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Polycyclic aromatic hydrocarbons in the occupational environment

With special reference to benzo[a]pyrene measurements in Swedish industry

by Gösta Lindstedt, PhD, Jan Sollenberg, PhD ¹

LINDSTEDT G, SOLLENBERG J. Polycyclic aromatic hydrocarbons in the occupational environment: A review with special reference to benzo[a]pyrene measurements in Swedish industry. *Scand j work environ health* 8 (1982) 1—19. A review is given of measurements of polycyclic aromatic hydrocarbons (PAH) in the work environment in general with emphasis upon Swedish measurements of benzo[a]pyrene not previously published in international literature. Finally, epidemiologic investigations on PAH-exposed workers, as well as threshold limit values for PAH, are discussed.

Key terms: coal tar pitch volatiles exposure, epidemiology, threshold limit values.

During recent decades, much attention has been focused on polycyclic aromatic hydrocarbons (PAH) in the environment. The main reason for this interest is the carcinogenic activity displayed by some PAH. PAH are supposedly responsible in part for a cancer frequency that is higher for smokers than nonsmokers, higher for urban populations than rural populations, and higher for some groups of workers than for the general population (33). The first chemical substance of known constitution shown to be a carcinogen was a PAH component, dibenzo [a, h] anthracene (17). Coal tar was shown to be carcinogenic to animals about 1915, and in 1933, a pure carcinogen, benzo[a]pyrene (BaP), was isolated from tar by Cook et al (16). Since then, thousands of papers have been published about the occurrence, formation, biochemistry, and toxicology of PAH. Several review articles on the PAH prob-

lem are available (27, 38).

PAH are formed by the incomplete combustion or pyrolysis of organic material. Such procedures always lead to a mixture of a large number of products. Among the PAH, compounds with three or four aromatic rings dominate. The carcinogens, however, are to be found among the higher PAH, mainly those with five or six rings. One of these (BaP) has been the subject of much more study than all the others. It is the most frequent of the carcinogenic PAH, and analytical methods for its determination have been available for a long time.

PAH are widely distributed in the environment, the main sources being industrial activities such as coking and the combustion of carbonaceous materials. In cities, exhaust gases from combustion engines contribute to the PAH pollution of the air. Natural sources are forest fires and volcanoes (10).

Since the 1950s the results of numerous investigations on the occurrence of PAH in the environment have been published. The highest content of PAH is to be found in occupational atmospheres. Even in in-

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dustrial areas, outdoor air contains two or three magnitudes less PAH than some workplaces, eg, coke works. Surprisingly enough, rather few investigations of PAH in work atmospheres were carried out before 1970 in comparison to the number of investigations concerning outdoor air. Since then, however, the number of investigations on PAH in occupational environments has steadily increased.

Many of the field investigations on PAH, especially the earlier ones, have been limited to BaP. In later years, more sophisticated methods of analysis, especially glass capillary gas chromatography, have made possible a simultaneous determination of a large number of PAH (50 or more) in air samples from work atmospheres.

In Sweden BaP determinations in the occupational environment were started in the early 1960s by Gerhardsson. Thus far many thousands of air samples have been analyzed for BaP, but data about other PAH are still lacking in Sweden. In Norway, some very extensive PAH studies have been published from aluminum works (5), coke plants (6), iron works (7), and other industries.

This review was written to give a summary of the BaP determinations in Swedish workplace atmospheres during a 15-a period, and to compare them with similar investigations of BaP and PAH in general in other countries.

In addition some epidemiologic investigations of PAH-exposed workers have been discussed, as well as different threshold limit values for PAH exposure. A more-detailed review has already been published in Swedish (50).

Sources of polycyclic aromatic hydrocarbons in the work environment

The most important sources of PAH emission in the work environment are coal tar and pitch. In many industrial processes these products are heated to high temperatures, and the PAH are vaporized. The lower PAH have a considerable vapor pressure at ordinary temperatures and essentially remain in the vaporized state. The higher PAH, however, soon condense to a solid state again. These PAH are

often adsorbed on the surface of soot particles that are generated simultaneously.

Important industrial processes in which coal tar is evaporated include coking or gas production (essentially the same process), roofing or tar-insulating work, electrolysis with so-called Söderberg or self-baking electrodes (for production of aluminum or steel), the making of graphite electrodes from pitch and other materials, and the pouring of molten iron or steel through runners or into molds covered with tar-containing preparations.

In other processes PAH are generated on the spot by pyrolysis, above all in combustion engines. Work atmospheres with air contaminated by motor-exhaust gases generally have a much lower content of PAH than those in which tar is evaporated.

Skin exposure to PAH, often in combination with air exposure, occurs in some professions. Many oils contain PAH, especially the crude oils used as lubricants many years ago. Modern, refined oils are much poorer in PAH and thus less carcinogenic. But sometimes PAH can accumulate in oil during use. For example, up to 10 mg of BaP per kilogram of oil has been found in used motor lubrication oil (81). A great part of a person's body may be exposed to oil if clothes become contaminated.

Sampling and analysis

For the sampling of higher PAH in the air, different types of filters are generally used. Glass fiber or silver membrane filters are preferred, since they are suited for solvent extraction or vacuum sublimation (58).

The lower PAH (three or four rings) have a considerable vapor pressure at ordinary temperatures. For sampling these substances, a wash bottle filled with a solvent must be connected in series with the filter. The losses of higher PAH, such as BaP, on filters are rather small (15).

To liberate PAH from the dust collected on filters, solvent extraction is generally used. Long-time extraction in a Soxhlet apparatus was preferred in earlier investigations, but later ultrasonic treatment in cold solvents was found to be more rapid and effective (14).

In place of extraction, vacuum sublimation of the material collected on the filter can be used at least for higher PAH such as BaP. This method needs only minute amounts of solvent to dissolve the sublimate, and therefore concentrating the solution is unnecessary. It is quick, and is a purification step in itself.

In many cases, the determination of individual PAH is not needed or wanted. Nonspecific methods of analysis, such as weighing the benzene extract after evaporation to dryness in a vacuum, are used for a general estimation of the overall PAH exposure. Such a procedure is the official method for determining coal tar pitch volatiles (CTPV), upon which the threshold limit value (TLV) for PAH exposure is based in the United States (20).

If individual PAH are to be determined analytically, separation of the very complex mixture in the extract is generally carried out by chromatographic methods. Nowadays, gas or high pressure liquid chromatography (HPLC) are preferred. In early works, paper or thin-layer chromatography (TLC) was used. The latter method is rather convenient if complete separation is not required. Individual PAH on TLC plates are generally quantitated with fluorimetry, either directly on the plate or in solution after elution from the plate. The most detailed and characteristic fluorescence spectra of PAH are obtained in alkane solutions at 77 K (Shpol'skii effect) (23).

In the Swedish studies of BaP in different work atmospheres, the methods of sampling and analysis have changed during the last 15–20 a. Initially, short-time sampling on large filters, followed by benzene extraction and separation by column and paper chromatography, was used. BaP was quantitated with fluorimetry in a sulfuric acid solution according to Sawicki et al (72). Directly after the extraction, the benzene extract was evaporated and weighed and thus provided a rough estimate of the CTPV. Later collection on small (37-mm) filters and separation by thin-layer chromatography, as described by Schaad (73), were introduced. Finally, in 1975 vacuum sublimation of the dry filter was substituted for extraction, and

the recovery of BaP was determined with the isotope dilution technique (77).

Benzo[a]pyrene and polycyclic aromatic hydrocarbons in different workplace atmospheres

Gas and coke works

In gas and coke works large amounts of PAH are released from the ovens in which coal is pyrolyzed. The workers in the vicinity of the ovens are highly exposed to these PAH. Most investigations of PAH in the work environment have been made in gas and coke works. In most cases, only BaP has been analyzed, but there are also some investigations available on a number of other PAH.

Generally, the mean BaP content in the air above the ovens is below $10 \mu\text{g}/\text{m}^3$, as found by Kreyberg (44), Lawther et al (47), Tanimura (79), Petrova (61), and Jackson et al (34), and as reported by the British Coke Research Association (12). Mašek (53) reported higher BaP figures in four Czechoslovakian coke works, in some cases up to $32 \mu\text{g}/\text{m}^3$, on the average, in the close vicinity of the coke ovens. At pitch batteries still higher BaP contents were found, up to $40 \mu\text{g}/\text{m}^3$.

In Sweden, BaP measurements were made at a city gas works in 1964 and at two coke works in 1976 and 1977 (50). At the gas works, the mean of 134 1-h samples was $4.3 \mu\text{g}/\text{m}^3$ (maximum 33) at the top of the ovens and $0.15 \mu\text{g}/\text{m}^3$ (344 samples) 25 m from the ovens. Oven top means at the two coke works were 13.5 and $9.4 \mu\text{g}/\text{m}^3$. Three larry drivers were exposed to levels of 17, 4.7, and $5.2 \mu\text{g}/\text{m}^3$. All city gas works in Sweden are now closed. Only the two coke works remain.

In a German coke works, Thielen (80) found a high BaP content on and under the larry. The median value of 28 samples was $25 \mu\text{g}/\text{m}^3$ (range 8–78 $\mu\text{g}/\text{m}^3$). On the roof of the ovens, the median of 10 samples was $23 \mu\text{g}/\text{m}^3$ (range 2–40 $\mu\text{g}/\text{m}^3$). In the vicinity of the coke battery, the BaP concentration never exceeded $7 \mu\text{g}/\text{m}^3$. The air above the flues and the tar precipitator was extremely rich in BaP, up to concentrations of $500 \mu\text{g}/\text{m}^3$.

In 1978, Bjørseth et al (6) published a very detailed investigation on PAH in a

Norwegian coke plant. Stationary sampling showed the BaP concentration on the battery top to be 38 and 47 $\mu\text{g}/\text{m}^3$ in two series, respectively. The exposure of some workers was also investigated by personal air sampling. The highest values were found for the larry driver (12–43 $\mu\text{g}/\text{m}^3$), the wharfman (21 $\mu\text{g}/\text{m}^3$), and the jamb cleaner (20 $\mu\text{g}/\text{m}^3$). Other categories such as coke car operators, door cleaners, and push car operators had a lower degree of BaP exposure, in general below 5 $\mu\text{g}/\text{m}^3$.

Complete analyses of the PAH components were made in the Norwegian investigation by the aid of capillary gas chromatography. Volatile components were trapped with ethanol in a wash bottle in series with the filter. The entire PAH fraction was dominated by the most volatile members, such as naphthalene (40 %) and phenanthrene (about 20 %). The main components of the particulate fraction were fluoranthene, phenanthrene, pyrene, and anthracene. On the battery top, the sum of identified particulate PAH components in the air was 1.0–1.7 mg/m^3 . If this fraction is estimated to be 20 % of the benzene solubles (7), it would correspond to 5–9 mg of CTPV/ m^3 , whereas the TLV in the United States and other countries is 0.2 mg/m^3 . In personal sampling, the mean exposure of the worker operating the larry was found to be 0.37 mg of PAH/ m^3 .

The particle size distribution was also studied in the same investigation, and 99 % of the particles were $\leq 3 \mu\text{m}$. Consequently, almost the entire particulate fraction in the coke works atmosphere is respirable.

Jackson et al (34) determined the weight of the cyclohexane-soluble part of the particulates in a coke works. On the top of the ovens this fraction was 0.4–1.7 mg/m^3 . At two sampling stations on the top of the ovens, the respective BaP content of the cyclohexane-soluble fraction was 0.78 and 0.63 %, on the average.

Fannick et al (22) measured CTPV (CTPV = benzene solubles) in ten by-product coking industries in Pennsylvania; 319 personal samples were taken from 11 different categories of workers. The average was 2.08 mg/m^3 . The most exposed groups were lidmen (3.22 mg/m^3), tar chasers (3.14 mg/m^3), and larry opera-

tors (3.05 mg/m^3). Individual peak values of up to 18 mg/m^3 were found. Only 7.8 % of all the samples were below the TLV of 0.20 mg/m^3 .

In the investigations of the aforementioned Swedish gas works, the benzene-soluble fraction was evaporated to dryness and weighed. The average was 0.69 mg/m^3 ($N = 134$, maximum 7.6 mg/m^3). The mean content of BaP in this fraction was 0.62 %. Thus, in two independent investigations, the BaP content in the benzene or cyclohexane extract was found to be between 0.5 and 1.0 %.

It is evident that some of the workers in the gas and coke industry are exposed to PAH at rather high levels, even in modern installations. In industrialized countries, this industry has been working for more than 100 a, and a large number of workers have been exposed for many years. Epidemiologic investigations have shown an elevated risk of lung cancer for these workers. (See the section dealing with this subject.)

Iron and steel works

In the iron and steel industry there are operations other than coking which involve PAH exposure. In Sweden a series of BaP measurements has been made at blast furnaces, electric steel furnaces, open hearth furnaces, and some other places in steel works. The results are summarized in table 1.

In Japan, Tanimura (79) found BaP levels of 1.1–1.6 $\mu\text{g}/\text{m}^3$ at a blast furnace, 0.43–0.58 $\mu\text{g}/\text{m}^3$ at an electric steel furnace, 0.3 $\mu\text{g}/\text{m}^3$ at an open hearth furnace, and 0.2–0.3 $\mu\text{g}/\text{m}^3$ at a Bessemer converter. Close to the ingot molds for pig iron he found BaP concentrations of 0.7–0.8 $\mu\text{g}/\text{m}^3$. The highest level, 4.2 $\mu\text{g}/\text{m}^3$, was found at a rolling mill plant in winter (1.0 in summer). Thus the BaP levels found in Swedish and Japanese iron and steel works seem to be of the same magnitude.

Other PAH measurements have been published from a Norwegian iron works (7), where pig iron is produced in electric furnaces. Total PAH exposure was found to be 0.0017–0.093 mg/m^3 for the personnel tapping the ovens. All other workers were exposed to PAH levels that were

below 0.04 mg/m³. On the average, BaP was 7 % of all the PAH components of the particulate fraction. The composition of the PAH fraction from these iron works was rather similar to that from the Norwegian coke works.

Mašek & Neiser (54) analyzed dust which had been collected close to a blast furnace. On the average, they found BaP levels of 3.1 µg/g in the respirable fraction and 9.1 µg/g in the coarse fraction. If it is assumed that the total dust content was below the TLV (10 mg/m³), the BaP content would have been well below 0.1 µg/m³. Sometimes, however, the TLV for dust was exceeded.

Rondia (69) studied the PAH exposure of the workers spraying the inside of ingot molds for steel with a tar-containing product. In all, nine PAH components were determined. Very high contents of BaP (90–126 µg/m³) were found. To eliminate the strong PAH exposure, Rondia recommended substitution of the tar product by mineral oil.

In all, some workers in iron and steel works are exposed to PAH originating from coal tar products in contact with molten iron. Generally, however, the PAH exposure in these industries seems to be lower than in coke and gas works.

Aluminum works

Aluminum is manufactured in an electrolytic process in which a mixture of molten cryolite and alumina is electrolyzed at a

temperature of about 970°C. There are two types of anodes: the Söderberg anode and the graphite ("prebaked") anode. The former type, which is the most commonly used, is the main cause of PAH exposure in aluminum works. The Söderberg electrode consists of a mass containing coal-tar pitch and coke. During electrolysis it is graphitized ("baked") in its lower, hotter part and finally consumed by electrolytic oxidation to carbon oxides. Fresh electrode mass is added from above to keep the electrode running continuously. PAH components are liberated from the pitch at the high temperature, and they escape to the work area in spite of ventilation arrangements. The PAH exposure in aluminum works has been studied by several investigators. The results are summarized in tables 2–4.

The analyses of benzene-soluble particulates in table 2 are to be compared with the American TLV of 0.2 mg/m³. It is evident that this limit value is greatly exceeded for many workers in the aluminum industry. More-detailed PAH analyses, including the determination of PAH components other than BaP, have been carried out in some laboratories. Bjørseth et al (5) carefully identified and quantified more than 30 PAH and heterocyclic compounds by glass capillary gas chromatography. The major part of the PAH fraction by weight was always the volatile components (two to three rings), such as naphthalene, biphenyl, fluorene, and phenanthrene. The particulate fraction

Table 1. Benzo[a]pyrene in some Swedish iron and steel works (50).

Sampling site, year	Sampling time	Mean BaP (µg/m ³)
Two blast furnaces, 1969	~ 9 min	0.03–6.2 (means of 5 series, N = 224)
Two blast furnaces, 1976	1.5–4.2 h	0.88–1.7
Electric steel works, 1969	~ 9 min	0.44–2.4 (means of 3 series, N = 222)
Five electric steel works, 1976–1977		
Smelters ^a	2.5–6 h	0.02–0.52
Repairing of furnace walls ^a	2–6 h	0.1–4.9
Mold operators ^a	6–7 h	2.6
Open hearth furnace, 1977		
Smelters ^a	6–7 h	0.17
Crane operators ^a	6–7 h	0.58
Mold operators ^a	6–7 h	2.5

^a Personal air sampling.

seldom exceeded 10 % of the whole amount of PAH. In addition to BaP the carcinogens benzo[b] and [k] fluoranthenes (up to 123 $\mu\text{g}/\text{m}^3$) and benzo[c]phenanthrene (up to 77 $\mu\text{g}/\text{m}^3$) were found. In the Söderberg potroom, BaP was 3.1—6.6 % of the total particulate PAH in the stationary samples and 4.2—9.6 % of the total in the personal samples.

The figures of total PAH in table 3 were obtained by adding the individual PAH components determined by capillary gas chromatography, except for the personal samples from the prebaked anode plant,

which were analyzed by a liquid chromatography method. The total PAH fraction was estimated to be about 20 % of the benzene-soluble extract. The "PAH profile" was also studied by Bjørseth et al (5). The Söderberg plant was found to have a PAH mixture more rich in high-boiling components than that of the prebaked anode plant.

In a study of four American aluminum plants (76), a number of PAH were determined in one plant. The strongly carcinogenic benzo[b]fluoranthene was, in general, slightly superior to BaP by weight, and

Table 2. Benzene soluble particulates in aluminum plants.

Country, year	Type of electrodes	Sampling method	Coal tar pitch volatiles (mg/m^3)	Reference
Sweden 1968	Söderberg	Stationary	0.42	Lindstedt & Sollenberg (50)
1970	Söderberg	Stationary	0.14	
United States, 1974	Söderberg (Vertical)	Personal	Range for 11 categories of workers: 0.5—12.0 Tappers 12.0 Head pin setters 7.5	Schuler & Bierbaum (76)
	Söderberg (Horizontal)	Personal	Range for 13 categories of workers: 1.2—18.5 Flex raiser 18.5 Hijackers 17.0 Anode cranemen 17.5	
	Prebaked	Personal	Range of 3 categories of workers: 0.2—0.5	
Poland, 1977	Söderberg	Stationary Personal	0.49 0.65 Potmen 18	Adamiak-Ziemba et al (1)

Table 3. Total polycyclic aromatic hydrocarbons (PAH) in an aluminum plant, as found by Bjørseth et al (5).

Type of electrodes, sampling site	Sampling method	Mean PAH ($\mu\text{g}/\text{m}^3$)	
		Gaseous	Particulate
Vertical Söderberg Potroom	Stationary	972 (86.0—1,564)	99.9 (19.7—202)
			37.7
			927 2,790
Prebaked Potroom	Stationary	56.8 (4.6—124)	1.5 (1.3—1.7)
			0.87
			2.0
			0.87
			0.52
Crust breaker	Personal		

the less carcinogenic *k* isomer roughly half of the *b* isomer.

Extraction of metals (other than iron, steel and aluminum)

A few BaP analyses from Swedish metal industries are available (50). At a copper works, the mean BaP concentration of 14 samples taken in 1973–1974 was 7 $\mu\text{g}/\text{m}^3$. The origin of PAH must be tar preparations used to cover runners and ingot molds, as was found in the iron and steel works.

In an industry making alloys containing chromium and molybdenum, most samples had a low BaP content ($< 0.1 \mu\text{g}/\text{m}^3$), except in one place where tar-containing plugs were made. In the latter the BaP level was 2–4 $\mu\text{g}/\text{m}^3$.

In the making of chromium-iron alloys, Pokrovskaja & Shabynina (64) found BaP levels to be 0.6–1.5 $\mu\text{g}/\text{m}^3$. In the electrode manufacturing department, however, the concentration was 35.1 $\mu\text{g}/\text{m}^3$.

Foundries

The PAH exposure problems in foundries are principally the same as in the iron and steel industry, the main source being tar or pitch preparations coming into contact with molten metal. In 1969, the BaP level was determined in a Swedish iron foundry (50). Near the high-frequency furnaces, the mean of BaP in the air was 0.93 $\mu\text{g}/\text{m}^3$ (range 0.16–4.3). Eight 1-h periods were covered by 9-min samples. During the shaking-out, the mean was 2.1 $\mu\text{g}/\text{m}^3$ (range 0.15–11.4).

The Swedish Founders' Association has published a few BaP measurements from iron and steel foundries (78). Out of nine samples from an iron foundry and 18 samples from a steel foundry, all but one (0.12 $\mu\text{g}/\text{m}^3$) were $< 0.06 \mu\text{g}/\text{m}^3$.

Slightly higher BaP figures were obtained during the high-pressure die-casting of brass alloys. In the same investigation, an experimental study of the effect of casting in molds with, and without, petroleum pitch was made. If molding

Table 4. Benzo[a]pyrene ($\mu\text{g}/\text{m}^3$) in aluminum plants.

Country, year	Type of electrodes ^a		Reference
	Self-baking (Söderberg)	Prebaked	
Sweden, 1968–1978	St: 1.8–5.3 P: Pin setters 10–24 Flex raisers 23–51 Anode service 4–22 Cathode repair 2–17		Lindstedt & Sollenberg (50)
Norway, 1978	St: 0.7–9.0 P: Tapper 3.4 Pin setters 53.7–116	St: 0–0.05 Detectable only in 2 samples out of 6	Bjørseth et al (5)
United States, 1974	P: Pin setter 53.0 Pin craneman 28.6 Tapping craneman 3.1 7 other categories < 1	P: Potmen 0.03–0.5 Craneman 0.1	Shuler & Bierbaum (76)
Soviet Union, 1966–1979	St: 13.7–22.1 P: Cranemen 11–73 3.6–19 (AC) Potmen 18–29 9–10 (AC) Pin setters 221–975 28–230 (AC)	St: 0.01–0.03 P: Cranemen 0.09–0.17 Potmen 0.08–0.20 Anodemen 0.02–0.20	Filatova et al (24), Konstantinov (40), Konstantinov & Kyz'minykh (42)
Poland, 1977	St: 1.85–3.7 P: Potmen 36–38 Cranemen 13–800 Anode plant workers 4–5		Adamiak-Ziemba et al (1)

^a St = stationary sampling, P = personal sampling, AC = anode chilled.

sand without pitch was used, no BaP was found in the smoke from the molding box. Adding pitch to the sand resulted in the release of BaP, the level of which increased as the percentage of pitch increased. Fresh molding sand containing 3.5 % pitch gave smoke containing a BaP concentration of $81 \mu\text{g}/\text{m}^3$ (length of measurement = 45 min).

Gwin et al (31) studied the volatile components generated from a molding sand called green sand containing 6 % bentonite clay, 1 % cereal binder, and 3 % sea coal. Several PAH components were identified in the pyrolysis products in a laboratory iron-casting experiment, but they were not quantified.

A large number of PAH was identified qualitatively, but not quantitatively, by Schimberg et al (74) in the gases from iron casting. Pitch was used as an additive to the molding sand. The relations between different PAH components were essentially the same for different sampling sites. Therefore the authors suggested that the analysis of one or two PAH components be used to estimate the whole PAH exposure in foundries.

Zdrasil & Picha (86) studied the BaP content in the air of two iron foundries. In one foundry, BaP was $0.12 \mu\text{g}/\text{m}^3$ or less for all work operations. In the other foundry, the highest value found was $0.47 \mu\text{g}/\text{m}^3$ (during tumbling). Higher figures, up to $4.1 \mu\text{g}/\text{m}^3$, were measured during pressure die-casting of aluminum alloys. In the tools, mineral lubricating oil was heated to $590\text{--}660^\circ\text{C}$ under high pressure, and PAH was formed by pyrolysis. The same authors also found that a great part of the BaP formed during the casting process is absorbed by the molding sand.

Welding

During the welding of painted or plastic-coated metal, the formation of PAH by pyrolysis of the organic material might be expected. In international literature, however, no studies of PAH generated by welding seem to have been published.

In Sweden, an investigation of BaP exposure has been carried out during the welding of railroad rails directly on the track (82). The PAH came from creosote-impregnated wooden ties, which were un-

avoidably heated during the welding. Of the 189 filters used during personal sampling (sampling time 4–7 h), 81 showed no signs of BaP ($< 0.01 \mu\text{g}/\text{m}^3$). Thirty-five samples had more than $0.1 \mu\text{g}/\text{m}^3$, and four had more than $0.5 \mu\text{g}/\text{m}^3$. The highest value found was $2.9 \mu\text{g}/\text{m}^3$. Thus this type of welding may cause moderate PAH exposure in rare cases.

Making of carbon electrodes

As has already been mentioned, prebaked or graphite electrodes are used in aluminum reduction plants, in electric steel furnaces, and in other metallurgical processes. The raw material for these electrodes is generally petroleum coke with tar or pitch as a binder. The "baking" consists of heating this mixture in ovens to temperatures above $1,000^\circ\text{C}$. If real graphite electrodes are to be made, a second heating step (up to about $2,700^\circ\text{C}$) must follow. During the baking procedure, large quantities of PAH are liberated from the electrode mass. The second step, the graphitization, involves rather little PAH exposure, since the volatile components are given off during the first heating.

BaP measurements were made in two Swedish graphite electrode plants in 1974–1976 (50). Close to the ovens, the median of 27 samples was about $5 \mu\text{g}/\text{m}^3$ in one plant, but in the other BaP did not exceed $1.3 \mu\text{g}/\text{m}^3$. Peak values were observed in the pitch impregnation department in both plants, $19\text{--}40 \mu\text{g}/\text{m}^3$. In the graphitization department, only 3 samples out of 24 were above $0.1 \mu\text{g}/\text{m}^3$.

Two recent Russian publications, available to us only in abstracts, report BaP values between 0.03 and $95 \mu\text{g}/\text{m}^3$ from different graphite electrode plants (35, 41). Griest et al (30) found only $\leq 1.3 \mu\text{g BaP}/\text{m}^3$ in a graphite production operation.

Bjørseth et al (5) investigated PAH exposure in an anode plant for making prebaked electrodes. At five stationary sampling sites, total gaseous PAH was between 10.5 and $262 \mu\text{g}/\text{m}^3$, and total particulate PAH between 3.4 and $73.3 \mu\text{g}/\text{m}^3$ (more than 30 components were analyzed). The particulate PAH exposure of four workers was measured with personal sampling. A pitch bin worker had

the highest exposure, 374 μg of PAH/ m^3 and 27.9 μg of BaP/ m^3 . The other three workers investigated were exposed to PAH levels of 10.6–36.8 $\mu\text{g}/\text{m}^3$ and BaP levels of 0.80–2.97 $\mu\text{g}/\text{m}^3$.

Shuler & Bierbaum, in the aforementioned NIOSH report (76), found high values of the benzene-soluble fraction for some workers in prebaked anode block production. In one plant a batch car operator was exposed to a level of 4.5 mg/m^3 (personal sampling), and in the other anode block pullers and cleaners were exposed to 5.3–10.4 mg/m^3 . Several other workers were exposed to concentrations above the TLV for CTPV (0.2 mg/m^3). Surprisingly high figures were found by the same authors during the production of Söderberg anode paste in two other aluminum reduction plants. The mean exposure of eight workers in one plant was 4.1 mg/m^3 (range 1.0–9.5 mg/m^3).

Bjørseth & Lunde (9) investigated PAH exposure in a Norwegian Söderberg paste plant. Two particulate samples had a value of about 0.3 mg/m^3 each (calculated by adding the individual components). The phenanthrene-anthracene fraction accounted for more than 50 % of all the particulate PAH. The benzo[a] and [e] pyrene value was 0.8 $\mu\text{g}/\text{m}^3$ (isomers not separated). It is evident that higher PAH are liberated to a much lower degree in the production of Söderberg paste than in the baking of electrodes.

Carbon black

Carbon black is the commercial name of a carbonaceous material manufactured by the partial combustion or pyrolysis of natural gas or petroleum. It consists mainly of elemental carbon (90–99 %), but, depending on the process of manufacture, amounts of PAH are always to be found in it. In industry carbon black is mainly used as an additive to rubber, eg, in tires. In the United States 1.3 million tons were consumed by the rubber industry in 1969. Qazi & Nau (65) identified 14 PAH components in a carbon black sample. Anthanthrene, coronene, and pyrene were the most frequent 150, 95, and 45 mg/kg , respectively). Four carcinogens were found, among which was BaP (6.5 mg/kg). Lee

& Hites (48) identified more than 30 PAH components, some of which were sulfur-containing, in so-called furnace black. Total PAH accounted for 0.1–0.2 % of the samples.

Pikovskaya et al (63) found rather high BaP contents in some Russian carbon blacks, 60–200 mg/kg , along with benzo[e]pyrene (BeP), perylene, anthracene, and phenanthrene.

There are very few investigations of PAH in the literature from workplaces where carbon black is manufactured or handled. Gabor et al (26) analyzed some airborne PAH components in a carbon black production plant. No other reports are available to contradict or confirm their extremely high PAH concentrations, such as 260–510 μg BaP/ m^3 .

Nutt (59) investigated BaP in a tire manufacturing plant. The 48-h mean from 49 sampling sites within the plant was 12.3 ng/m^3 (maximum 55 ng/m^3). This very low BaP figure could not be significantly distinguished from that of the outdoor air. Thus, it could not be proved that carbon black contributed to the BaP content in the workplace atmosphere.

Asphalt

The asphalt used for paving streets and roads mainly comes from the distillation residue of petroleum crude oils. In some cases, however, it is mixed with coal tar. Since it is handled at elevated temperatures, the smoke may be suspected to contain PAH components. The petroleum asphalt in itself is rather poor in higher PAH. According to some analyses cited by Zorn (88), bitumen asphalt has a BaP content of 4.7 mg/kg , compared to the 500 mg/kg in coal tar.

Adamiak-Ziemba & Kesy-Dabrowska (2) investigated PAH in the air of asphalt production plants. During the oxidation of asphalt by air-blowing, benzene-soluble particulates reached levels of up to 17 mg/m^3 when hot asphalt was poured. The BaP concentration was never above 0.05 $\mu\text{g}/\text{m}^3$, but, when asphalt was burned off tubes, a BaP concentration of 0.7 $\mu\text{g}/\text{m}^3$ was measured. BeP and perylene had a little higher concentration than BaP. Some other PAH were also identified.

von Lehmden et al (49) found high

amounts of pyrene and anthracene in the exhaust gases from asphalt air-blowing but were unable to detect any higher PAH. In an asphalt hot-road mix plant (where a mixture of 6 % asphalt and 94 % sand and crushed stone is prepared) BaP and benzo-[ghi]perylene were found in the effluent gases from the mixer, but they could be removed by water spraying.

During the asphalt paving of German highways, Zorn (88) found very high BaP exposure for some workers (50–350 $\mu\text{g}/\text{m}^3$) when an asphalt-tar mixture was used. He also pointed out that there is considerable skin exposure from contaminated clothes. In a Norwegian study (8) the PAH exposure for asphalt-paving workers was 1.3–27.2 $\mu\text{g}/\text{m}^3$. If total PAH is estimated to be 20 % of the whole benzene-soluble particulate fraction, these levels would correspond to about 0.14 mg of benzene solubles per cubic meter of air at the most. The TLV is 0.2 mg/m^3 in the United States and many other countries.

Pipeline protective coating

Larson (46) studied exposure at eight plants where metallic pipes were coated by hot coal tar and wrapped with a special paper to provide an anticorrosive coating. Six different categories of workers were distinguished, all of which had a CTPV exposure in excess of the TLV (0.2 mg/m^3). The most exposed category, the coating operators, had a mean exposure of 6.53 mg/m^3 , the highest individual exposure being 23.7 mg/m^3 . The mean CTPV exposure for all personnel in the pipeline coating industry was found to be 1.89 mg/m^3 , almost equal to that in the coke oven industry (22).

In a laboratory study of the emission from the same tar mixture used in industry, and under identical conditions, 85 % of the aerosol was found to consist of particles less than 10 μm in size. The emission was totally dominated by the lower PAH. BaP accounted for 0.46 % of the benzene solubles in the total particulates and 0.57 % of the fraction $< 10 \mu\text{m}$.

Mines and tunnels

In Sweden, large series of BaP samples have been taken in iron mines since the

early 1960s. The main source of PAH in mines is the exhaust gases from diesel trucks and other vehicles. During the first period, 1961–1969, 679 short-time (~ 10 min) samples were taken in seven different investigations. Without any traffic near the sampling sites, the mean BaP values per sampling site never exceeded 0.011 $\mu\text{g}/\text{m}^3$. When traffic was passing, means between 0.010 and 0.039 $\mu\text{g}/\text{m}^3$ were observed. The highest 10-min value was 0.55 $\mu\text{g}/\text{m}^3$.

After 1970 the sampling technique was changed. Samples were taken continuously on the same sampling site for 8–32 h, the filter being replaced after a few hours to avoid clogging by dust. The results are summarized in table 5.

On the average, the BaP exposure in Swedish iron mines is a little above the all-year mean exposure in crowded city streets. Other air pollutants in the mines, such as different dusts, nitrogen oxides, and radon, must be more hazardous for the workers' health.

In the 1960s, some BaP samples were taken in tunnels and rock chambers under construction. In five investigations, 164 short-time samples were taken. The BaP means of each investigation were in the interval 0.012–0.063 $\mu\text{g}/\text{m}^3$. The highest value for a 10-min sample was 0.11 $\mu\text{g}/\text{m}^3$.

Garages and automobile repair shops

In other places, the air is polluted mainly by gasoline engines. In 1964–1970, some BaP investigations were carried out in Swedish automobile repair shops and in garages (table 6).

In the two garages investigated, BaP was on the same level as in the city streets. In the car repair shops, the BaP figure was a little elevated.

Electric discharge machining

Electric discharge machining is a process in which an electric discharge takes place between a graphite electrode and a piece of metal, both immersed in mineral oil. Locally, the temperature at the site of discharge is very high, and the oil is pyrolyzed and gives rise to smoke containing PAH components. Arvidson, Spjut & Solenberg (1977, unpublished) found varying

contents of BaP in smoke above the oil bath. The highest 4.5-h sample had a BaP concentration of $9.1 \mu\text{g}/\text{m}^3$; the corresponding levels of the other samples were much lower. The time-weighted average (TWA) of four samples was $2.2 \mu\text{g}/\text{m}^3$. The oil bath was well ventilated by a hood, and personal samples from the operators did not contain detectable amounts of BaP. In the oil, however, BaP was enriched during use. Fresh oil had no detectable BaP, but two samples taken after 20 and 26 weeks of use contained 136 and $149 \mu\text{g}/\text{l}$, respectively. Thus it is important for workers in electric discharge machining to avoid skin contact with the oil, air exposure being eliminated by a good ventilation hood.

Chimney sweeping

Chimney sweeping was the first profession with PAH exposure for which cases of cancer were observed. This was done already in 1775 by Sir Percival Pott, who found a remarkable frequency of scrotum cancer among chimney sweeps. Surprisingly, measurements of PAH exposure seem to be lacking except for a recent paper by Bagchi & Zimmerman (4). During cleaning from the top of the chimney, they found a CTPV value of $14.53 \text{ mg}/\text{m}^3$ and a BaP

level of $40 \mu\text{g}/\text{m}^3$ in the breathing zone of the chimney sweep. Cleaning from the hearth was less exposed work (CTPV = $2.16 \text{ mg}/\text{m}^3$). The authors recommended spraying the chimney top with water during the sweeping to reduce dust exposure. They were also fully aware that chimney sweeps have considerable skin exposure, especially on the face, neck, and hands.

Miscellaneous

In some operations, tar is melted in an open vessel and later spread over a large area. Personnel in the vicinity of the hot tar may be very heavily exposed to PAH. A few investigations of BaP in the air from such operations have been published.

Bonnet (11) studied a process in which tar was melted and mixed with cork powder to be spread out on walls as insulation. Very high BaP figures ($> 1 \text{ mg}/\text{m}^3$) were found, which surpass all other BaP measurements ever made in an occupational environment, as far as we know.

Sawicki et al (71) observed BaP values of up to $78 \mu\text{g}/\text{m}^3$ during the tarring of a sidewalk and $14 \mu\text{g}/\text{m}^3$ during roof tarring. These operations also involve the handling of hot tar close to the worker.

High PAH concentrations were found by Goldsmith et al (29) during a hot forg-

Table 5. Benzo[a]pyrene (BaP) analyses (time-weighted averages) from three Swedish iron mines 1975 (50).

Mine	Number of sampling sites	Number of samples	Sampling time/site (h)	BaP ($\mu\text{g}/\text{m}^3$)	
				Mean	Range
A	25	180	12—33	0.009	0—0.058
B	25	104	8—32	0.008	0—0.032
C	5	32	25—29	0.005	0.003—0.006

Table 6. Benzo[a]pyrene (BaP) in Swedish automobile repair shops and garages (50).

Location	Number of sampling sites	Number of samples	Sampling time (h)	BaP ($\mu\text{g}/\text{m}^3$)	
				Mean	Maximum
Repair shop A	4	24	1	0.028	0.14
Repair shop B	4	24	1	0.044	0.088
Repair shop C	4	24	8	0.035	0.070
Industrial garage	5	60	4	0.004	0.024
Underground public garage	3	60	2.5	0.011	0.029

ing operation (BaP: 1.6–2.9 $\mu\text{g}/\text{m}^3$; CTPV: 1.3–6.0 mg/m^3) and by Zdrazil & Picha (85) during the turning of iron castings having an anticorrosive layer of coal tar (BaP up to 290 $\mu\text{g}/\text{m}^3$). In the latter case, the tar had to be substituted by asphalt, which is poorer in higher PAH.

Review of benzo[a]pyrene exposure levels for different workplace categories

To summarize the measurements from all types of workplaces, it might be of interest to range them according to the degree of exposure. Since most investigations have concerned BaP only, we prefer to base the classification on BaP analyses. Other analyses, eg, CTPV, would very likely lead to the same hierarchy.

1. *Very high BaP exposure* ($> 10 \mu\text{g}/\text{m}^3$)
Gas and coke works (topside work)
Aluminum works (some jobs, eg, pin setters, potmen, cranemen, etc)
Manufacturing of carbon electrodes (pitch bin workers, etc)
Handling of molten tar or pitch (roofing, paving, insulation coating, etc)
Chimney sweeping (from top)
Asphalting if asphalt is mixed with tar (some jobs)
2. *Fairly high BaP exposure* ($1\text{--}10 \mu\text{g}/\text{m}^3$)
Gas and coke works in general (nontopside work)
Blast furnaces
Steel works (some jobs)
Manufacturing of carbon electrodes (in general)
Aluminum works (in general)
Asphalting if asphalt is mixed with tar (in general)
3. *Moderate BaP exposure* ($0.1\text{--}1 \mu\text{g}/\text{m}^3$)
Steel works (in general)
Foundries (some jobs)
Welding of rails on track
Manufacturing of Söderberg electrode paste
4. *Low BaP exposure* ($0.01\text{--}0.1 \mu\text{g}/\text{m}^3$)
Automobile repair shops
Asphalt manufacturing (from petroleum)
Foundries (in general)
Construction of tunnels and rock chambers

Aluminum electrolysis halls with prebaked electrodes

5. *Very low BaP exposure* ($< 0.01 \mu\text{g}/\text{m}^3$)

Iron mines
Garages

Epidemiologic studies of workers exposed to polycyclic aromatic hydrocarbons

Since it has been known for many years that coal tar, as well as some isolated PAH components, are carcinogens, many investigators have studied the cancer frequency of workers known to be exposed to tar vapors in rather high concentrations. The largest and best studied category is the workers of the gas and coke industries.

Early investigations by Kuroda & Kawahata in 1936 (45), Kennaway & Kennaway in 1947 (37), Bruusgaard in 1959 (13), and Kawai et al in 1967 (36) revealed a clear tendency towards excess lung cancer death for gas and coke workers in comparison to the population in general. On the contrary, Reid & Buck (67) did not find any significant excess frequency of cancer among British coking plant workers.

Doll et al (21), in a series of investigations finally reported in 1972, studied the mortality of British gas workers in the period 1957–1965. The death rate from lung cancer for workers dealing with coal carbonization was about twice as high as for the average population. (Only workers employed for more than 5 a were followed.) The corresponding excess frequency of bladder cancer was about 2.5 times. The correlation between length of employment and cancer frequency was not investigated further. Two jobs, topman and hydraulic main attendant, seemed to be especially dangerous as regards cancer risk. These types of workers are working at places where the exposure to tar fumes is rather heavy. Unfortunately, smoking habits were only investigated for 10 % of the men studied, but they were not unusual and could not explain the excess lung cancer rate.

In an extensive study of coke oven employees of some American steel works, Lloyd (51) and Redmond et al (66) found a significant correlation between coal tar

exposure and cancer frequency. The lung cancer death rate was increased 2.5 times for all coke oven workers, 5 times for oven topside workers, and 10 times for full-time topside workers with more than 5 a of employment. Cancer of the kidneys was also increased, as well as colon and pancreas cancer for nonoven workers.

Sakabe et al (70), in 1975, reported an investigation of 2,201 Japanese coke oven workers retired between 1947 and 1973. For the whole group, the excess of lung cancer death was very small (1.28 times) and statistically nonsignificant. When the coke oven workers from the iron and steel industry were studied separately, a significant excess of lung cancer death (2.37 times) was observed. Workers from city gas companies had no excess lung cancer at all. Most of the workers dying from lung cancer were smokers, but information was incomplete on this point. However, the excess lung cancer death rate for coke oven workers in the iron and steel industry coincided rather well with that found in the British and American investigations already cited.

Contrary to other investigators, Davies (18) did not find any excess lung cancer death rate for coke oven workers in two steelworks in South Wales. A total of 610 workers was studied over the period 1954–1965. An explanation may be that it was impossible to arrange the material according to different degrees of tar exposure.

Mazumdar et al (55), in 1975, published an epidemiologic study of cancer death rate among coke oven workers in comparison to their degree of exposure to coal tar vapors. Their lifetime exposure was estimated in the following way: The different jobs were divided into three classes of decreasing exposure: topside jobs, side oven 1 jobs, and side oven 2 jobs. The average levels of CTPV for the different classes, calculated from the data of Fannick et al (22), were found to be 3.15 mg/m³ for topside jobs, 1.99 mg/m³ for side oven 1 jobs, and 0.88 mg/m³ for side oven 2 jobs. From the work history of each employee, the lifetime CTPV dose was calculated and expressed as (mg/m³) × months. White and nonwhite workers were studied independently of each other. Total death rate was not significantly cor-

related to the exposure for any of these groups. For nonwhite workers, however, a strong dose-response relationship was found both for cancer in general and for lung cancer. The group exposed below 200 (mg/m³) × months showed no excess cancer death in comparison to the controls. The authors therefore proposed that this life dose of CTPV be the highest allowed, which would lead to a TLV of about 0.2 mg/m³ if the average exposure period is assumed to be 30 a. For white coke oven workers, however, no significant correlations between exposure and cancer death rate could be found. Smoking habits were not studied for either of the two groups of workers.

Many authors have found an excess rate of bladder cancer among tar-exposed workers. Generally, the presence of β -naphthylamine in the tar is held responsible for that type of cancer. This problem has been discussed by Zorn (87), Manz (52), and others.

Another category heavily exposed to PAH is workers in aluminum reduction plants. A few epidemiologic investigations have been carried out on these workers.

Konstantinov & Kyz'minykh (42) investigated cancer frequency among electrolysis hall workers of an aluminum reduction plant with self-baking electrodes. Total cancer mortality was 1.85 times higher than expected. Cancer of the respiratory organs was 8.3 times higher than expected in the youngest age group (< 40 a) and 1.6 times higher for workers more than 40 a of age. The corresponding figures for skin cancer were 39 times for the youngest group and 10.5 times for all workers. The number of workers investigated and the number of cancer incidences were not stated in the paper.

A large study of American aluminum plant workers employed for at least 5 a between 1946 and 1973 has been published (3). For all potroom workers, a slight and nonsignificant excess of lung cancer was observed (1.2 times). For horizontal Söderberg electrode plants, however, this excess was 1.62 times. A slight and nonsignificant excess frequency of leukemia was also observed.

In 1979, Gibbs & Horowitz (28) published an epidemiologic study of lung cancer mortality in two Canadian aluminum re-

duction plants. In that paper, an attempt was made to relate lung cancer frequency to length and intensity of tar exposure. The different jobs were divided into three categories: A (no tar exposure), B (some exposure, degree 25 %), and C (definitive tar exposure, degree 100 %). With knowledge of the occupational history of each worker, the total tar vapor dose was estimated as "tar years" (years times degree of exposure). Work in prebake electrolysis halls was classified as A. For the group with 21 or more "tar years" of exposure, lung cancer was increased 2.9 times, and for 11–20 "tar years," the increase was 1.7 times. No excess frequency of lung cancer was found for workers with 1–10 "tar years" of exposure. If only years of exposure were taken into account, the corresponding quotients were 2.4 for 21 or more years of exposure and 1.4 for 11–20 a. Smoking habits were not investigated, but it seems unlikely that they could explain the excess lung cancer observed.

In 1979, Milham (56), as well as Konstantinov (40), studied cancer frequency among workers from aluminum reduction plants with prebaked electrodes. The PAH content in the electrolysis halls of such plants is negligible, but a strong PAH exposure may occur in the department where the electrodes are manufactured. Both these authors found a slight excess frequency of cancer of different sites, especially respiratory cancer (1.7–1.9 times). Milham studied the correlation between length of employment and cancer frequency and found a maximum for workers employed 15–19 a.

Milham (personal communication, 1981) has said that the number of workers in the electrode manufacturing department of his study was too small to account for the excess cancer in the prebake plants. Therefore the presence of carcinogens other than PAH is indicated for the aluminum industry. This important question must be investigated further.

Only a few epidemiologic investigations on other categories of PAH-exposed workers have been published. Hammond et al (32) investigated a group of workers (5,939 individuals) who were mainly engaged in applying hot pitch or asphalt to roofs or in waterproofing basements. All of

them had been members of the corresponding union for at least 9 a. The mortality within this group in 1960–1971 was studied, and the cancer deaths were correlated to the length of employment of each individual. The cancer death rate was normal for those employed less than 20 a, but 1.45 times higher than expected for workers with 20 or more years of employment. Cancer of different sites showed an increase in all cases (lung cancer 1.59 times, skin cancer 4 times, etc). The lung cancer death rate was further studied, and for those employed for more than 40 a, it was 2.47 times higher than expected. Some pilot experiments showed that the average daily inhaled dose of BaP was 16.7 μg . For some operations the level reached 50 μg .

Pierre et al (62) found malignant skin tumors on the face of 20 % of the workers daily exposed to coal pitch in a briquette factory. Out of 10 skin tumor cases, 5 appeared after 1–10 a of exposure. These five workers had a more intense exposure at work than the others. A truck driver developed a skin tumor after 43 a of exposure.

An investigation of the mortality of Finnish foundry workers has been published (43). Out of 224 deaths in 1950–1973, 21 were due to lung cancer, against the 12 expected. The highest excess frequency was observed for molders and coremakers exposed for more than 5 a and working in iron foundries. As already stated, pitch and other additives to the molding sand may yield PAH on pyrolysis. A detailed review on lung cancer in ferrous foundry workers has recently been published by Palmer & Scott (60).

Robertson & Ingalls (68) studied mortality among carbon black workers (34,739 person-years between 1935 and 1974). Within this cohort, 29 deaths from malignant neoplasms were observed against 41 expected. No excess death rate could be found even when the workers were divided into groups according to years of employment.

In the 1910s and 1920s, scrotum cancer cases were found among mule spinners of the cotton industry, who came in contact with mineral oils used as lubricants. Later, scrotum and skin cancers were observed among workers exposed to cutting oils.

[For a review of this subject see Waterhouse (84) or Kipling & Waldron (39).] These cancer cases may have been caused by PAH components of the oils, although it has not yet been proved. Modern solvent-refined oils are much less carcinogenic than older preparations.

Wahlberg (83) studied 34 cases of scrotal cancer (16 fatal) in Swedish hospitals. Seven of the cases had been exposed to oil for several years as automatic lathe operators, and six had had some hand contact with motor oils. The rest of the patients were apparently not occupationally exposed.

Decoufle (19), in a study of 5,189 metal-machining workers exposed to oil mists, was unable to find any excess respiratory cancer in the period 1938–1967. A slight excess of digestive cancer (1.76 times) was observed only for those exposed 10–14 a.

Thus, some categories of PAH-exposed workers definitely have a higher risk of cancer than nonexposed persons of the same age. Most of the epidemiologic investigations cited may be criticized for no or insufficient knowledge of the smoking habits of the subjects studied. A marked difference in smoking habits between the subjects and the reference groups does not seem likely in most cases. Future epidemiologists ought, however, to place more stress upon exploring the smoking history of their subjects.

Threshold limit values for polycyclic aromatic hydrocarbons

The long latency between first exposure and symptoms and many other factors make the establishment of TLVs for carcinogens in the work atmosphere an extremely difficult task. TLVs for PAH were practically nonexistent until 1967, when the American Conference of Governmental Industrial Hygienists (ACGIH) adopted a TLV of 0.2 mg/m³ for CTPV, which was defined as the benzene-soluble fraction of the particulates collected on a filter. This TLV has remained unchanged on the ACGIH list thus far. Some years later, the same TLV was introduced on the official list of the US Occupational Safety and Health Administration (OSHA). In 1976, however, OSHA issued the standard

"Exposure to Coke Oven Emissions" (20), in which a lowering of the TLV to 0.15 mg/m³ was recommended. That level of benzene solubles was regarded to be the lowest possible to maintain at coke ovens at the present stage of technology. This lowering of the TLV has not, so far, been legally accepted in the United States, and the latest edition of the OSHA TLV list still has 0.2 mg/m³.

The US National Institute for Occupational Safety and Health, in a criteria document (57), proposed to substitute benzene with cyclohexane for the extraction, since the latter solvent is far less toxic. It was proposed to put the TLV at 0.10 mg of cyclohexane-soluble per cubic meter of air because this was the lowest concentration which could be determined with reasonable accuracy by the method proposed. This TLV still remains a proposal.

In the 1970s, the Soviet Union issued a TLV for BaP (0.15 µg/m³). The documentation of this value has been published by Shabad (75). It is based upon laboratory experiments with animals.

In Sweden, a TLV of 10 µg/m³ was introduced for BaP in 1978. It has been lowered to 5 µg/m³ in 1982. The choice of BaP as the PAH indicator in Sweden mainly depends on the great number of BaP measurements made in this country during a 15 a period, very few other data about PAH being available. Most other countries have adopted the American TLV for CTPV.

In the oldest Swedish investigations, both benzene solubles and BaP were determined. The average content of BaP in the benzene fraction was 0.71 % in gas works and 1.3 % in aluminum electrolysis halls. If BaP is assumed to be 1.5 % of CTPV at the most, the American TLV for CTPV of 0.2 mg/m³ would correspond to a BaP concentration of 3 µg/m³.

Thus there are two different systems in use for TLVs of air pollutants containing PAH components. The CTPV method measures a fraction of mainly unknown composition. Only about 20 % of it consists of identified PAH, as found by Bjørseth et al (7) with the aid of gas chromatographic analysis. This method has been adopted because it is rather simple and gives a general view of the total exposure to tar vapors. It is not applicable to atmospheres

polluted by other sources of PAH, eg, motor exhaust gases. The determination of BaP gives information about one well-defined, strongly carcinogenic PAH component. Of course, knowledge of BaP alone is not sufficient for estimating the cancer risk of a given environment. There are always many other carcinogens present, and the influence of other substances and external factors on carcinogenesis is largely unknown. A third alternative, complete PAH analysis by gas or liquid chromatography, gives superior information on the chemical environment, but at the present state of knowledge the cancer risk cannot be much better estimated from this information than from the BaP or CTPV values alone. For further research, of course, a more-detailed chemical analysis of the air pollutants must be the base of a better understanding of carcinogenesis. Therefore, this work must be continued, but for routine control a complete analysis is out of the question.

The practical purpose of exposure measurements is to protect the workers and to study the effect of elimination arrangements. From that aspect, it is not very important which method of controlling PAH exposure is chosen. The "ranking list" of the different jobs presented earlier would very likely have been the same if CTPV or some other criterion had been used instead of BaP. A still simpler method, enabling small laboratories to control PAH exposure, would be of great value. Such methods have been proposed, eg, the thin layer chromatography method described by Fjeldstad & Halgard (25). It gives the sum of PAH in a rather short time with cheap equipment. In the future, exposure control would be greatly aided if a TLV could be based upon such a simplified analytical method.

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