating conditions on polynuclear aromatic hydrocarbon emissions. J. Japan Soc. Air Pollut. 14: 334-339 (1979).
17. Chipman, J. C., and Massey, M. T. Proportional sampling system for the collection of an integrated auto exhaust gas sample. J. Air Pollution Control Assoc. 10: 60-61 (1960).
18. Spindt, R. S. First Annual Report on Polynuclear Aromatic

Content of Heavy Duty Diesel Engine Exhausts Gases. Gulf Research and Development Co., CAPE-24-72, July 1974.
19. Stenberg, U., Alsberg, T., and Bertilsson, B. M. A comparison of the emission of polynuclear aromatic hydrocarbons from automobiles using gasoline or a methanol/gasoline blend. Society of Automotive Engineers, Warrendale, PA, 1981, Paper no. 810441.
20. Stenberg, U. The emission of polynuclear aromatic hydrocarbons from gasoline powered vehicles. Report to the Swedish EPA, February 1, 1979.
21. Habbi, K. Characterization of particulate lead and vehicle exhausts-experimental techniques. Environ. Sci. Technol. 4: 239-259 (1970).
22. Habbi, K. Characterization of particulate matter in vehicle exhausts. Environ. Sci. Technol. 7: 223-234 (1973).
23. Newhall, H. K., Jentoft, R. E., and Ballinger, P. R., The effect of unleaded fuel composition on polynuclear aromatic hydrocarbon emissions, Society of Automotive Engineers, Warrendale, PA, 1981 paper no. 7308334.
24. Gibson, T. L. Nitroderivatives of polynuclear aromatic hydrocarbons in airborne and source particulate. Atmos. Environ. 16: 2037-2040 (1982).
25. Williams, R. L., and Swarin, S. J. Benzo(a)pyrene emissions from gasoline and diesel automobiles. Society of Automotive Engineers, Warrendale, PA, 1981 paper no. 790419.
26. Lee, F. S.-C., Prater, T. J., and Ferris, F. PAH emission from a stratified-charge vehicle with and without oxidation catalyst: sampling and analysis evaluation. In: Polynuclear Aromatic Hydrocarbons, P. W. Jones and P. Leber (Eds.), Ann Arbor Science Press, Ann Arbor, MI, 1979, pp. 83-110.
27. Pedersen, P. S., Ingversen, J., Nielsen, T., and Larsen, E. Effects of fuel, lubricant and engine operating parameters on the emission of polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 14: 71-79 (1980).
28. Stenberg, U., Westerholm, R., Alsberg, T., Rannug, U., and Sundvall, A. Enrichment of PAH and PAH derivatives from automobile exhausts by means of a cryogradient sampling system. Paper presented at 6th International Symposium on PAH, Columbus, OH, Oct. 23-27, 1981.
29. Anonymous. Enflüsse der Betriebszeit des Motors sowie des Motorschmieröles auf die Emission von polyzyklischen aromatischen Kohlenwasserstoffe aus Kraftfahrzeugen mit Ottomotoren. DGMK Berichte 110, Hamburg, 1977.
30. Handa, T., Yamamura, T., Kato, Y., Saito, S., and Ishii, T. Factors analysis and derivation of an experimental equation on polynuclear aromatic hydrocarbons emissions from automobiles. Environ. Sci. Technol. 13: 1077-1081 (1979).
31. Candeli, A., Mastrandrea, V., Morozzi, G., and Toccaceli, S. Carcinogenic air pollutants in the exhausts from an European car operating on various fuels. Atmos. Environ. 8: 693-705 (1974).
32. Candeli, A., Morozzi, G., Paolacci, A., and Zoccolillo, L. Analysis using thin layer and gas liquid chromatography of polynuclear aromatic hydrocarbons in the exhausts products from an European car running on fuel containing a range of concentrations of these hydrocarbons. Atmos. Environ. 9: 843-849 (1975).
33. Research program initiated by a Swedish Governmental Committee.
34. Ames, B. N., McCann, J., and Yamasaki, E. Methods for detecting carcinogens and mutagens with the *Salmonella*/mammalian-microsome mutagenicity test. Mutat. Res. 31: 347-364 (1975).
35. Rannug, U. Data from short-term tests on motor vehicles. Environ Health Perspect. 47: 000-000 (1982).
36. Egebäck, K. E. (Ed.). Chemical and Biological Characterization of Vehicle Exhaust Emissions, When Using Different Engine/Fuel Combinations. National Swedish Environment Protection Board, Stockholm, Dec. 1982.
37. Pitts, J. N., Jr. Formation and fate of gaseous and particulate mutagens and carcinogens in real and simulated atmospheres. Environ. Health Perspect. 47: 115-140 (1983).
38. Nielsen, T. A study of the reactivity of polycyclic aromatic hydrocarbons. Nordic PAH project, report 10, Oslo 1981.
39. Jäger, J. Detection and characterization of nitro derivatives of some polycyclic aromatic hydrocarbons by fluorescence quenching after thin layer chromatography: application to air pollution analysis. J. Chromatogr. 152: 575-578 (1978).
40. Stump, F., Bradow, R., Ray, W., Dropkin, D., Zweidinger, R., Sigsby, J., and Snow, R. Trapping gaseous hydrocarbons for mutagenic testing, EPA, Research Triangle Park, Draft copy, Oct. 1981.
41. Jonsson, A., and Persson, K. Analysis of alcohols and alkylnitrites. In: Chemical and Biological Characterization of Vehicle Exhaust Emissions when Using Different Engine/Fuel Combinations, K. E. Egebäck (Ed.), National Swedish Environment Protection Board, Stockholm, Dec. 1982.
42. Stenberg, U., Alsberg, T., Blomberg, L., and Wännman, T. Gas chromatographic separation of high molecular PAH in samples from different sources, using temperature-stable glass capillary columns. In: Polynuclear Aromatic Hydrocarbons, P. W. Jones and P. Leber (Eds.), Ann Arbor Science Press, Ann Arbor, MI, 1979, pp. 313-326.
43. Lindskog, A. Transformation of polynuclear aromatic hydrocarbons during sampling. Environ. Health Perspect. 47: 81-84 (1983).
44. Handa, T., Kato, Y., Yamamura, T., and Ishii, T. Correlation between the concentration of polynuclear aromatic hydrocarbons and those of particulates in an urban atmosphere. Environ. Sci. Technol. 4: 416-422 (1980).
45. Cautreels, W., and van Cauwenberghe, K. A. Experiments on the distribution of organic pollutants between airborne particulate matter and the corresponding gas phase. Atmos. Environ. 12: 1133-1141 (1978).
46. Thrane, K. E., and Mikalsen, A. High volume sampling of airborne polycyclic aromatic hydrocarbons using glass fibre filters and polyurethane foam. Atmos. Environ. 15: 909-918 (1981).
47. Lee, F. S.-C., and Schuetzle, D. Sampling, extraction and analysis of PAH from internal combustion engines. In: Handbook of PAH, A. Björseth (Ed.), Marcel Dekker, New York, in press.