SOME NON-HETEROCYCLIC POLYCYCLIC AROMATIC HYDROCARBONS AND SOME RELATED EXPOSURES

The compounds covered in this monograph are listed in Table 1.1

1. Exposure Data

Polycyclic aromatic hydrocarbons (PAHs) are very widespread environmental contaminants, due to their formation during the incomplete combustion or pyrolysis of organic material. They are found in air, water, soils and sediments, generally at trace levels except near their sources. Tobacco smoke contains high concentrations of PAHs. They are present in some foods and in a few pharmaceutical products that are applied to the skin.

Occupational exposure to PAHs in several work environments can lead to body burdens among exposed workers that are considerably higher than those in the general population. In particular, industrial processes that involve the pyrolysis or combustion of coal and the production and use of coal-derived products are major sources of PAHs and are the focus of this monograph.

1.1 Chemical and physical data

1.1.1 *Nomenclature, structure and properties*

The term polycyclic aromatic hydrocarbons (PAHs) commonly refers to a large class of organic compounds that contain only carbon and hydrogen and are comprised of two or more fused aromatic rings.

The PAHs that have been chosen for inclusion in this monograph are presented in the Appendix; their nomenclature is listed in Table 1 and their structures are given in Figure 1 therein. The International Union of Pure and Applied Chemistry (IUPAC) Systematic Name (IUPAC, 1979; Sander & Wise, 1997), the Chemical Abstracts Services (CAS) Registry Number, the molecular formula and the relative molecular mass for each compound are given in Table 1 of the Appendix. The chemical and physical properties, the latest Chemical Abstracts Primary Name (9th Collective Index), common synonyms and sources for spectroscopic data are given in Table 2 and the main text of this Appendix. The nomenclature of PAHs has been inconsistent and the more commonly used names that appear in this monograph may not be those used in the primary CAS Index or by IUPAC.

Table 1.1. *IARC Monographs* volume[a] and evaluation of the polycyclic aromatic hydrocarbons covered in this monograph

Common name	Volume(s)	Group
Acenaphthene	–	–
Acepyrene	–	–
Anthanthrene	32	3
Anthracene	32	3
11*H*-Benz[*b*,*c*]aceanthrylene	–	–
Benz[*j*]aceanthrylene	–	–
Benz[*l*]aceanthrylene	–	–
Benz[*a*]anthracene	3, 32	2A
Benzo[*b*]chrysene	–	–
Benzo[*g*]chrysene	–	–
Benzo[*a*]fluoranthene	–	–
Benzo[*b*]fluoranthene	3, 32	2B
Benzo[*ghi*]fluoranthene	32	3
Benzo[*j*]fluoranthene	3, 32	2B
Benzo[*k*]fluoranthene	32	2B
Benzo[*a*]fluorene	32	3
Benzo[*b*]fluorene	32	3
Benzo[*c*]fluorene	32	3
Benzo[*ghi*]perylene	32	3
Benzo[*c*]phenanthrene	32	3
Benzo[*a*]pyrene	3, 32	2A
Benzo[*e*]pyrene	3, 32	3
Chrysene	3, 32	3
Coronene	32	3
4*H*-Cyclopenta[*def*]chrysene	–	–
Cyclopenta[*cd*]pyrene	32	3
5,6-Cyclopenteno-1,2-benzanthracene	–	–
Dibenz[*a*,*c*]anthracene	32	3
Dibenz[*a*,*h*]anthracene	3, 32	2A
Dibenz[*a*,*j*]anthracene	32	3
Dibenzo[*a*,*e*]fluoranthene	32	3
13*H*-Dibenzo[*a*,*g*]fluorene	–	–
Dibenzo[*h*,*rst*]pentaphene	3	3
Dibenzo[*a*,*e*]pyrene	3, 32	2B
Dibenzo[*a*,*h*]pyrene	3, 32	2B
Dibenzo[*a*,*i*]pyrene	3, 32	2B
Dibenzo[*a*,*l*]pyrene	3, 32	2B
Dibenzo[*e*,*l*]pyrene	–	–
1,2-Dihydroaceanthrylene	–	–
1,4-Dimethylphenanthrene	32	3
Fluoranthene	32	3
Fluorene	32	3
Indeno[1,2,3-*cd*]pyrene	3, 32	2B

Table 1.1 (contd)

Common name	Volume(s)	Group
1-Methylchrysene	32	3
2-Methylchrysene	32	3
3-Methylchrysene	32	3
4-Methylchrysene	32	3
5-Methylchrysene	32	2B
6-Methylchrysene	32	3
2-Methylfluoranthene	32	3
3-Methylfluoranthene	32	3
1-Methylphenanthrene	32	3
Naphtho[1,2-*b*]fluoranthene	–	–
Naphtho[2,1-*a*]fluoranthene	–	–
Naphtho[2,3-*e*]pyrene	–	–
Perylene	32	3
Phenanthrene	32	3
Picene	–	–
Pyrene	32	3
Triphenylene	32	3

[a] Vol. 3 published in 1973, Vol. 32 in 1983 and Suppl. 7 in 1987 (IARC, 1973, 1983, 1987).

The chemical structures and ring numbering shown in the Appendix follow the IUPAC rules for fused-ring systems. Structures are typically oriented such that (i) the greatest number of rings in a row are aligned horizontally, (ii) the maximum number of rings is positioned in the upper right quadrant and (iii) the least number of rings is positioned in the lower left quadrant. Numbering begins with the uppermost ring the furthest to the right; the most counterclockwise carbon atom is not involved with ring fusion. The numbering proceeds clockwise around the structure with hydrogenated carbon atoms. The numbering of anthracene and phenanthrene are 'retained exceptions' to this rule. Numbering of atoms engaged in ring fusion (numbers not shown in this monograph) are given letters, such as *a*, *b* and *c*, after the number of the preceding atom.

The 35 IUPAC 'parent compounds' are used in the nomenclature, and structures are built from these by adding prefixes (e.g. benzo-, cyclopenta- or a group of rings such as indeno-), followed by an italic letter or letters denoting the bond or bonds of the base (which has as many rings as possible) at which fusion occurs. The letter *a* refers to the 1,2-bond, and all bonds are then lettered sequentially whether or not they carry hydrogen atoms (Lee *et al.*, 1981). The IUPAC parent compounds are given an order of increasing priority with increasing ring number. The parent with the highest priority is used to name the structure. An exception to this rule is the choice of benzo[*a*]pyrene over benzo[*def*]chrysene.

The important chemical and physical properties of each pure PAH are summarized in Table 2 of the Appendix and include, where available: melting-point, vapour pressure, partition coefficient for *n*-octanol:water (log K_{ow}), water solubility, and Henry's law constant. These physicochemical properties of PAHs — namely, very low water solubility, low vapour pressure and high log K_{ow} — control the transport and distribution of PAHs in the environment. A more complete set of data that includes the available descriptions of crystals, and data on boiling-point, density and rate constant for atmospheric gas-phase reactions (low molecular weights only) are given in the Appendix. Only experimental data are reported here and, for consistency, log K_{ow} values generally include evaluated values only (Sangster Research Laboratories, 2005).

1.1.2 *Analysis*

(a) *Analysis of ambient exposure to PAHs*

Chemical analysis of PAHs often requires extensive separation schemes because of their lack of distinct functional groups, the existence of numerous structural isomers and the need to analyse PAHs in diverse environmental matrices. Methods for the analysis of PAHs were described in detail in the 1980s (for example, Lee *et al.*, 1981; Bjorseth, 1983; IARC, 1983; Bjorseth & Ramdahl, 1985) and have recently been updated (IPCS, 1998; Neilson, 1998). Unfortunately, the PAHs that have been quantified in ambient and occupational samples are often very limited in number; for example, the 16 'US Environmental Protection Agency priority pollutant PAHs' are often measured, and the larger PAHs (molecular weight >300), which have been suggested to have an important carcinogenic impact (Grimmer *et al.*, 1984), have been addressed only recently (Schubert *et al.*, 2003).

(i) *Collection and sampling*

Two- to four-ring PAHs are present, at least partially, in the gas phase in ambient and industrial atmospheres (Coutant *et al.*, 1988), and sampling of total PAHs requires that an adsorbent be placed downstream from the filter that samples the particle-associated PAHs. In addition, air stripping, that is caused by the passage of large volumes of air, can cause volatile components to be lost from the filter, and, again, it is very important that sampling techniques include adsorbents downstream of the filter (NIOSH, 2000). Common adsorbents used include Amberlite XAD resins, polyurethane foam and Tenax-GC (Chuang *et al.*, 1987; Reisen & Arey, 2005). Size-fractionated sampling of particles is now often used to apportion the sources of ambient particles and to investigate the health impact of ambient particles. The US Environmental Protection Agency classifies particle diameters as 'coarse' (2.5–10 μm), 'fine' (≤2.5 μm) and 'ultrafine' (<0.1 μm).

During ambient sampling, reaction of the PAHs on the filter with ambient gaseous species such as ozone can result in an underestimation of the actual concentrations (Schauer *et al.*, 2003). Such 'artefacts' are probably less important in workplace atmospheres where higher PAH concentrations allow shorter sampling times.

(ii) *Extraction*

Extraction techniques used include solvent, Soxhlet, ultrasonic, microwave-assisted, supercritical fluid, accelerated solvent and solid-phase extraction, and these have been evaluated for use with different sample matrices (Colmsjö, 1998). The addition of deuterated internal standards of specific PAHs and quantification by 'isotope-dilution' mass spectrometry (MS) is one technique that is often employed to correct for losses of analyte during sample preparation (Boden & Reiner, 2004).

(iii) *Quantification and identification of PAHs in isolated mixtures of polycyclic aromatic compounds*

Due to the existence of numerous structural isomers of the PAHs, chromatographic separation either by gas chromatography (GC) or high-performance liquid chromatography (HPLC) is generally employed for isomer-specific identification and quantification. In addition, HPLC provides a useful fractionation technique for isolating PAHs from complex sample mixtures and allows quantification with universal or selective detectors after further separation, for example, by GC with MS (GC–MS) (Reisen & Arey, 2005). The development of standard reference materials (SRMs) with certified values for PAHs in complex environmental matrices allows evaluation of new analytical techniques (Wise *et al.*, 1993; Schubert *et al.*, 2003).

(iv) *Liquid chromatography (LC)*

The development of reverse-phase (RP) HPLC columns coupled with ultraviolet (UV) absorbance and fluorescence detection has improved the analysis of a range of PAHs including high-molecular-weight species (Fetzer & Biggs, 1993; Wise *et al.*, 1993). The length:breadth ratio is a shape-descriptive parameter that has been used in numerous studies of PAH retention in both LC and GC (see Poster *et al.*, 1998 and references therein), and a useful listing of length:breadth ratio for many of the PAHs has been compiled (Sander & Wise, 1997). For a comprehensive review of the selectivity of monomeric and polymeric C_{18} RP HPLC columns for PAH analysis, the reader is referred to Poster *et al.* (1998).

(v) *Gas chromatography*

High-efficiency capillary GC columns with thermally stable stationary phases are used routinely for the analysis of PAHs. Using GC–MS and three different GC stationary phases, 23 isomers of molecular weight 302 and four isomers of molecular weight 300 were recently quantified in four different environmental–matrix SRMs: coal tar (SRM 1597), sediment (SRM 1941) and air particulate matter (SRMs 1648 and 1649a) (Schubert *et al.*, 2003).

(vi) *Other methods of quantification*

Laser-excited time-resolved Shpol'skii spectroscopy has recently been reported as a method for the unambiguous determination of dibenzo[*a*,*e*]pyrene, dibenzo[*a*,*h*]pyrene, dibenzo[*a*,*i*]pyrene, dibenzo[*a*,*l*]pyrene and dibenzo[*e*,*l*]pyrene in HPLC fractions (Yu &

Campiglia, 2004). The use of multidimensional GC, LC, coupled LC–GC and supercritical fluid chromatography have been reported (Sonnefeld *et al.*, 1982; Benner, 1998; Poster *et al.*, 1998; Marriott *et al.*, 2003). The use of single-particle or particle-beam MS offers the possibility of real-time analysis of PAHs on size-resolved particles but, without chromatographic separation, complete information on structural isomers cannot be achieved (Noble & Prather, 2000).

(b) Analysis of occupational exposure

Since the 1940s, the exposure of workers to PAHs has been assessed by measurements of workroom air. In the 1970s, personal air sampling of inhalable dust replaced static air sampling (Kenny *et al.*, 1997). In many studies, a surrogate — namely coal-tar pitch volatiles as benzene-soluble or cyclohexane-soluble matter — has been used as an indicator of airborne PAH. Only in the last decade has the direct determination of the 16 ‘priority pollutant’ PAHs or that of a single marker — namely benzo[*a*]pyrene — in workroom air been chosen to measure industrial exposure to PAHs. The sampling method used to evaluate PAH exposures has been changed so that not only the particulates are sampled, but also the gaseous fraction of the PAH (Notø *et al.*, 1996). Methods for the extraction and analysis of ambient air samples are also applied to occupational air samples.

There are currently no standardized methods to measure dermal exposures to PAH. Using polypropylene pads as adsorbing materials, Jongeneelen *et al.* (1988a) evaluated dermal exposures among workers exposed to coal-tar pitch. Wolff *et al.* (1989) measured dermal exposures among roofers by collecting pre- and post-shift skin wipes from measured areas of each worker’s forehead. These samples are extracted and analysed by methods similer to those used for air samples.

(c) Analysis of PAH metabolites in urine

A specific metabolite of pyrene, 1-hydroxypyrene, in urine has been suggested as a biomarker of human exposure to PAHs (Jongeneelen *et al.*, 1985; Jongeneelen, 2001). Recently, the glucuronide of 1-hydroxypyrene has also been used as an indicator of exposure, since the majority of 1-hydroxypyrene is conjugated and the fluorescence intensity of the conjugate is higher, but its additional value has not yet been assessed (Strickland *et al.*, 1996). The measurement of various hydroxylated phenanthrenes has also been reported as a biomarker of exposure; analysis by GC–MS (Grimmer *et al.*, 1991, 1993) and HPLC has been used to measure hydroxylated phenanthrenes and 3-hydroxybenzo[*a*]pyrene (Gundel *et al.*, 1996; Popp *et al.*, 1997; Gendre *et al.*, 2002). A recent attempt at immunoaffinity separation of PAH metabolites from the urine of exposed workers showed the presence of both 1-hydroxypyrene and several hydroxyphenanthrenes (Bentsen-Farmen *et al.*, 1999). Urinary 1-hydroxypyrene remains, at the present time, the most reliable and pratical marker for monitoring individual exposures or exposures of the population to PAHs (Dor *et al.*, 1999).

1.2 Occurrence and exposure

1.2.1 *Sources of exposure to PAHs for the general population*

Sources of PAH exposure for the general population have been reviewed previously (IARC, 1983) and also more recently (IPCS, 1998). Exposures to PAHs can occur through tobacco smoke, ambient air, water, soils, food and pharmaceutical products. PAHs are ubiquitous in the environment, and result in measurable background levels in the general population (IPCS, 1998). Biological monitoring of 1-hydroxypyrene in the urine of occupationally non-exposed individuals or representative samples of the general population has shown detectable levels in nearly all individuals at median concentrations that are typically less than 0.1 μmol/mol creatinine (reported in Huang *et al.*, 2004). In the USA, the National Health and Nutrition Examination Survey (NHANES) analysed 2312 urine samples collected from the general population in 1999–2000 and showed a geometric mean concentration of 1-hydroxypyrene of 0.039 μmol/mol creatinine (95% confidence interval (CI), 0.034–0.046 μmol/mol). Adult smokers had a three-fold higher level than nonsmokers (geometric mean, 0.080 versus 0.025 μmol/mol). These data are comparable with other recent data on occupationally non-exposed populations in Europe and Canada (Huang *et al.*, 2004). Occupational exposures in some industries can result in urinary levels of 1-hydroxypyrene that are orders of magnitude higher (see Section 1.2.2). The NHANES survey data for 2001–2002 (CDC, 2005) also include urinary analyses of 22 PAH metabolites in over 2700 individuals.

Mainstream tobacco smoke is a major source of exposure to PAHs for smokers (IARC, 2004). A recent study (Ding *et al.*, 2005) reported PAH levels in mainstream smoke from 30 US domestic brands of cigarette. The 14 PAHs measured (of the 16 priority PAHs of the Environmental Protection Agency) had either *sufficient* or *limited evidence* of carcinogenicity in experimental animals. Levels of total PAHs in mainstream smoke ranged from 1 to 1.6 μg/cigarette. Sidestream smoke is a source of PAHs in indoor air; levels of benzo[*a*]pyrene in sidestream smoke have been reported to range from 52 to 95 ng/cigarette — more than three times that in mainstream smoke (IARC, 2004).

PAHs are widely detected as ambient air pollutants, primarily bound to particulate matter but also in the gas phase (especially the lower-molecular-weight PAHs). Average concentrations of individual PAHs in the ambient air of urban areas typically range from 1 to 30 ng/m^3 (excluding naphthalenes), and the more volatile PAHs are generally more abundant; however, concentrations up to several tens of nanograms per cubic metre have been reported in road tunnels or in large cities that use coal or other biomasses as residential heating fuels extensively (IPCS, 1998). Estimates of annual emissions of PAHs from anthropogenic sources in the 1990s were 8600 tonnes/year in Europe (Boström *et al.*, 2002) and 2000 tonnes/year in Canada (Government of Canada, 1994). Major sources of PAHs in ambient air (both outdoors and indoors) include residential and commercial heating with wood, coal or other biomasses (oil and gas heating produce much lower quantities of PAH), other indoor sources such as cooking and tobacco smoke, motor vehicle exhaust (especially from diesel engines), industrial emissions and forest fires (IARC, 1983; IPCS, 1998). PAHs present in ambient air in the gas phase generally have durations of less than a day, whereas particle-associated PAHs may persist for weeks and undergo long-range atmospheric transport (Arey & Atkinson, 2003).

Most PAHs in water originate from surface run-off, particularly in urban areas; smaller particles derive from atmospheric fall-out and larger particles from the abrasion of asphalt pavement. Industrial effluents can also contribute to PAH loads in surface waters, and sediment levels may range up to several thousand micrograms per kilogram. Although concentrations of PAHs in water are usually very low because of the low solubility of these compounds, surface water concentrations are typically 1–50 ng/L, with higher concentrations in some contaminated areas (IPCS, 1998). Comparison of PAH levels in rainwater with those in surface waters showed higher levels in rainwater (10–200 ng/L, with levels up to 1000 ng/L in snow and fog) (IPCS, 1998). Recently, it has been reported that urban run-off from asphalt-paved car parks treated with coats of coal-tar emulsion seal could account for the majority of PAHs in many watersheds in the USA (Mahler *et al.*, 2005). PAH levels in drinking-water are typically much lower (IPCS, 1998).

Food is a major source of intake of PAHs for the general population (see Section 1.2.3). Estimates of PAH intake from food vary widely, ranging from a few nanograms to a few micrograms per person per day. Sources of PAHs in the diet include barbecued/grilled/broiled and smoke-cured meats; roasted, baked and fried foods (high-temperature heat processing); breads, cereals and grains (at least in part from gas/flame drying of grains); and vegetables grown in contaminated soils or with surface contamination from atmospheric fall-out of PAHs (IARC, 1983; IPCS, 1998; JECFA, 2005).

Skin contact with PAH-contaminated soils and the use of dermal pharmaceutical products based on coal tar have also been identified as sources of exposure to and uptake of PAHs for the general population (Jongeneelen *et al.*, 1985; Wright *et al.*, 1985; Viau & Vyskocil, 1995; IPCS, 1998).

1.2.2 *PAHs in occupational settings: production processes and exposure*

(a) Processing and use of coal and coal-derived products

The processing and use of coal and coal-derived products is fundamental to many of the industries described below. A brief introduction to coal pyrolysis and liquefaction is informative.

Pyrolysis (also called thermolysis) is the thermal decomposition of organic substances such as coal during heating to more than 300 °C in an oxygen-free atmosphere. It is the generic term for carbonization, coking and devolatilization. It is also the primary reaction in gasification, combustion and direct liquefaction. The decomposition products of pyrolysis are pyrolysis gas (mainly hydrogen, carbon monoxide, carbon dioxide, methane and C_2–C_5 hydrocarbons), liquid products (tar, oil, crude benzene and water) and coke as a solid residue and the main product. Depending on the properties of the coal, different sulfur and nitrogen compounds are formed during the pyrolysis process. The distribution and composition of pyrolysis products are mainly determined by the type of coal but can be influenced by parameters in the process such as heating rate, temperature, atmosphere and pressure (Crelling *et al.*, 2005).

Low-temperature carbonization and coking involve the heating of coal with the exclusion of air. This process removes condensable hydrocarbons (pitch, tar and oil), gas and gas liquour, which leaves a solid residue of coke. Low-temperature carbonization (up to 800 °C) and coking (> 900 °C) are differentiated by the final temperature. The two processes also differ considerably in the rate of heating of the coal and the residence time in the reactor. These parameters have a direct effect on the product yields. Low-temperature carbonization produces fine coke and fairly large quantities of liquid and gaseous products, whereas high-temperature coking is used primarily for the production of a high-temperature lump coke for blast furnaces and cupola ovens (Crelling *et al.*, 2005).

High-temperature coking of coal is carried out entirely in batch-operated coke ovens, the majority of which are of the horizontal chamber type. The feedstock is a coking coal of given size and composition. The coking properties depend chiefly on softening and resolidification temperatures and on swelling behaviour. Coking takes place at 1000–1300 °C for 15–30 h. The coking time depends on the operating conditions and width of the oven. The main product is metallurgical coke that is required for the production of pig iron. Metallurgical coke is characterized by its suitable size and high resistance to abrasion even under the conditions of a blast furnace. Coke-oven gas and liquid by-products are also produced. In western Europe, these by-products influence the economy of coking and, therefore, are reprocessed (Crelling *et al.*, 2005). High-temperature coking is associated with higher levels of exposure to PAHs than low-temperature processes (Price *et al.*, 2000).

Considerable technical improvements in coke production have led to greater cost effectiveness. These include the mechanization and automation of oven operations, the reduction of coking time and an increase in specific throughput by the use of thinner bricks of higher thermal conductivity and larger oven sizes (Crelling *et al.*, 2005).

Tables 1.2–1.13 summarize the information available on exposures from 1983 to 2005 for the 10 industrial sectors addressed in this monograph. Each table was constructed to identify the country in which the sampling was carried out, the year in which measurements were made, the identity of the job or task sampled, the number subjects for whom measurements were made, the number of measurements taken, tobacco-smoking status of the subjects (when reported), levels of total PAHs, pyrene and benzo[*a*]pyrene in the air and dermal levels of pyrene and benzo[*a*]pyrene, as well as composite measures such as benzene-soluble fractions and cyclohexane-soluble material. The air samples reported are personal exposure measurements. In most cases, the study did not take into account concomitant exposures in the workplace; however, when this information was reported, it has been indicated in the text on the relevant industrial sector. Approximately one-third of the studies reported measurements of urinary metabolites, usually 1-pyrenol

(1-hydroxypyrene). These have also been indicated below, together with results of the dermal sampling that was usually conducted to measure levels of pyrene and benzo[*a*]pyrene on the skin surface.

(b) General considerations

Based on the CAREX database, it has been estimated that in 15 countries in Europe in 1990–93 almost 1 000 000 people were exposed to PAHs above background levels through their occupations (Kauppinen *et al.*, 2000). A study in Costa Rica showed that 17 700 men and women were occupationally exposed to PAHs, excluding environmental tobacco smoke and diesel exhaust (Partanen *et al.*, 2003).

The production and use of coal tar and coal tar-derived products are major sources of occupational exposure to PAHs. Crude coal tar is a by-product of coke production and was formerly also a by-product of gas works. Crude coal tar is usually distilled, and blends of distillation fractions are used for various purposes, such as wood conservation, paints, road tars and roofing materials. PAH concentrations in coal-tar products may range from less than 1% up to 70% or more (Jongeneelen, 2001; ATSDR, 2002).

Most PAHs are relatively non-volatile compounds. Airborne PAHs with fewer than four aromatic rings (molecular weight range, 128–178) are sufficiently volatile to be present as gaseous compounds in the working environment. PAHs with four rings (molecular weight, 202) may be present both in the gas phase and as adsorbed particulates. PAHs with higher molecular weights (>228) are typically bound to airborne particulates (Jongeneelen, 2001).

Occupational exposure to PAHs occurs primarily through inhalation and skin contact. Monitoring of workplace air and personal air sampling for individual PAHs, sets of PAHs or surrogates (e.g. coal-tar pitch volatiles) have been used to characterize inhalation exposures; more recently, biological monitoring methods have been applied to characterize the uptake of certain PAHs (e.g. pyrene, benzo[*a*]pyrene) as biomarkers of total exposure (see Sections 1.1.2 and 1.3).

There is growing awareness that occupational uptake of PAHs through the skin is substantial (Jongeneelen, 2001). For example, uptake of pyrene by the dermal route was estimated to account for as much as 75% of total body dose for coke-oven workers (VanRooij *et al*, 1993a); for creosote-impregnating workers, dermal pyrene uptake was on average 15-fold higher than the estimated respiratory uptake (VanRooij *et al.*, 1993b).

Geographical distribution of the industries described in the following sections varies considerably from industry to industry and over time within an industry. Coke production increased more than fivefold in the People's Republic of China between 1970 and 1995, with concomitant decreases in Europe and North America. In 1995 and 1999, the People's Republic of China provided over one-third of the world's production of coke and more than half of global coke exports (Terjung, 2000).

(c) Coal liquefaction

Coal liquefaction is a conversion process in which liquid fuels and liquid chemicals are obtained from solid coal. Coal liquefaction can be accomplished in two ways. In the first, which is called direct liquefaction or coal hydrogenation, the coal is suspended in suitable oils and treated with either hydrogen in the presence of a catalyst or hydrogenating solvents to yield oil products and some unreactive residue. In the second, which is called indirect liquefaction, coal is gasified to yield a mixture of hydrogen and carbon monoxide (synthesis gas) from which liquid products can be synthesized in one or more steps. Both methods were developed into industrial-scale processes during the 1930s and were used extensively during the Second World War in Germany. Currently, (indirect) coal liquefaction is employed on an industrial scale only in South Africa. Further improvements were made to develop large pilot plant operations, mainly in Germany, Japan and the USA. These activities reached their peak between 1975 and 1985, and have continued at lower levels since that time (Quinlan *et al.*, 1995a,b,c; Crelling *et al.*, 2005).

Concentrations of PAHs in the air and the skin and urine of workers in coal liquefaction are summarized in Table 1.2.

Quinlan *et al.* (1995a) studied a pilot coal liquefaction plant. Inhalation exposures to cyclohexane-soluble material were measured and spot urine samples were collected. There were no statistically significant relationships between the levels of cyclohexane-soluble material and those of 1-hydroxypyrene, and the authors attributed elevated levels of 1-hydroxypyrene primarily to dermal absorption of PAHs among engineers.

Quinlan *et al.* (1995b) also conducted an in-depth study to investigate the relationships between work activities, exposures to PAHs and excretion of 1-hydroxypyrene among coal liquefaction workers. The study demonstrated that there was an increase in the daily (pre- versus post-shift) levels of 1-hydroxypyrene excretion, as well as an increase in the day-to-day levels (shift 1 to shift 4). The levels of exposure to cyclohexane-soluble material ranged from < 5 to 49 $\mu g/m^3$. Pyrene was reported to comprise 7% of the extract; its concentration in the particulate phase ranged from 0.8 to 2.8 $\mu g/m^3$, while benzo[*a*]pyrene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and dibenzo[*a*,*h*]pyrene totalled 0.5% of the cyclohexane-soluble extract.

(d) Coal gasification

Coal gasification is the process of reacting coal with oxygen, steam and carbon dioxide to form a gas that contains hydrogen and carbon monoxide. Gasification is essentially incomplete combustion. The chemical and physical processes in gasification and combustion are quite similar, the main difference being the nature of the final products. With regard to processing, the main difference in operations is that gasification consumes the heat evolved during combustion. Under the reducing environment of gasification, sulfur in the coal is released as hydrogen sulfide rather than sulfur dioxide and nitrogen in the coal is converted mostly to ammonia rather than nitrogen oxides. These

Table 1.2. Concentrations of PAHs in the air, skin and urine of workers in coal liquefaction in the United Kingdom [year of study not reported]

Reference	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^3)		Dermal levels (ng/cm^2)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range	Mean	Range
Quinlan *et al.* (1995a)	Engineer	5	6	2		0.07	NR				
	Technician	5	9	3							
	Engineer	5	6	2	1-Hydroxypyrene					8.53	< 1*–72.8
	Technician	5	9	3						3.74	0.5*–7*
Quinlan *et al.* (1995b)	Operators[a]	5	NR	NR	16 individual PAHs, vapour-phase only		ND–3340[b]				
			10	NR	CSM		ND–49				
			[b]	NR	Pyrene[c]	1323	630–2870				
										Geometric mean	
	Operators[d]	5	38	NR	1-Hydroxypyrene					NR	0.59–20.02
	Maintenance[d]	5	35	NR						NR	0.24–13.72
	Laboratory[d]	2	16	NR						NR	0.29–2.22
	Operators[e]	7	7	NR						2.9	0.87–6.58
	Maintenance[e]	9	9	NR						3.35	0.56–14.18
	Laboratory[e]	9	9	0						0.53	0.22–2.28
	Office[e]	10	10	1						0.26	0.15–2.06

Table 1.2 (Contd)

Reference	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels ($\mu g/m^3$)		Dermal levels (ng/cm^2)		Urinary levels (μmol/mol creatinine)	
						Mean	Range	Mean	Range	Mean	Range
Quinlan *et al.* (1995c)	Engineer	5	10	0	Pyrene			21.5	ND–47.7		
	Technician	5	10	3				17.8	ND–78.3		
	Engineer	5	20	0	Benzo[*a*]pyrene			ND	ND		
	Technician	5	20	3				ND	ND		
	Engineer	5	20	0	1-Hydroxypyrene						0.73–48.47
	Technician	5	20	3							2.19–15.43

CSM, cyclohexane-soluble material; ND, not detected; NR, not reported; PAH, polycyclic aromatic hydrocarbon

* Read from graph

[a] Values measured over 1 week

[b] Value measured for phenanthrene

[c] Calculated from mean CSM value, assuming 7% pyrene content in CSM extract

[d] Values measured over 4 weeks

[e] Spot measurements at the end of working period

reduced forms of sulfur and nitrogen are easily isolated, captured and used, and thus gasification is a clean-coal technology with better environmental performance than coal combustion (Shadle *et al.*, 2002).

Depending on the type of gasifier and the operating conditions, gasification can be used to produce a fuel gas that is suitable for a number of applications. A low heating-value fuel gas is produced from an air-blown gasifier for use as an industrial fuel and for power production. A medium heating-value fuel gas is produced from enriched oxygen-blown gasification for use as a synthesis gas in the production of chemicals such as ammonia, methanol and transportation fuels. A high heating-value gas can be produced by passing the medium heating-value gas product over catalysts to produce a substitute or synthetic natural gas (Shadle *et al.*, 2002).

The earliest gasification processes were developed using a countercurrent, fixed-bed gasifier. In a fixed-bed gasifier, coal is fed onto the top of the bed and travels downwards against the current to the flow of gases. Atmospheric fixed-bed gasifiers of various design are still occasionally found in small-scale industrial use. On a large scale, some Lurgi fixed-bed pressurized gasification plants are currently operating commercially, e.g. in the Republic of South Africa and in the USA (Shadle *et al.*, 2002; Crelling *et al.*, 2005).

Fluidized-bed gasification, invented in 1922 by Winkler at BASF, has the advantage of a fairly simple reactor design. In this process, the reactor vessel is designed so that the air and steam flow required for gasification is sufficient to fluidize the bed of coal, char and ash. Fluidization occurs when the velocity of the gas flow lifts the particles and causes the gas–solid mixture to flow like a fluid (Shadle *et al.*, 2002; Crelling *et al.*, 2005).

Entrained-flow gasification takes place in a flame-like reaction zone, usually at a very high temperature, to produce a liquid slag. For economical operations, a high-standard heat recovery system is mandatory, but the gas product typically has a very low methane content and is free of tars, oils and phenols, which thereby simplifies gas and water treatment considerably. Entrained-flow gasifiers of the Koppers-Totzek design that are operated at atmospheric pressure are used industrially in many countries to produce hydrogen or synthesis gas (Shadle *et al.*, 2002; Crelling *et al.*, 2005).

The moving-bed gasifiers produce tars, oils, phenols and heavy hydrocarbons, and the concentrations in the gas product are controlled by quenching and water scrubbing. Fluidized-bed gasifiers produce significantly smaller amounts of these compounds because of higher operating temperatures. Entrained-flow gasifiers that operate at even higher temperatures (in excess of 1650 °C) can achieve carbon conversions of more than 99.5% while generating essentially no organic compounds heavier than methane (Shadle *et al.*, 2002).

Concentrations of PAHs in the air of workers in the coal gasification industry were reported by Gustavsson and Reuterwall (1990) to be similar to those described by Lindstedt and Sollenberg (1982) in American plants [data not presented in Tables or Figures]. In addition to PAHs, workers in coal gasification may be exposed to many compounds, including asbestos, silica, amines, arsenic, cadmium, lead, nickel, vanadium, hydrocarbons, sulfur dioxide, sulfuric acid and aldehydes (IARC, 1984).

(e) Coke production and coke ovens

Coke was first produced commercially in England in the early eighteenth century. By the early to mid-1800s, coke was being widely produced in Europe and the USA as the major fuel for blast furnaces.

Coal carbonization is the process of producing metallurgical coke for use in iron-making blast furnaces and other metal-smelting processes. Carbonization entails heating the coal to temperatures as high as 1300 °C in the absence of oxygen in order to distill out tars and light oils. A gaseous by-product, referred to as coke-oven gas, together with ammonia, water and sulfur compounds are also removed thermally from the coal. The coke that remains after this distillation largely consists of carbon in various crystallographic forms, but also contains the thermally modified remains of various minerals that were in the original coal. These mineral residues, commonly referred to as coke ash, do not combust and are left after the coke is burned. Coke also contains part of the sulfur from the coal. Coke is principally used as a fuel, a reductant and a support for other raw materials in iron-making blast furnaces. A much smaller amount of coke is used similarly in cupola furnaces in the foundry industry. The carbonization by-products are usually refined, within the coke plant, into commodity chemicals such as elemental sulfur, ammonium sulfate, benzene, toluene, xylene and naphthalene. Subsequent processing of these chemicals produces a large number of other chemicals and materials. Coke-oven gas is a valuable heating fuel that is used mainly within steel plants, for example, to fire blast-furnace stoves, to soak furnaces for semi-finished steel, to anneal furnaces and lime kilns as well as to heat the coke ovens themselves (Kaegi *et al.*, 1993).

The vast majority of coke is produced from slot-type by-product coke ovens. Individual coke ovens are built of interlocking silica bricks that are produced in numerous shapes for special purposes. It is not uncommon for batteries of modern coke ovens to contain 2000 different shapes and sizes of brick. Typical coke ovens are 12–14 m in length, 4–6 m in internal height and be less than 0.5 m in internal width. On each side of the oven are heating flues that are also built of silica brick. Batteries of adjacent ovens, where ovens share heating flues, contain as many as 85 ovens. At each end of each oven, refractory-lined steel doors are removed and re-seated for each oven charge and push. Coke batteries are generally heated with part of the coke-oven gas that is generated in the process of coke production; however, they can also be heated with blast-furnace gas and natural gas. Once heated, the battery generally remains hot for its entire life because cooling causes a mineralogical change in the silica that lowers the strength of the silica brick (Kaegi *et al.*, 1993).

Above the ovens is a roof system that is capable of supporting the moving Larry car from which coal is discharged into each oven through three to five charging holes in the top of each oven. The Larry car is filled for each oven charge from a large blended coal silo that is constructed above the rail of the Larry car, usually at one end of the coke battery. Modern Larry car technology includes telescopic charging chutes to minimize dust emissions during charging. Many facilities also include automatic removal and replacement of the charging-hole lid. After completion of charging and replacement of the charging-hole lids, a small flap at the top of one of the oven doors is opened and a steel levelling bar is inserted along the length of the oven above the coal charge. The levelling bar is moved back and forth over the coal to produce a level charge that has sufficient free space above it. This free space is important to ensure balanced heating of the coal and is needed to convey the volatile carbonization products out of the oven. Most coke batteries charge wet coal into the ovens; however, a few facilities are equipped with pre-heaters that not only remove all moisture from the coal, but pre-heat it to 150–200 °C in order to expedite the carbonization process. The pre-heated charge facilities function very similarly to wet charge facilities except that more attention is paid to potentially higher levels of charging emissions caused by the dryness of the coal (Kaegi *et al.*, 1993).

On top of the battery, at either one or both ends of each oven, refractory-lined standpipes are mounted on additional roof openings into each oven. The volatile gases generated from the coal during carbonization flow to the top of the oven, into the free space and out through the standpipes. The standpipes are all connected to large collecting mains that run along the length of the battery. These mains transport the gases to the by-product plant in which they are processed into various materials. Water is sprayed into the mains in order to cool the gases and to condense out some of the tar (Kaegi *et al.*, 1993).

At the end of the coking cycle, which ranges from about 15 to 30 h depending on production needs and on the condition of the battery, the doors are removed from each oven. A pusher machine equipped with a large water-cooled ram then pushes the coke from the oven into a hot or quench car. After the coke is pushed from the oven, the doors are replaced to maintain oven heat and oven carbon content. The hot car may or may not have a moveable or partial roof to minimize gaseous and particulate emissions. The car moves on rails and positions the hot coke beneath a large water tank that is equipped with nozzles on its underside. The water flow is regulated to quench the coke with a minimal amount of excess water remaining on the cooled coke. After quenching, the hot car moves again to dump the coke onto a refractory, covered coke wharf that is sloped away from the hot car. The coke flows to the bottom of the wharf, at which point it drops onto a conveyor system for transportation to a blast furnace, storage pile or out of the plant (Kaegi *et al.*, 1993; Crelling *et al.*, 2005).

In 1990, total worldwide coke production was about 378 million tones and was essentially unchanged since that in 1970. In 1990, the former USSR was the largest coke producer (80 million tonnes), followed closely by the People's Republic of China (73 million tonnes). Japan produced 53 million tonnes and the USA produced about 27 million tonnes. Since 1970, production in the former USSR has remained in the range of 75–85 million tonnes, but massive shifts in production have occurred in the USA, Japan and the People's Republic of China. Between 1970 and 1990, production in the USA decreased by more than 50% while Japanese production increased by 50%. During the same period, the People's Republic of China increased coke production by over 300%

(Kaegi *et al.*, 1993). By 1999, worldwide coke production had declined to about 326 million tonnes, of which 121 million tonnes were produced in the People's Republic of China (Terjung, 2000).

Concentrations of PAHs in the air and urine of workers in coke ovens are summarized in Table 1.3 and Figure 1.1.

More than 30 studies of exposure among coke-oven workers have been reported since 1983, six of which included profiles of three or more PAHs; seven others reported levels of pyrene, benzo[*a*]pyrene or both; and the remainder reported composite measurements (benzene-soluble fraction, cyclohexane-soluble material) or urinary measurements only. A variety of sites in the coke plants were sampled, and the overall pattern (regardless of the exposure that was measured) was that topside workers (including lidmen, tar chasers and Larry car operators) had the highest exposures, followed by workers by the side of the ovens (such as coke-side machine operators, benchmen, door repairers, wharfmen, quenchers, pushers and temperature controllers). Workers in other areas of the plant such as maintenance, office and control workers had the lowest exposures (see Table 1.3). It has been reported that modernization of coke plants, including improved control measures, can substantially reduce exposures (Quinlan *et al.*, 1995c).

In addition to PAHs, coke-oven workers may be exposed to a large number of compounds, including asbestos, silica, amines, arsenic, cadmium, lead, nickel, vanadium, hydrocarbons, sulfur dioxide, sulfuric acid and aldehydes (IARC, 1984).

(f) Coal-tar distillation

Coal tar is the condensation product obtained by cooling the gas that evolves from the destructive distillation of coal to approximately ambient temperature. It is a black, viscous liquid that is denser than water and is composed primarily of a complex mixture of condensed-ring aromatic hydrocarbons. It may contain phenolic compounds, aromatic nitrogen bases and their alkyl derivatives, and paraffinic and olefinic hydrocarbons. Coal-tar pitch is the residue from the distillation of coal tar. It is a black solid that has a softening-point of 30–180 °C (Betts, 1997). Figure 1.2 portrays the process of coal-tar production and its conversion to coal-tar distillates and residual coal-tar pitch, and also illustrates the uses of creosote (see this section) and of coal-tar pitch (see Sections 1.2.2(*e*),(*g*),(*h*)).

The largest source of tar and pitch is the pyrolysis or carbonization of coal. The importance of coal tar as an industrial raw material dates back to the first half of the eighteenth century, when the carbonization of coal and the production of tar as a by-product were expanding rapidly in the United Kingdom. Initially, the crude tar was subjected to a simple flash distillation in pot stills to yield a solvent (naphtha), creosote for timber preservation and a residue of pitch that was used as a binder for coal briquettes. Later, coal tar was the main source of aromatic hydrocarbons, phenols and pyridine bases that were needed by the rapidly expanding dyestuffs, pharmaceuticals and explosives industries. The development of by-product coke ovens and recovery of crude benzene at both coke ovens and gas works greatly increased the supplies of crude tar and tar distillates

Table 1.3. Concentrations of PAHs in the air, skin and urine of workers in coke ovens

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^3)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Andersson *et al.* (1983), Sweden, NR	Top side	1	1	NR	11 PAHs	1513 (total)			
					Benzo[*a*]pyrene	38			
Haugen *et al.* (1986), Norway, NR	Top side	4	4	22	38 PAHs	Outside RPE, 266	212–315		
						Inside RPE, 110	51–162		
Hemminki *et al.* (1990), Poland, NR	Top side	NR	NR	NR	Benzo[*a*]pyrene	39.1	9.4–90		
	Side	NR	NR	NR		4.09	0.54–13.6		
	Pusher side	NR	NR	NR		6.42	2.5–11.2		
	Sorting	NR	NR	NR		0.82	0.25–1.4		
	Office	NR	NR	NR		0.19	0.03–0.45		
	Distillation	NR	NR	NR		0.06	0.06		
Jongeneelen *et al.* (1990), Netherlands, NR	Side	5		NR	13 PAHs; pyrene	6.9[a]; < 0.6[a]	< 1–46; < 0.6–4.8		
	Top side oven 1	20		55%		17.0[a]; 2.0[a]	7.3–39; < 0.6–4.4		
	Push side	7		29%		13.9[a]; 1.6[a]	3.6–77; < 0.6–9.8		
	Maintenance	10		NR		13.6[a]; 1.8[a]	< 1–43; < 0.6–6.1		
	Top side oven 2	9		56%		12.9[a]; 1.7[a]	1.8–37; 1.8–7.3		
	Side	7		57%	1-Hydroxypyrene: end of shift; increase over shift			2.0[a]; 0.13[a]	0.7–2.6; –1.2–1.5
	Top side oven 1	19		NR				3.3[a]; 2.0[a]	0.8–7.5; 0–4.9
	Push side	7		29%				1.9[a]; 0.67[a]	0.6–3.5; –0.4–2.0
	Maintenance	11		64%				1.9[a]; 1.2[a]	1.31–4.1; 0.33–3.0
	Top side oven 2	9		56%				2.7[a]; 1.3[a]	1.3–6.5; –1.3–4.6
Reuterwall *et al.* (1991), Sweden, NR	Oven in steel mill	12	NR	0	14 PAHs; benzo[*a*]pyrene	NR; [3.5 estimated]	6–570		

Table 1.3 (Contd)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^3)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Buchet *et al.* (1992), Belgium, NR	Oven bench side	10	10	6	13 PAHs	14.2^{b}; 25.1^{c}	0.7–74.2		
	Oven top side	6	6	3		198.7^{b}; 241.2^{c}	26.6–959		
	Oven bench side	10	10	6	Pyrene	0.05 NS^{b}; 0.09 S^{b}			
	Oven top side	6	6	3		15.9 NS^{b};5.62 S^{b}			
	Oven bench side	10	10	6	1-Hydroxypyrene			*Nonsmoker*^{b} 2.27 pre; 2.36 post	*Smoker*^{b} 0.46 pre; 1.45 post
								4.67 pre; 10.91 post	3.22 pre; 11.72 post
	Oven top side	6	6	3					
Assennato *et al.* (1993), Italy, 1992		69	NR	45.6%					
	Supervisor	1	1	NR	Benz[*a*]anthracene; chrysene; benzo[*a*]pyrene; total PAHs		0.41; 0.29; 0.32; 6.98		
	Door maintenance	NR	NR	36.4%			4.26–14.79; 2.31–6.37; 2.34–6.53; 30.37–96.96		
	Machine operator	NR	NR	NR			0.11–33.19; 0.08–13.17; 0.03–12.63; 2.94–218.9		
	Gas regulator	NR	NR	NR			0.21–2.1; 0.12–1.61; 0.13–1.6; 7.24–26.48		
	Temperature operator	NR	NR	NR		NR	1.77–10.07; 1.37–5.03; 0.98–4.78; 20.98–64.48		
	Top side	NR	NR	NR		NR	0.45–3.4; 0.47–4.73; 0.23–2.42; 8.91–47.93		

Table 1.3 (Contd)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^3)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Grimmer *et al.* (1993), Germany, NR		4	16	3/4	19 PAHs	Summary data not reported			
	Battery top	1	4	0	Pyrene metabolites			60.5	43.7–80.3
	Battery top	1	4	1				33.4	29.2–39.2
	Driver of containers	1	4	1				16.9	6.1–26.3
	Machinist	1	4	1				4.3	3.1–5.2
Van Hummelen *et al.* (1993), Belgium, NR		33	33	26/33	13 PAHs	23.7	SE, 10.8		
					1-Hydroxypyrene			0.51 pre; 0.75 post	SE, 0.08 SE, 0.17
VanRooij *et al.* (1993a), Netherlands, 1990		12	60	8/12	Pyrene	1.53	0.09–5.37		
						Total dermal levels (µg)			
					Pyrene (8-h)	74.4	21.2–165.9		
					1-Hydroxy-pyrene (7-day)			111.4 nmol	36–239 nmol
Ferreira *et al.* (1994), Belgium, NR		56	56	31/56	Total 13 PAHs	15.9	0.5–1106.4		
					1-Hydroxypyrene			0.8 pre 1.5 post	0.04–29.3 0.02–93.5

Table 1.3 (Contd)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (μg/m^3)		Urinary levels (μmol/mol creatinine)	
						Mean	Range	Mean	Range
Clonfero *et al.* (1995), Italy NR		95	95	54	1-Hydroxypyrene			1.28	0.04–5.59
Levin *et al.*	Various	10	10	6/10	Benzo[*a*]pyrene	4^c	0.9–37		
(1995),					Sum of 7 PAHs		20–480		
Sweden,					1-Hydroxypyrene			14 ng/mL^c	4–90 ng/mL
1988									
1990					Benzo[*a*]pyrene	0.7^c			
					Sum of 7 PAHs		< 10–70		
					1-Hydroxypyrene			3.8 ng/mL^c	1–17 ng/mL
Øvrebø *et al.*		*Jan; June*			1-Hydroxypyrene			*Jan; June*	
(1995),	Top side	18; 13		50%				4.26; 5.53	
Norway,	Bench side	26; 18		61%				1.80; 2.93	
NR	Maintenance	23; 17		56%				1.11; 1.32	
Popp *et al.*		29	29	16/29	Benzo[*a*]pyrene	1.7	0.5–3.6		
(1995),					Total 19 PAHs	49.2	14.0–127.4		
Germany,	Top side				Benzo[*a*]pyrene	2.3			
NR					Total 19 PAHs	67.1			
	Coke side				Benzo[*a*]pyrene	1.4			
					Total 19 PAHs	38.7			
Pyy *et al.* (1995),		160	Dust, 510;	NR	Fluorene	0.58–24.64			
Finland,	10 working areas		gas, 90		Phenanthrene	0.16–18.76			
1987–90					Benzo[*a*]pyrene	0.05–10.30			

Table 1.3 (Contd)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^3)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Malkin *et al.*		10	10	NR	CTPV		ND–350		
(1996),					Pyrene		ND–1		
USA,	Coal-tar sludge	18	18	9	1-Hydroxy-			1.0; 1.7	0.16–3.0; 0.24–4.85
1994	handling area				pyrene (pre; post)			1.6; 3.7	
	Labourer	2	2	NR				0.4; 0.6	
	Coal handler	6	6	NR					
	operator							1.4; 2.4	
	Coal handler maintenance	5	5	NR					
	Other	5	5	NR				1; 1.6	
Winker *et al.* (1996), Austria, NR		24	1	14/24	Sum of 16 PAHs	*Old facility* *New facility*	101 32		
Mielzyńska *et al.*	Total	24		> 50%	Benzo[*a*]pyrene	2.1^{c}	0.1–15.1		
(1997),	Top side oven	7	25	NR	(air) and	3.97	0.6–14.1	2.0; 3.57	0.1–7.76; 0.14–10.74
Poland,	Side of oven	8	28	NR	1-Hydroxy-	2.57	0.2–15.1	1.54; 2.37	0.09–4.94; 0.08–18.92
NR	Gas fitting operators	3	10	NR	pyrene (pre; post urine)	1.27	0.3–4.5	1.24; 2.96	0.15–2.66; 0.92–5.3
	Dry quenching	6	11	NR		0.27	0.1–1.5	0.46; 0.87	0.07–1.76; 0.06–2.2
Pan *et al.* (1998),		75	95	51/75					
China,	Topside	25		15	Total PAHs;	264.9^{c}; 4.27^{c}; 4.30^{c}		12.0	
NR					pyrene; benzo[*a*]-				
	Push side	10		8	pyrene;	139.3^{c}; 1.6^{c}; 2.0^{c}		9.1	
	Coke side	15		10	1-hydroxypyrene	82.4^{c}; 0.46^{c}; 0.58^{c}		5.7	
	Bottom	25		18	(pre urine)	134.0; 0.86; 4.0		4.0	

Table 1.3 (Contd)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m³)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Romundstad *et al.*		NR	594	NR	Total particulate				
(1998),	Top side				PAH		*95% CI*		
Norway,	1976		12			300	139–461		
1976–87	1978–87		221			125	113–138		
	Inside helmet, 1977–87		212			37	33–41		
	Side oven								
	1976–87		75			44	25–63		
	Inside helmet		60			10	7–12		
	Ram car								
	1976		5			30	5–55		
	1978		5			6	0–17		
	Quench, 1976		4			2	0–6		
Wu *et al.* (1998),	Top side	18	54	12	BSF (air) and	528^b	144–6309	29^d; 199^d	1–101^d; 8–3261^d
Taiwan, China,	Side oven	41	123	21	1-hydroxy-pyrene	74^b	11–1130	5^d; 13^d	0.7-23^d; 0.2–520^d
1995–96	Side/control	21	63	11	(pre; post urine)	49^b	16–111	3^d; 11^d	0.3-24^d; 3–31^d
Brescia *et al.*		76			PAH; benzo[*a*]-	18.98; 1.72	12.58–42.66; 0.87–2.88	1.44	0.04–3.75
(1999),	Top side	27	27	55.6%	pyrene,				
Italy,	Bench	32	32	62.5%	1-hydroxypyrene	20.03; 1.56	12.58–63.66; 0.48–6.33	1.30	0.051–5.59
NR	Bottom	17	17	45.0%		15.37; 0.78	6.9–16.86; 0.32–0.86	1.35	0.068–4.18

Table 1.3 (Contd)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^3)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Chen *et al.* (1999), Taiwan, China, 1995–96		88	264	NR	BSF				
	Lidman		33			515[b]	72–18181		
	Tar chaser		21			432[b]	51–4334		
	Larry car operator		15			185[b]	55–649		
	Cokeside machine operator		21			121[b]	32–2965		
	Benchman		18			97	33–488		
	Door repair		30			82	11–352		
	Wharfman		15			42	10–117		
	Quencher		24			29	ND–395		
	Pusher		24			25	ND–98		
	Temperature controller		12			55	30–156		
	Body repairman		21			55	10–136		
	Heater		12			38	21–85		
	Supervisor		18			26	ND–91		
Pavanello *et al.* (2000), Italy, NR	Top side	30	30	0	1-Hydroxypyrene			0.82	0.12–5.15
	Other workers	30	30	0				0.39	0.03–1.23

Table 1.3 (Contd)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^3)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Price *et al.* (2000), United Kingdom, 1998	Low-temperature	13	13	6	Sum of 19 PAHs	50.03	5.87–131.6		
					HSE11^e	7.03	0.01–19.4		
					Benzo[*a*]pyrene	1.15	0.01–3.2		
					Pyrene	2.03	0.05–7.44		
					1-Hydroxy-pyrene			2.64	0.41–6.91
	High-temperature	11	11	5	Sum of 19 PAHs	79.26	8.8–184.7		
					HSE11^e	16.45	1.27–44.8		
					Benzo[*a*]pyrene	2.26	0.18–6.26		
					Pyrene	2.12	0.43–9.90		
					1-Hydroxy-pyrene			1.72	0.25–5.42
	High-temperature	13	13	5	Sum of 19 PAHs	70.73	9.94–294.7		
					HSE11^e	5.77	0.226–29.25		
					Benzo[*a*]pyrene	0.81	0.02–4.13		
					Pyrene	0.63	0.05–2.49		
					1-Hydroxy-pyrene			2.07	0.25–7.1
van Delft *et al.* (2001), Netherlands, 1997									*SD*
	Oven (high exposure)	35	35	15	1-Hydroxypyrene			51.04 (NS); 1.52 (S)	0.67 (NS); 1.40 (S)
	Distilleries and maintenance (low exposure)	37	37	18				0.27 (NS); 0.7 (S)	0.22 (NS); 0.39 (S)
Zhang *et al.* (2001), China, NR		162	NR	108	1-Hydroxypyrene			9.86^b	0.9–89.8

Table 1.3 (Contd)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^3)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Lu *et al.* (2002), Taiwan, China, NR	Top side	24	72	15	BSF 1-Hydroxypyrene	483.0[b]		S pre: 6.6	2.3–16.7
								S post: 17.0	6.0–32.5
								NS pre: 3.8	0.4–18.6
								NS post: 7.3	1.0–35.0
	Coke side	50	150	23		70.8[c]		S pre: 0.9	0.3–2.7
								S post: 1.6	0.3–5.0
								NS pre: 0.8	0.2–2.4
								NS post: 1.4	0.3–11.5
	Office	14	42	6		43.4[c]		S pre: 1.0	0.4–2.2
								S post: 1.3	0.7–3.1
								NS pre: 1.2	0.5–3.0
								NS post: 1.5	0.7–3.6
Marczynski *et al.* (2002), Germany, NR		20	20	15	Sum of 16 PAHs	54.26	4.51–316.4		
					Benzo[*a*]pyrene	2.77	0.12–16.26		
Strunk *et al.* (2002), Germany, NR		24	24	16	Sum of 16 PAHs (air); 1-hydroxypyrene; sum of hydroxyphenanthrene (urine)				
	Top side	5	5			491.2	82.81–1679	19.7; 39.18	6.84–34.82; 19.06–79.36
	Bench side	8	8			26.61	1.65–88.53	7.01; 12.95	1.22–15.03; 5.87–23.66
	Complete area	11	11			76.18	1.04–237.8	3.57; 8.70	0.51–10.2; 3.31–21.26
Waidyanatha *et al.* (2003), China, NR	Side and bottom	13	13	8	Phenanthrene[d]; pyrene[d]			1.70; 0.003	0.037–8.66; 0.001–0.007
	Top side	15	15	9				3.42; 0.005	0.013–19.3; 0.0005–0.017

Table 1.3 (Contd)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^3)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Pavanello *et al.* (2004), Poland, 2002		95	95	57	1-Hydroxypyrene			6.93	0.25–31.4

BSF, benzene-soluble fraction; CI, confidence interval; CTPV, coal-tar pitch volatiles; ND, not detected; NR, not reported; NS, nonsmoker; PAH, polycyclic aromatic hydrocarbon; pre, pre shift; post, post shift; RPE, respiratory protective equipment; S, smoker; SD, standard deviation; SE, standard error

[a] Geometric mean of the mean of three or fewer observations per worker

[b] Geometric mean

[c] Median

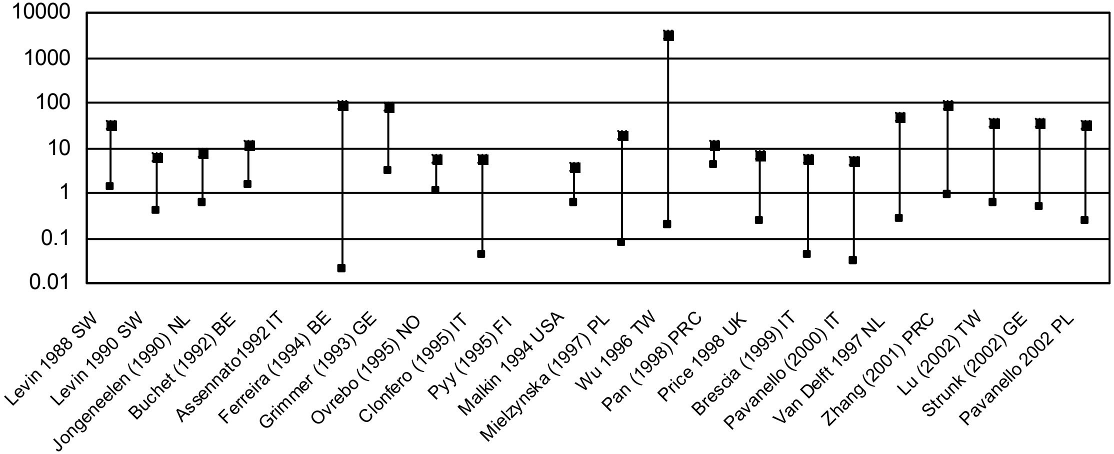
[d] Reported in µg/L

[e] Benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, dibenzo[*a,h*]anthracene, anthanthrene, cyclopenta[*cd*]pyrene

Figure 1.1. Range in concentrations of post-shift urinary 1-hydroxypyrene (in µmol/mol creatinine) and benzo[*a*]pyrene (in µg/m^3) in occupational settings with exposure to PAHs[a]

Coke ovens

1-Hydroxypyrene



Benzo[*a*]pyrene

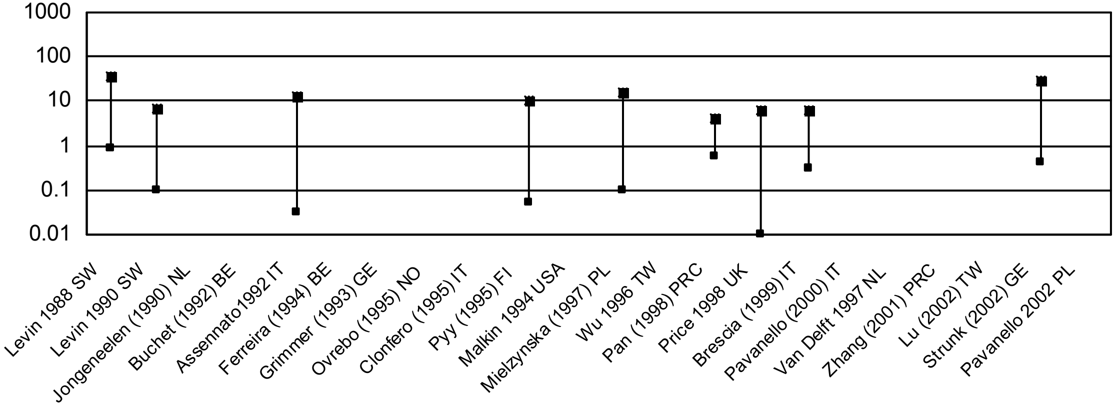
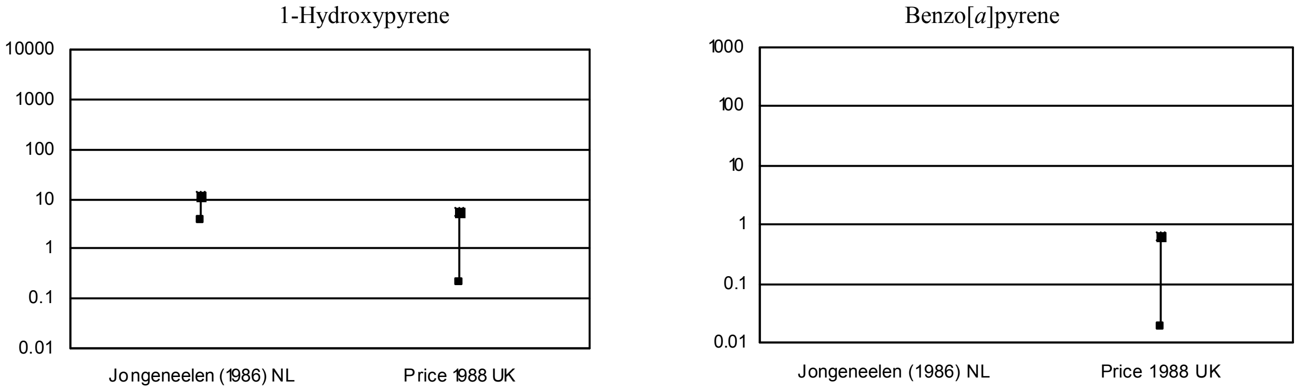


Figure 1.1 (contd)

Coal tar distillation



Roofing and paving

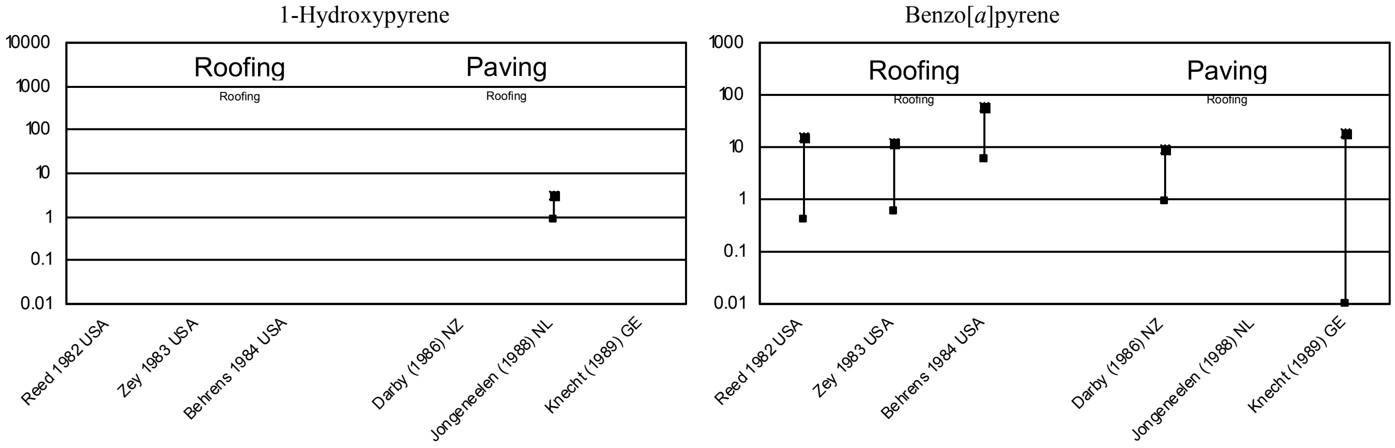
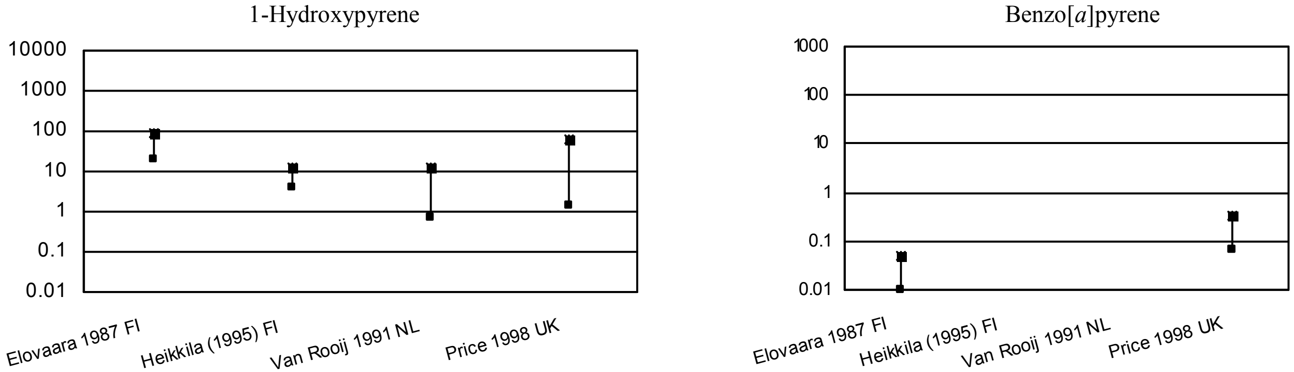


Figure 1.1 (contd)

Wood impregnation with creosote



Aluminium production

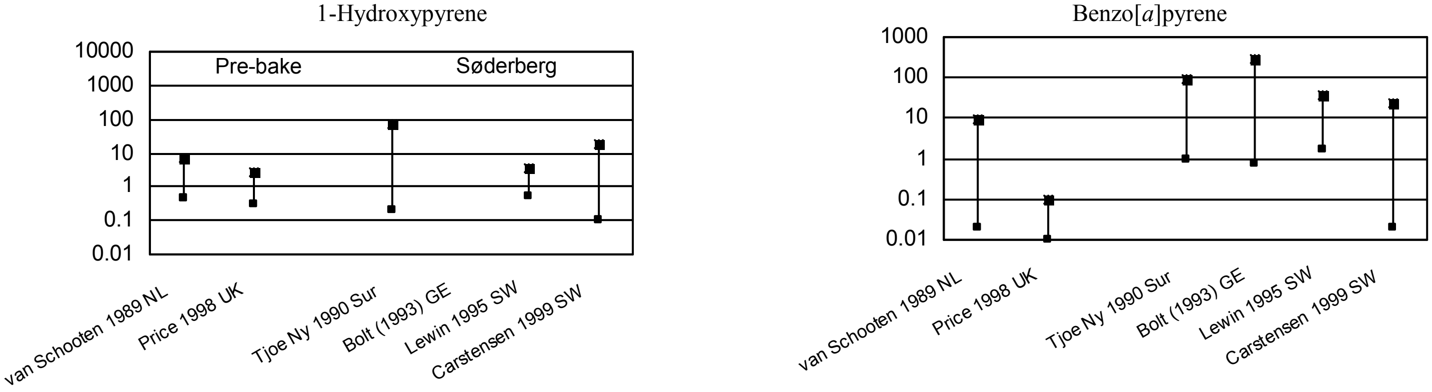
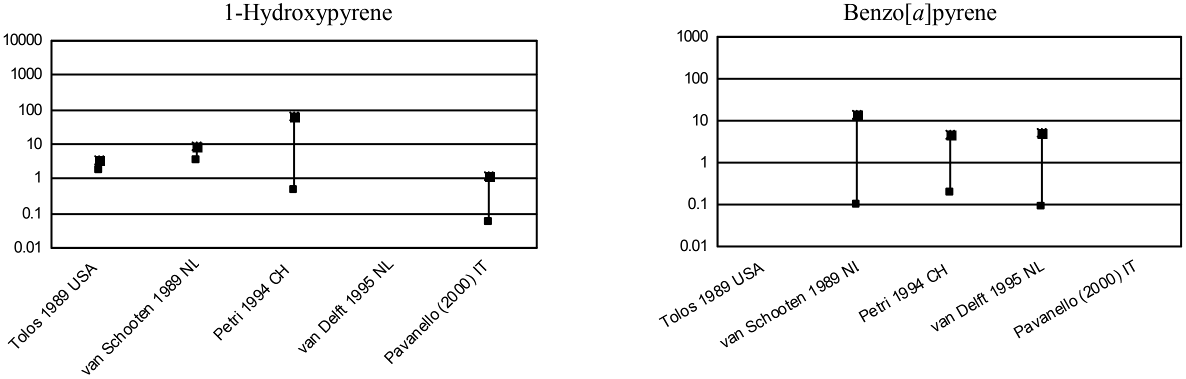


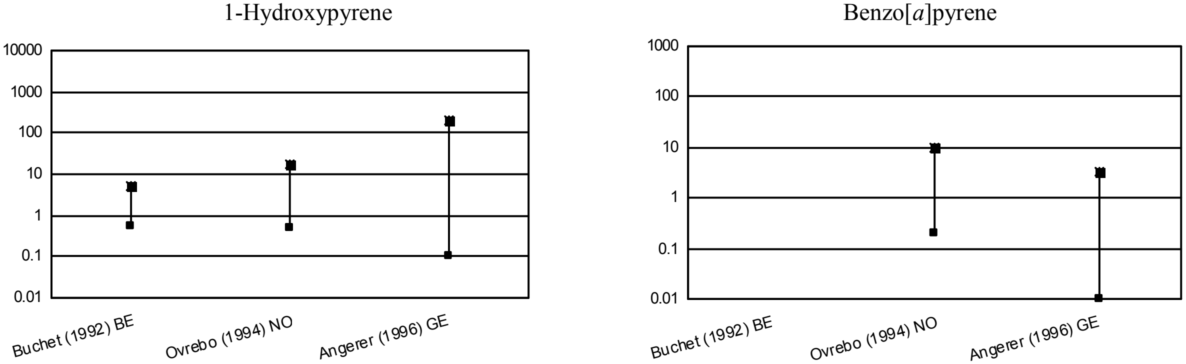
Figure 1.1 (contd)

Anode manufacturing for aluminium


1-Hydroxypyrene

Benzo[*a*]pyrene

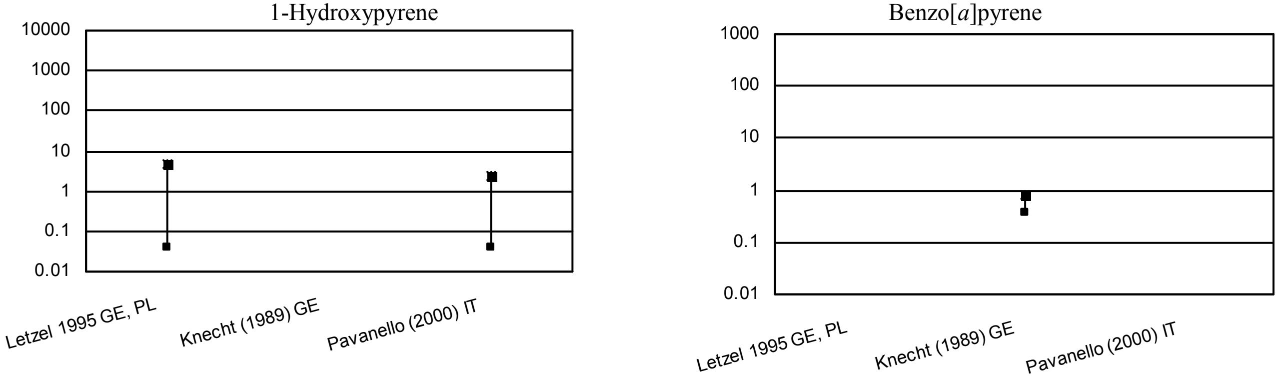
Carbon electrode manufacturing


1-Hydroxypyrene

Benzo[*a*]pyrene

Figure 1.1 (contd)

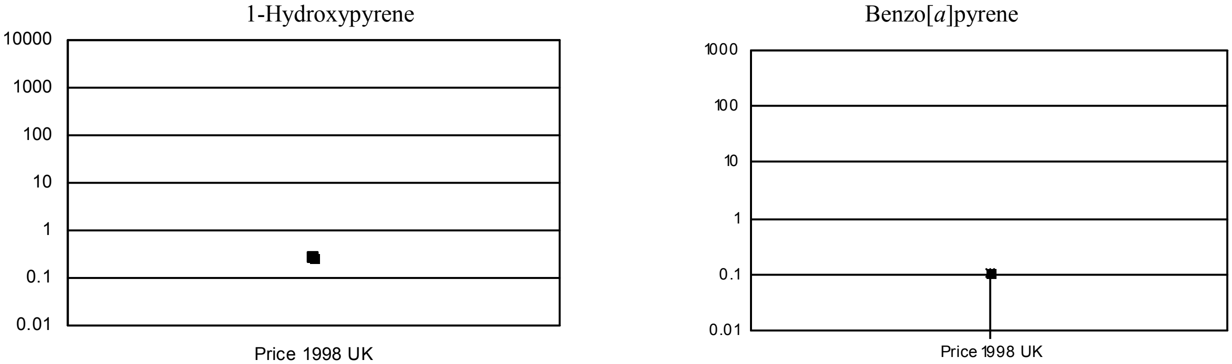
Chimney sweeps



1-Hydroxypyrene

Benzo[*a*]pyrene

Power plants

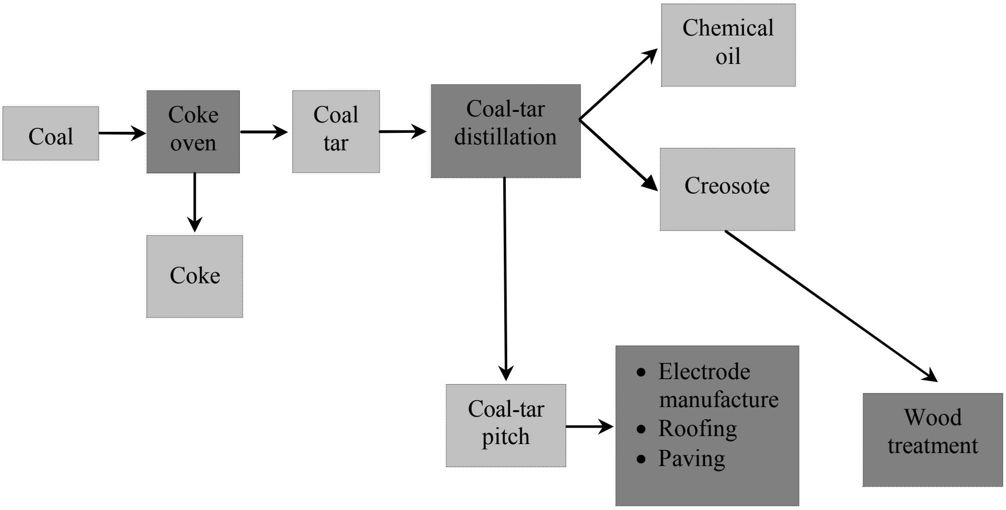


1-Hydroxypyrene

Benzo[*a*]pyrene

[a] Data in brackets are publication date; data without brackets are study date, not every study had data for both 1-Hydroxypyrene and Benzo[*a*]pyrene
BE, Belgium; CH, Switzerland; FI, Finland; GE, Germany; IT, Italy; NL, Netherlands; NO, Norway; NZ, New Zealand; PL, Poland; PRC, People's Republic of China; SUR, Surinam; SW, Sweden; TW, Taiwan, China; UK, United Kingdom; USA, USA

Figure 1.2. Simple schema for generation of coal tar and coal-tar products



for the recovery of tar chemicals, i.e. benzene, toluene, xylenes, phenol, cresols and cresylic acids, pyridine and methylpyridines, naphthalene and anthracene, in addition to the so-called bulk products, e.g. creosote, tar paints, road tars and pitch binders (Betts, 1997).

Until the end of the Second World War, coal tar was the main source of these aromatic chemicals. However, the large increase in demand from the rapidly expanding plastics and synthetic fibre industries has greatly surpassed the potential supply from coal carbonization, which has led to the development of petroleum-based processes. This situation was exacerbated in the early 1970s by the cessation of the manufacture in Europe of town gas from coal, a process that was carried out preponderantly in continuous vertical retorts. By the 1990s, over 90% of the world production of aromatic chemicals was derived from the petrochemical industry, and coal tar became chiefly a source of anti-corrosion coatings, wood preservatives, feedstocks for the manufacture of carbon black and binders for electrodes (Betts, 1997).

Apart from the presence of a few per cent (usually below 5%) of aqueous liquor that contains inorganic salts and 1 or 2% of coal–char–coke dust that arises from the carry-over of particles in the carbonization process, coal-tar distillation products comprise essentially two components: (i) the distillate, which distills at up to ~400 °C at atmospheric pressure, is primarily a complex mixture of mono- and polycyclic aromatic hydrocarbons, a proportion of which are substituted with alkyl, hydroxyl and amine and/or hydro sulfide groups and, to a lesser extent, their sulfur-, nitrogen- and oxygen-containing analogues. For those tars produced from coal carbonization at lower temperatures, the distillate also contains hydroxy aromatic compounds, alkanes and alkenes. The distillate is typically removed by way of several fractions, which include 'chemical oils' and creosote; (ii) the second product is the residue from the distillation (pitch), which represents at least 50% of the coal-tar products formed by high-temperature carbonization and consists of a continuation of the sequence of mono- and polycyclic aromatic and heterocyclic compounds, but also extends to molecules containing 20–30 rings (Betts, 1997).

Crude coal tar is of value only as a fuel. Although large amounts were formerly burned, this practice has largely been abandoned. In the 1990s, 99% of the tar produced in the United Kingdom and Germany and 75% of that produced in the USA were distilled. In the USA, most of the crude tar is first topped in simple continuous stills to recover a chemical oil, i.e. a fraction that distills at 235 °C and contains most of the naphthalene (Betts, 1997).

Although smaller mild-steel or wrought-iron pot stills, that are equipped with fractionating columns, may still be used, continuous stills that have daily capacities of 100–700 tonnes are the primary means of coal-tar distillation worldwide (Betts, 1997).

The various designs of continuous tar stills are basically similar. The crude tar is filtered to remove large-sized solid particles, dehydrated by heat exchange and passage through a waste-heat coil, then heated under pressure to ~360 °C and flashed to separate volatile oils from the non-volatile pitch. The volatile oils are separated into a series of fractions of increasing boiling range by fractional condensation in a sidestream column or a series of columns. The diverse designs differ in the extent to which heat exchange is used, in the plan of the pipe-still furnace, in the distillation pressure (i.e. atmospheric pressure or reduced pressure) and the recycling or not of pitch or base tar (Betts, 1997).

The tars recovered from commercial carbonization plants are not primary products of the thermal decomposition of coal, since the initial products undergo a complex series of secondary reactions. Even tars produced at the lowest commercial carbonization temperatures are very different from primary tars. Low-temperature tar, continuous vertical-retort tar and coke-oven tar form a series in which the yield of tar decreases, the aromaticity of the tar increases, the content of paraffins and phenols decreases and the ratio of substituted aromatic and heterocyclic compounds to their unsubstituted parent molecules decreases. These differences are reflected in the densities and carbon:hydrogen ratios of the tars. Higher aromaticity correlates with higher density and carbon:hydrogen ratio. The reactions that account for these changes (i.e. cracking and cyclization of paraffins, dehydration of phenols and dealkylation of aromatic and heterocyclic ring compounds) are those that would be expected, on thermodynamic grounds, to occur at the temperatures that prevail in carbonization retorts (Betts, 1997).

The part of coke-oven tar that is normally distillable at atmospheric pressure boils at up to ~400 °C and amounts to up to 50% of the whole. It contains principally aromatic hydrocarbons. In particular, benzene, toluene and the xylene isomers, tri- and tetramethylbenzenes, indene, hydrindene (indane) and coumarone occur in the first fraction that is normally removed; this represents about 3.5% of the tar and boils at up to ~200 °C. This fraction also contains polar compounds including tar acids (phenol and cresols) and tar bases (pyridine, picolines (methylpyridines) and lutidines (dimethylpyridines)). The most abundant component of this type of tar is naphthalene, which is taken in the second fraction and represents about 10% of the tar. It is contaminated with small but significant amounts of thionaphthene, indene and other compounds. The next fraction contains the two methylnaphthalene isomers and is equivalent to 2% of the tar. Subsequent fractions contain biphenyl, acenaphthene and fluorene (each in the range of 0.7–1% of the tar) and then diphenylene oxide (about 1.5% of the tar). Anthracene and phenanthrene are usually present at about 1 and 6%, respectively. The series continues with components that boil at up to 400 °C, which represents approximately the limit of the usual commercial distillation range, i.e. pyrene and fluoranthene (Betts, 1997).

Continuous vertical-retort tars differ from coke-oven tars in that, whereas the latter contain relatively small amounts of non-aromatic hydrocarbons, continuous vertical-retort tars contain a relatively high proportion of normal straight-chain or slightly branched-chain paraffins, alkylated aromatics and phenols (Betts, 1997).

Of the total tar bases in coke-oven and continuous vertical-retort tars in the United Kingdom, pyridine makes up about 2%, 2-methylpyridine, 1.5%, 3- and 4-methylpyridines, about 2%, and ethylpyridine and dimethylpyridines, 6%. Primary bases, anilines and methylanilines account for about 2% of the bases in coke-oven and continuous vertical-retort tars and 3.5% of the bases in low-temperature tars. The main basic components in coke-oven tars are quinoline (16–20% of the total), isoquinoline (4–5%) and methylquinolines. These dicyclic bases are less prominent in continuous vertical-retort and low-temperature tars, in which only a minority of the basic constituents have been identified (Betts, 1997).

Much less is known about the composition of pitch, the residue from coal-tar distillation. Studies of coke-oven pitch indicate that it contains the following high-molecular-weight constituents: aromatic hydrocarbons with four rings, e.g. chrysene, fluoranthene, pyrene, triphenylene, naphthacene and benzanthracene; five-membered ring systems are represented by picene, benzopyrenes (benzo[*a*]pyrene and benzo[*e*]pyrene), benzofluoranthenes and perylene; the main components of the next highest fraction are six-membered ring systems such as dibenzopyrenes, dibenzofluoranthenes and benzoperylenes; seven-ring systems, e.g. coronene, have also been identified. These basic hydrocarbon structures are accompanied by methyl and polymethyl derivatives and, in the case of the pitches from continuous vertical-retort and low-temperature tars, by mono- and polyhydroxy derivatives. As in the case of the distillate oil range, heterocyclic compounds are also present (Betts, 1997).

Above this relatively low-molecular-weight range, which constitutes approximately 40–50% of a medium-soft coke-oven pitch, the information concerning the chemical structure of pitch is only qualitative and is derived mainly from statistical structural analysis and mass spectra. As molecular weight increases, more heterocyclic atoms appear in the molecule, whereas the number and length of alkyl chains decreases and the hydrocarbon structures are not fully condensed. In the lower-temperature pitches, some ring structures appear to be partly hydrogenated (Betts, 1997).

Concentrations of PAHs in the air and urine of workers in coal-tar distillation are summarised in Table 1.4 and Figure 1.1. The levels of exposure to PAHs overall were similar among the high-temperature processes and much lower in the low-temperature distillation facility.

(g) Paving and roofing involving coal-tar pitch

The exposures associated with roofing are the result of two operations. First, the old roof is removed by cutting, prying and scraping the existing roofing material from the roof, and discarding it. A new roof is then installed by melting solid blocks of coal-tar pitch, then pumping or carrying buckets of the molten material to the roof, where layers of roofing felt and liquid coal-tar pitch are spread upon the surface to produce a build-up. In recent years, coal-tar pitch has been removed from paving and roofing asphalts and has been replaced by bitumen (NIOSH, 2000; IPCS, 2004).

Concentrations of PAHs in the air of workers who used coal-tar pitch in roofing are summarized in Table 1.5 and Figure 1.1.

NIOSH conducted three health hazard evaluations (Reed, 1982; Zey, 1983; Behrens & Liss, 1984) between 1982 and 1984 of the tear-off and installation of coal-tar roofs. In the three investigations, air samples were collected to measure exposures to total PAHs, the benzene-soluble fraction and six to 12 individual PAHs. Exposures varied widely between sites. In one study, the majority of exposures were below the limits of detection; in another study, exposures ranged up to 64.5 μg/m^3 for benzo[*a*]pyrene.

Wolff *et al.* (1989) evaluated dermal and inhalation exposure among roofers by collecting pre-shift and post-shift skin wipes from a measured area of each worker's forehead and air samples from the workers' breathing zone. Samples were collected during the portion of each job when old coal-tar roofs were cut into pieces, ripped up and cleared away. Substantial increases were measured in the levels of skin contamination (pre- to post-shift) for seven PAHs and total PAHs (mean pre-shift, 83.9 ng/9 cm^2 skin area versus post-shift, 1521 ng/9 cm^2 skin area). Mean inhalation exposure levels during the tear-off of coal-tar roofs ranged from 9.6 to 23.0 μg/m^3 for the sum of eight PAHs.

Other exposures of roofers include silica, diesel exhaust, asbestos and organic solvents.

Roadway paving can be conducted by several methods, including hot-mix laying and chip sealing. In hot-mix laying, the mixture of a binder (coal tar, bitumen or a blended product containing both) and aggregate (stone chips) is spread on the roadway by a paving machine, followed by a roller. In the chip-sealing process (also known as surface dressing), the liquid binder (coal tar, bitumen or a mix) is sprayed directly onto the road, then the aggregate stone is spread on top and rolled (Darby *et al.*, 1986).

Detailed information on cessation of the use of coal tar in the European paving industry has been collected in the course of an IARC study on cancer mortality among asphalt workers. In Table 1.6, the last reported year of use of coal tar in paving by any company that participated in the cohort study is presented. The data originated from a company questionnaire and its ensuing evaluation by country-specific experts (Burstyn *et*

Table 1.4. Concentrations of PAHs in the air and urine of workers in coal-tar distillation

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air (µg/m³)		Urinary 1-hydroxypyrene (µmol/mol creatinine)	
						Mean	Range	Mean	Range
van de Ven & Nossent (1984), Netherlands, NR	Operators, cleaners, maintenance	NR	49	NR	Sum of 11 PAHs	31	<1–277		
Jongeneelen *et al*. (1986), Netherlands, NR			*Air; urine*		Sum of 11 PAHs; pyrene				
	Operator pitch unit	1	8; 2	0		26; 8.5	<2–280; <2–96	3.7	NR
	Operator batch distillery	1	6; 2	1		14; 5.1		11.8	NR
	Operator pump station	1	5; 4	0		4.7; 1.4		4.0	NR
	Cleaner	1	4; 4	1		16; 5.2		4.6	NR
Price *et al*. (2000), United Kingdom, 1998	Low-temperature	8	8	1	Total 19 PAHs	12.17	3.99–38.59	0.36	0.21–1.05
					HSE 11[a]	0.008	<0.004–0.008		
					Benzo[*a*]pyrene	ND	ND		
					Pyrene	0.037	0.013–0.068		
	High-temperature	12	12	4	Total 19 PAHs	279.04	51.9–1130.5	2.60	0.78–5.69
					HSE 11[a]	0.95	0.15–4.87		
					Benzo[*a*]pyrene	0.283	0.019–0.642		
					Pyrene	1.24	0.14–6.73		

PAHs, polycyclic aromatic hydrocarbons; ND, not detected; NR, not reported

[a] Benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, dibenzo[*a,h*]anthracene, anthanthrene, cyclopenta[*cd*]pyrene

Table 1.5. Concentrations of PAHs in the air of workers in roofing involving coal-tar pitch

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^3)	
						Mean	Range
Reed (1982), USA, 1982	Coal-tar roof tear-off	7	11	NR	BSF	720	300–1100
					Phenanthrene	8.3	0.8–22.0
					Anthracene	2.4	0.2–6.7
					Fluoranthene	13.1	1.5–39.5
					Pyrene	11.6	1.0–34.7
					Benzo[*a*]anthracene	5.7	0.5–14.4
					Chrysene	6.4	0.6–15.6
					Benzo[*a*]pyrene	5.9	0.4–15.7
Zey (1983)[a], USA, 1983	Coal-tar roof tear-off and application	13	24	NR	BSF	ND	140–2970
					Acenaphthene	24	ND–91.6
					Fluorene	25	ND–26
					Phenanthrene	12	ND–21
					Anthracene	22	ND–16.8
					Fluoranthene	9	ND–47.3
					Pyrene	9	ND–31.3
					Benzo[*c*]phenanthrene	29	ND–3
					Benzo[*a*]anthracene	14	ND–8.4
					Chrysene	15	ND–17.6
					Benzo[*b*]- + benzo[*k*]-fluoranthene	17	ND–11.5
					Benzo[*e*]pyrene	30	ND–4.5
					Benzo[*a*]pyrene	23	ND–11.9
					Total PAHs	42.7	ND–388

Table 1.5 (Contd)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^3)	
						Mean	Range
Behrens & Liss (1984), USA, 1984	Coal-tar roof tear-off	6	6	NR	BSF	2.2	600–5300
					Fluoranthene	69.0	13.3–186.6
					Pyrene	52.8	10.6–140.6
					Benzo[*a*]anthracene	32.7	6.8–82.9
					Chrysene	27.9	6.0–71.4
					Benzo[*a*]pyrene	23.7	6.0–59.9
					Benzo[*e*]pyrene	21.8	4.3–64.5
					Phenanthrene	59.2	10.6–161.3
					Benzo[*ghi*]pyrene	17.9	3.3–43.8
Wolff *et al.* (1989)[b], USA, 1987	Tear-off of coal-tar roofs						*SD*
	Morning job	NR	8	NR	Sum of 8 PAHs	23.0	9.5
	Afternoon job	NR	2			9.6	0.9
	Single job	NR	1			15.3	–
	Morning job	NR	7			14.5	5.2
	Single job	NR	2			13.4	7.1
						Dermal levels (ng)	
	Skin wipe	3	6		pre	83.9	37.7
					post	1521	1373

BSF, benzene soluble fraction; ND, not detected; NR, not reported; PAH, polycyclic aromatic hydrocarbons; pre, pre-shift; post, post-shift; SD, standard deviation

[a] The Working Group noted some inconsistency and lack of information in the article, which made determination of number of workers, number of samples and PAH air levels difficult.

[b] The paper presents some inconsistencies in the number of air and skin wipe samples that were taken.

Table 1.6. Cessation of use of coal tar in asphalt paving (surface dressing)

Country	Last year of use
Finland	1965
Denmark	1974
Sweden	1974
Norway	1984
Netherlands	1990
France	1992
Germany	1995

From Burstyn *et al.* (2003)

al., 2003). A gradient in cessation of use can be seen, with Scandinavian countries ending use earlier than central and southern European countries, such as the Netherlands, France and Germany. However, even within countries, large differences in the use of coal tar have occurred between companies, depending on the supplier of the asphalt mixes and the presence of coke ovens in the neighbourhood. Even after the cessation of use of coal tar, workers in paving have been exposed to coal tar due to the use of recycled asphalt that contained coal tar in some countries.

Concentrations of PAHs in the air and urine of workers in paving that involves coal tar are summarized in Table 1.7 and Figure 1.1.

Darby *et al.* (1986) investigated the exposure of workers who performed coal-tar chip sealing as part of road paving operations in New Zealand. Personal exposures to six PAHs were measured in two samples taken in the area of workers' breathing zones and were reported to contain up to 9 μg/m^3 benzo[*a*]pyrene.

Jongeneelen *et al.* (1988a) measured exposures in highway chip sealing with coal-tar and reported inhalation levels of cyclohexane-soluble material, dermal levels of pyrene and pre- and post-shift levels of urinary excretion of 1-hydroxypyrene. The geometric mean for inhalation exposures to cyclohexane-soluble material was 0.6 mg/m^3 and that for dermal exposure to pyrene was < 10 ng; mean pre- to post-shift urinary 1-hydroxypyrene levels increased from 0.7 to 0.9 μmol/mol creatinine. In another study of road surfacing with blends of bitumen with refined coal-tar, the mean increase between pre- and post-shift levels of urinary 1-hydroxypyrene was 0.54 μmol/mol creatinine (Jongeneelen *et al.*, 1988b).

Knecht and Woitowitz (1989) measured air samples located in the breathing zone of workers who applied a coal tar–bitumen blend in road paving. Median air concentrations of benzo[*a*]pyrene were reported to be 0.7 μg/m^3.

Table 1.7. Concentrations of PAHs in the air and urine of workers in paving involving coal-tar pitch

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^3)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Darby *et al.* (1986), New Zealand, NR	Coal-tar chip sealing	2	2	NR	Benzo[*a*]anthracene + chrysene		1.2–17.8		
					Benzo[*b,j,k*]fluorene		1.1–11.4		
					Benzo[*e*]pyrene		0.7–5.4		
					Benzo[*a*]pyrene		0.9–9.0		
					Dibenz[*a,j*]anthracene		0.2–1.6		
					Indeno[1,2,3-*cd*]pyrene		0.7–6.3		
Jongeneelen *et al.* (1988a), Netherlands, NR	Chip sealing with refined coal-tar and blended bitumens					*Geometric mean*		*Geometric mean*	
		3	2	2	CSM	0.25 mg/m^3			
			3		Pyrene (wrist)	<10 ng			
			9		1-Hydroxypyrene			pre 1.8	
			8					post 2.8	
		6	18	2	CSM	0.20 mg/m^3			
			23		Pyrene (wrist)	24 ng			
			23		Pyrene rinse post	97.5 µg			
			23		1-Hydroxypyrene			pre 1.2	
			23					post 1.5	
		3	6	1	CSM	0.2 mg/m^3			
			9		Pyrene (wrist)	24 ng			
			7		Pyrene rinse post	216 µg			
			8		1-Hydroxypyrene			pre 1.5	
			8					post 1.9	

Table 1.7 (contd)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels ($\mu g/m^3$)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Jongeneelen *et al*. (1988a) (contd)	Chip sealing with refined coal-tar	4	1	0	CSM	0.6 mg/m^3			
			4		Pyrene (wrist)	< 10 ng			
			5		Pyrene rinse post	37.4 ng			
			3		1-Hydroxypyrene			pre 0.7	
			4					post 0.9	
Jongeneelen *et al*. (1988b), Netherlands, NR	Road surfacing with blended bitumen and refined coal-tar	28	NR		1-Hydroxypyrene				pre 0.8–3.1 post 0.9–3.2
Knecht & Woitowitz (1989), Germany, NR	Road surfacing with blended 30% refined coal-tar + 70% bitumen	NR Stationary samples taken near work stations	250	NR		*Median*			
					Benzo[*a*]pyrene	0.7			
					Indeno[1,2,3-*cd*]pyrene	0.2			
					Benzo[*bjk*]fluoranthene	9.3			
					Dibenzo[*a*,*h*]anthracene	0.03			
					Chrysene	2.8			

CSM, cyclohexane-soluble matter; NR, not reported; PAH, polycyclic aromatic hydrocarbon; pre, pre-shift; post, post-shift

(h) Creosote as a wood preservative

Coal-tar creosote is a distillate of coal tar that generally distills in the 200–400 °C range and is composed primarily of about 85% PAHs and 2–17% phenolic compounds. PAHs in coal-tar creosote are mainly two- and three-ring structures (Price *et al.*, 2000; ATSDR, 2002).

Coal-tar creosote has been used as a wood preservative since the nineteenth century, and wood preservation accounts for over 97% of its current use. Coal-tar creosote is applied to wood by commercial pressure treatment at 50–60 °C or, at least in the past, by individuals dipping or brushing the wood by hand. It is applied to railroad ties, utility poles, marine pilings, fence posts and other wood products for outdoor use (Price *et al.*, 2000; ATSDR, 2002).

Several studies have investigated exposure to PAHs among workers involved in the treatment of timber with creosote (Table 1.8 and Figure 1.1). Total PAH concentrations can be very high, especially due to relatively high concentrations of low-molecular-weight PAHs such as naphthalene, acenapthene and phenanthrene. In this industry, exposure to PAHs may occur both through inhalation and via the skin by contact with treated timber and contaminated surfaces. Based on urinary 1-hydroxypyrene levels, Elovaara *et al.* (1995) showed that the major uptake of PAHs was attributable to exposure to creosote through the skin. An intervention study (VanRooij *et al.*, 1993b) also provided evidence that skin is the main route of uptake of PAHs in this industry. Workers who wore a coverall under their working clothes had a 35% reduction in dermal exposure to pyrene and their urinary concentration of 1-hydroxypyrene was halved from 6.6 µg to 3.2 µg over a period of 22 h.

Workers involved in the creosote industry are also exposed to diesel exhaust, asbestos, silica, sulfur-substituted hydrocarbons, solvents, aliphatic amines and aldehydes. Other potential exposures may include other wood preservatives such as inorganic arsenicals or pesticides based on pentachlorophenol.

(i) Aluminium production, including the manufacture of anodes

Aluminium, the third most abundant element in the earth's crust, is usually combined in nature with silicon and oxygen as aluminium silicate. When aluminium silicate is subjected to tropical weathering, aluminium hydroxide may be formed. Rock that contains high concentrations of aluminium hydroxide is called bauxite. Although bauxite is normally the starting material for the production of aluminium, the industry generally refers to metallurgical grade alumina (Al_2O_3) that is extracted from bauxite by the Bayer process as the ore, from which aluminium is obtained by electrolysis (Sanders, 2002).

Since the discovery of the process by Hall and Héroult in 1886, nearly all aluminium has been produced by electrolysis of alumina dissolved in a molten cryolite (Na_3AlF_6)-based bath. The aluminium is deposited in molten form on a carbon cathode, which also serves as the melt container. Simultaneously, oxygen is deposited on and consumes the carbon–carbon anode(s) of the cell. Pure cryolite melts at 1012 °C, but alumina and additives,

Table 1.8. Concentrations of PAHs in the air, skin and urine of workers in the timber impregnation industry (creosote)

Reference country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels ($\mu g/m^3$)		Dermal levels (µg)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range	Mean	Range
Heikkilä *et al*. (1987), Finland, [1985]	Plant 1	9	26		3–6 ring PAHs	3–106[a]					
					4–6 ring PAHs	0.3–8.1[a]					
	Plant 2	4	8		3–6 ring PAHs	0.1–104[a]					
					4–6 ring PAHs	0.06–7.5[a]					
VanRooij *et al*. (1993b), Netherlands, 1991	Assembly hall	7	7	5/7	Pyrene		0.3–3.0				
					1-Hydroxypyrene			440	47–1368	6.4 µg	0.7–12.7[c]
	Cylinder	3	3	0	Pyrene	1.1	0.9–1.3				
					1-Hydroxypyrene			649	120–1511	7.5 µg	2.6–12.2[c]
Elovaara *et al*. (1995), Finland, 1987	Wood impregnation plant	6	30	3	Total 10 PAHs[b]	5.7	1.23–13.74				
					Benzo[*a*]pyrene	0.01	0.01–0.05				
					Pyrene	0.97	0.23–2.10				
		6	18	3	1-Hydroxypyrene (end of shift)					64	19–85
Heikkilä *et al*. (1995), Finland, NR	Handling of creosote-impregnated timber	3	9	3	1-Hydroxypyrene					6.8	3.8–12.8

Table 1.8 (Contd)

Reference country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels ($\mu g/m^3$)		Dermal levels (μg)		Urinary levels ($\mu mol/mol$ creatinine)	
						Mean	Range	Mean	Range	Mean	Range
Price *et al.* (2000), United Kingdom, 1998	Several	11	11	6	Total of 19 PAHs	835	30.2–1913				
					HSE11[d]	0.28	0.07–0.38				
					Benzo[*a*]pyrene	0.22	0.07–0.35				
					Pyrene	0.33	0.06–0.69				
					1-Hydroxypyrene					16.0	1.44–60.0

PAH, polycyclic aromatic hydrocarbon

[a] Range of means

[b] Excluding naphthalene

[c] Sample covering 8 h-work shift and the 14 consecutive hours

[d] Benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, dibenzo[*a,h*]anthracene, anthanthrene, cyclopenta[*c,d*]pyren

namely 4–8% calcium fluoride, 5–13% aluminum fluoride, 0–7% lithium fluoride and 0–5% magnesium fluoride, lower the melting-point, which allows operations to proceed at 920–980 °C (Sanders, 2002). Commercialization of the Hall-Héroult process was rapid, and led to the swift growth of the aluminium industry in Europe and North America in the last decade of the nineteenth century (Frank *et al.*, 2005).

A modern alumina-smelting cell consists of a rectangular steel shell which is lined with refractory insulation that surrounds an inner lining of baked carbon. Few materials other than carbon are able to withstand the combined corrosive action of molten fluorides and molten aluminium. Thermal insulation is adjusted to provide sufficient heat loss to freeze a protective coating of electrolyte on the inner walls but not on the bottom, which must remain uncovered to allow for electrical contact with the molten aluminium cathode. Steel (collector) bars are joined to the carbon cathode at the bottom to conduct the electric current from the cell. The current enters the cell either through pre-baked carbon anodes or through a continuous self-baking Søderberg anode (Sanders, 2002).

The Søderberg anode is formed continuously from a paste of petroleum coke and coal-tar pitch which are typically added to the top of a rectangular steel casing. When it passes through the casing, the paste bakes to form carbon and replaces the anode that is being consumed. The baked portion extends past the casing into the molten electrolyte. The electric current enters the anode through vertical or sloping steel spikes (also called pins), and molten aluminium is generally removed from the cells daily by siphoning into a crucible. Normally, the metal is 99.6–99.9% pure, and the principal impurities (iron, silica, titanium, vanadium and manganese) derive mainly from the anode, but also from the alumina (Sanders, 2002).

Pre-baked anodes are produced by molding petroleum coke and coal-tar pitch binder into blocks which are baked at 1000–1200 °C. Petroleum coke is used because of its low impurity (ash) content. The more noble impurities, such as iron and silicon, deposit in the aluminium whereas less noble impurities, such as calcium and magnesium, accumulate as fluorides in the bath. Coal-based coke could be used, but extensive and expensive pre-purification would be required. Steel stubs seated in the anode that uses cast iron support the anodes (via anode rods) in the electrolyte and conduct electric current into the anodes (Sanders, 2002).

In industrial electrowinning (separation by electrolysis) of aluminium, part of the energy required to reduce the alumina is supplied by electricity and part derives from consumption of the carbon anode. Carbon is also used to line the cathode. For each kilogram of aluminium produced, 0.4–0.5 kg of anode is consumed and this represents the major carbon requirement. High-purity carbon is desirable because any ash from the carbon would contaminate either the aluminium produced or the electrolyte. In addition, certain impurities, such as vanadium, are particularly harmful because they catalyse air burning of the carbon; other impurities, such as phosphorus, accumulate in the electrolyte, undergo cyclic redox reactions (partial reduction followed by re-oxidation) and consume electric current unproductively. The coke residue from petroleum refining is reasonably pure and has therefore been used as the major source of carbon for anodes (Frank *et al.*, 2005).

Anthracite has been the major constituent of cathode blocks in the cells, although graphite and metallurgical coke have also been used to some extent. Anthracite is calcined at 1200 °C or above, crushed and sized, mixed with coal-tar pitch, molded into blocks and baked. These blocks, mortared together with a carbonaceous seam mix, form the pot lining, which is the container for both the aluminium and the electrolyte. High purity is not as important for the cathode blocks because leaching of impurities is very slow. Consumption of cathode carbon amounts to 0.02–0.04 kg per kilogram of aluminium produced (Frank *et al.*, 2005).

Workers in the aluminium industry and the related carbon-electrode manufacturing industry have been monitored most intensively for exposure to PAHs and large studies have recently been conducted in Europe and South America (Table 1.9 and Figure 1.1). Exposure studies up to the early 1980s were reviewed previously (IARC, 1984), and only studies published since that time are reviewed below.

Exposure to PAHs, sulfur dioxide and fluorides have decreased over time (Benke *et al.*, 1998). At two plants that operated the vertical stud Søderberg potrooms in Norway, exposures decreased on average by a factor of four between the late 1950s and the late 1980s (Romundstad *et al.*, 1999). The decrease in exposure is most probably a result of the implementation of improved technology in combination with increased use of effective personal protective devices. In addition, the increasing predominance of pre-bake potrooms also probably contributed to the decline of exposures to PAHs (Benke *et al.*, 1998), although this might apply to the anode pre-baking plants. Urinary levels of 1-hydroxypyrene in anode manufacturing for the aluminium industry did not decrease considerably between the mid-1980s and mid-1990s (Table 1.10 and Figure 1.1).

Dermal exposure to PAHs and consequent uptake through the skin may contribute to the internal exposure to PAHs of workers. VanRooij *et al.* (1992) showed that dermal exposure does not necessarily correlate with exposure by inhalation in workers in potrooms and the anode pre-bake plants. Levels of benzo[*a*]pyrene on the wrists of workers in the bake-oven area were twice as high as those of workers from the paste plant. The exposure of bake-oven workers to benzo[*a*]pyrene by inhalation, however, appeared to be four times lower than that of workers in the paste plant. Exposure to pyrene by both inhalation and dermal contact was higher in the paste plant. No information was available for temporal trends in dermal exposure in these workplaces.

In addition to exposures to sulfur dioxide and fluorides, several other exposures can occur among aluminium workers, including aluminium fluoride, fibrous sodium aluminium tetrafluoride particles, fluorspar, alumina, carbon monoxide, carbon dioxide and various trace metals (e.g. vanadium, chromium and nickel) (Benke *et al.*, 1998). Exposure to asbestos has also been reported (Dufresne *et al.*, 1996). In addition to these chemical exposures, workers in the aluminium industry are also exposed to extreme heat and high static magnetic fields (Benke *et al.*, 1998).

Table 1.9. Concentrations of PAHs in the air and urine of workers in the aluminium industry[a]

Reference, country	Year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m³)		Urinary levels (µmol/mol creatinine)	
							Mean	Range	Mean	Range
Bolt & Golka (1993), Germany	NR	Søderberg plant	16	NR	NR	Benzo[*a*]pyrene	NS	0.8–292		
Tjoe Ny *et al*. (1993), [Surinam]	1990	Technicians, engineers, electricians, laboratory workers	6	6	1	Total 16[d]	12	3–22		
						Benzo[*a*]pyrene	<1.0	<1.0–<1.0		
						Pyrene	3.5	<1.4–8.3		
			5	5	1	1-Hydroxypyrene			1.0	0.2–2.7
		Foremen, tappers	6	6	NR	Total 16[d]	38	12–60		
						Benzo[*a*]pyrene	0.93	<1.0–1.5		
						Pyrene	7.9	2.2–14		
			4	4	2	1-Hydroxypyrene			3.0	1.2–4.5
		Crane operators, all rounders	10	10	NR	Total 16[d]	328	59–715		
						Benzo[*a*]pyrene	14	1.5–43.2		
						Pyrene	39	16–121		
			8	8	4	1-Hydroxypyrene			18	3.7–39.6
		Potmen	10	10	NR	Total 16[d]	170	30–388		
						Benzo[*a*]pyrene	2.7	1.0–5.7		
						Pyrene	25	2.5–49		
			9	9	3	1-Hydroxypyrene			35	16.5–75.9
		Electrode men	6	6	NR	Total 16[d]	1040	256–2430		
						Benzo[*a*]pyrene	48	7.5–94		
						Pyrene	130	52–262		
			4	4	4	1-Hydroxypyrene			43	23.5–66.5

Table 1.9 (Contd)

Reference, country	Year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^{3})		Urinary levels (µmol/mol creatinine)	
							Mean	Range	Mean	Range
Levin *et al.* (1995), Sweden	NR	Several	9	9	1	Total 7	91	30–400		
						Benzo[*a*]pyrene	7.07	1.7–36		
			9	9	1	1-Hydroxypyrene			5.9	1.3–10.7 ng/mL
van Schooten *et al.* (1995), Netherlands	1989	Pot-relining	NR	41	NR	Total 12^{b}	150^{c}	0.9–1709		*SD*
						Benzo[*a*]pyrene^{b}	1.05^{c}	<0.02–9		
						Pyrene^{b}	32.3^{c}	0.15–223		
			8	NS	6	1-Hydroxypyrene			S, 6.72	4.25
									NS, 6.20	8.44
		Electrolysis	NR	23	NR	Total 12^{b}	1.0^{c}	0.3–4.6		
						Benzo[*a*]pyrene^{b}	0.03^{c}	<0.02–0.2		
						Pyrene^{b}	0.12^{c}	0.03–0.7		
			22	NR	13	1-Hydroxypyrene			S, 0.88	0.42
									NS, 0.48	0.27
Carstensen *et al.* (1999) Sweden	NR	Potroom workers	97	97	31%	Total 22^{b}	13.2^{e}	0.01–270		
			96	96		Total 7 (gaseous)	16.3^{e}	0.01–132		
			93	93		Benzo[*a*]pyrene^{b}	0.97^{e}	0.02–23.5		
			94	94		Pyrene^{b}	1.11^{e}	0.02–34.4		
			95	95		Pyrene (gaseous)	1.56^{e}	0.01–9.5		
			96	96		1-Hydroxypyrene			4.3	0.1–17.7

Table 1.9 (Contd)

Reference, country	Year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (μg/m^3)		Urinary levels (μmol/mol creatinine)	
							Mean	Range	Mean	Range
Romundstad *et al*. (1999), Norway	1978–87	Pot operator	195		NR	PAHs[b]	66			
	1980–86		60		NR		88			
	1987–95		201		NR		10			
	1988–96		98		NR		14			
	1980–86	Stud puller	54		NR		842			
	1986–87		35		NR		89			
	1987–89		30		NR		248			
	1988–96	Stud puller with one-man cabins with filtered air	130		NR		11			
	1990–95		49		NR		12			
	1978–79	Flex raiser	47		NR		145			
	1980–86		21		NR		120			
	1987–95		46		NR		9			
	1978–87	Tapper	90		NR		37			
	1986		2		NR		65			
	1987–95		60		NR		10			
	1988–96		97		NR		9			
	1978–87	Other jobs in potroom	288		NR		53			
	1980–86		161		NR		52			
	1987–95		193		NR		10			
	1988–89		15		NR		13			
	1978–87	Daytime maintenance	264		NR		86			
	1980–86		33		NR		219			
	1987–95		74		NR		24			
	1988–96		271		NR		23			

Table 1.9 (Contd)

Reference, country	Year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels ($\mu g/m^3$)		Urinary levels (µmol/mol creatinine)	
							Mean	Range	Mean	Range
Price *et al.* (2000), United Kingdom	1998	Several	10	10	1/9	Sum of 19 PAHs	60.9	0.01–138		
						HSE 11[f]	0.31	0.001–0.85		
						Benzo[*a*]pyrene	0.03	0.01–0.10		
						Pyrene	0.86	0.02–2.91		
						1-Hydroxypyrene			0.7	0.3–2.6

NR, not reported; NS, non-smoker; PAH, polycyclic aromatic hydrocarbon; S, smoker; SD, standard deviation

[a] All studies were of the Søderberg process, except those in the Netherlands (van Schooten *et al.*, 1995) and the United Kingdom (Price *et al.*, 2000), which were of the pre-baking process

[b] Only particulate PAHs were measured

[c] Geometric mean

[d] PAHs recommended for sampling by the US National Institute of Occupational Safety and Health

[e] Median

[f] Benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, dibenzo[*a,h*]anthracene, anthanthrene, cyclopenta[*cd*]pyrene

Table 1.10. Concentrations of PAHs in the air and urine of workers in anode manufacturing for the aluminium industry

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^{3})		Urinary levels (µmol/mol creatinine)	
						Mean	Range or SD	Mean	Range
Tolos *et al.* (1990), USA, NR	Anode bake area								
	Crane operators	9	9	NR	Total 17	25.8	13.8–56.4		
					Pyrene	2.5	1.2–6.5		
					1-Hydroxypyrene			2.9	2.0–3.6
	Packer-puller	7	7	NR	Total 17	24.7	10.1–57.2		
					Pyrene	2.8	1.5–7.4		
					1-Hydroxypyrene			2.4	1.9–3.3
	Equipment operators	2	2	NR	Total 17	52.1	9.5–94.6		
					Pyrene	2.1	1.5–2.8		
					1-Hydroxypyrene			3.0	2.5–3.5
van Schooten *et al.* (1995) Netherlands, 1989	Bake oven	NR	22	NR	Total 12^{a}	8.7^{b}	3.0–107		*SD*
					Benzo[*a*]pyrene^{a}	0.35^{b}	0.1–14.4		
					Pyrene^{a}	1.5^{b}	0.5–22.7		
		6	NR	6	1-Hydroxypyrene			8.43	4.08
		9	NR	0				3.65	2.11
	Anode factory	NR	40	NR	Total 12^{a}	23^{b}	1.1–854		
					Benzo[*a*]pyrene^{a}	1.51^{b}	0.1–11.6		
					Pyrene^{a}	5.6^{b}	0.3–318		
		2	NR	2	1-Hydroxypyrene			4.84	3.64
		5	NR	0				3.25	1.89
Petry *et al.* (1996), Switzerland, 1994	Green anode section; several jobs	6	30	4	Total 26	NR	4.0–121		
					Benzo[*a*]pyrene	NR	0.2–4.9		
					Pyrene	NR	0.4–12.8		
					1-Hydroxypyrene			NR	0.5–61.8

Table 1.10 (Contd)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m³)		Urinary levels (µmol/mol creatinine)	
						Mean	Range or SD	Mean	Range
van Delft *et al*. (1998), Netherlands, 1995	Anode plant (high exposure	5	18		Total 16	32	2.3–185		
					Benzo[*a*]pyrene	1.2	0.43–3.2		
					Pyrene	2.45	0.28–46		
		17	17	9	1-Hydroxypyrene[c]			13.2 µg/day	7.7–45.1
	Maintenance (medium exposure)	7	12		Total 16	8.4	1.8–80		
					Benzo[*a*]pyrene	0.37	0.09–5.0		
					Pyrene	0.51	0.10–4.4		
		19	19	7	1-Hydroxypyrene[c]			5.66 µg/day	2.2–20.2
	Laboratory and office (low exposure)	19	19	5	1-Hydroxypyrene[c]			1.59 µg/day	0.66–3.54
Pavanello *et al*. (2000), Italy, NR	Anode plant workers	22	22	0	1-Hydroxypyrene			0.32	0.06–1.17

NR, not reported; PAH, polycyclic aromatic hydrocarbon; SD, standard deviation

[a] Only particulate PAH were measured

[b] Geometric mean

[c] Conversions used for 1-hydroxypyrene: 1 µmol/mol creatinine = 1.93 µg/g creatinine = 0.013 µmol/L = 2.84 µg/L = 2.84 ng/mL

(j) Carbon-electrode manufacture other than for aluminium production

With the exception of the use of carbon in the manufacture of aluminium, the largest use of carbon and graphite is as electrodes in electric-arc furnaces. In general, the use of graphite electrodes is restricted to open-arc furnaces of the type used in steel production, whereas carbon electrodes are employed in submerged-arc furnaces used in the manufacture of phosphorus, ferroalloy and calcium carbide (Criscione *et al.*, 1992).

Graphite electrodes are produced commercially in many sizes ranging from 32 mm in diameter by 610 mm in length to 700 mm in diameter by 2800 mm in length; each diameter is generally available in two or three lengths. These electrodes are used in open-arc furnaces for the manufacture of steel, iron and steel castings, brass, bronze, copper and its alloys, nickel and its alloys, magnesium, lead, tin, fused cast refractories, fused refractory grain and mineral wool insulation and for the treatment of toxic wastes. The largest use of graphite electrodes by far is in the manufacture of steel and, as a consequence, the growth of graphite production has been closely related to the growth in steel production in electric furnaces. A small but growing number of arc furnaces now use direct current and a single-electrode column positioned in the centre of the furnace. In both cases, steel is produced by filling the cylindrical shell with ferrous scrap, directly reduced iron or occasionally molten pig iron, then melting and refining the metallic charge with the intense heat derived from the electric arc that is generated at the tips of the electrodes (Criscione *et al.*, 1992).

Before the mid-1940s, the arc furnace was used almost exclusively for the production of low-tonnage, high-quality steels such as stainless and alloy steels. Since then, its use has been extended to production of the more common high-tonnage steel grades, including sheet steels. The growth of steel production in arc furnaces in the USA has been dramatic; it rose from 6% of total steel production in 1950, to 20% in 1975 and 36% in 1990. Worldwide, over 210 million tonnes of steel were produced in electric-arc furnaces in 1990 (approximately 26% of total world steel production) and these furnaces consumed over 800 000 tonnes of graphite electrodes (Criscione *et al.*, 1992).

Graphite electrodes are consumed in the melting process. For iron and steel production, the average consumption is approximately 2–5 kg/tonne, depending on the quality of the charge material, the quality of the electrodes and numerous factors related to the productivity and operation of the arc furnace. A combination of these factors has resulted in a reduction of about 40% in specific electrode consumption over the past 15 years (Criscione *et al.*, 1992).

Graphite electrodes are produced in two broad-grade classifications — regular grade and premium grade. The principal differences between the two grades are that the premium grade is made from a super premium needle coke and is impregnated with pitch before graphitization. The premium-grade electrode is used when very high performance is required, such as in ultrahigh-powered arc furnaces. The capacity of an electrode column to carry current depends on many characteristics of the furnace operation as well as those of the electrode and electrode joint, and, over the years, significant progress has been achieved in improving this capacity (Criscione *et al.*, 1992).

Concentrations of PAHs in the air and urine of workers in the carbon-electrode industry are summarized in Table 1.11 and Figure 1.1. Exposure conditions in these carbon manufacturing plants are relatively similar to those in anode manufacturing for aluminium plants. Three recent studies from Belgium (Buchet *et al.*, 1992), Germany (Angerer *et al.*, 1997) and Norway (Øvrebø *et al.*, 1994) reported differences in PAH concentrations within the plants. Much higher exposures were observed at the beginning of the production process when raw materials are mixed and the electrode is dipped in liquid tar in the studies in Belgium and Germany.

(k) Chimney sweeping and other exposures to soot

For hundreds of years, chimneys have been swept with long steel brushes inserted manually into the chimney from the top and from the bottom. By this procedure, chimney sweepers are exposed to soot particulates.

Soots are black particulate matter that are formed as by-products of combustion or pyrolysis of organic (carbon-containing) materials, such as coal, wood, fuel oil, waste oil, paper, plastics and household refuse. Their chemical compositions and properties are highly variable and depend on the type of starting material and the conditions of combustion. Soots vary considerably with respect to their relative amounts of carbon, their particle type, size and shape, and the types of organic and inorganic compounds adsorbed to the particles. In general, soots have a total carbon content below 60% and a high content of inorganic material and soluble organic fraction. The soluble organic fraction of soot is extractable with organic solvents and consists of PAHs and their derivatives. Inorganic constituents may include oxides, salts, metals, sulfur and nitrogen compounds, water, and other adsorbed liquids and gases (IARC, 1985; Watson & Valberg, 2001).

Two German studies investigated the exposure of chimney sweeps to PAHs (Table 1.12 and Figure 1.1). Knecht *et al.* (1989) assessed exposures in the breathing zone of chimney sweeps during so-called 'dirty' or 'black work' over a period of 11 days. Samples were taken per 'job' that was classified based on the fuel fired: oil fuel, oil/solid or solid fuels. Twenty PAHs were quantified in a total of 115 samples. Higher concentrations were seen when solid fuels had been fired. A more recent biomonitoring study carried out in Germany and Poland in 1995 reported 1-hydroxypyrene levels in the urine ranging from below the detection limit of 0.1 μg/L to 12.8 μg/L (Letzel *et al.*, 1999). Urinary concentrations in Poland were on average five times higher, most probably due to the fact that coal and wood are more often used there as fuel. The urinary concentrations in workers in Germany were relatively low. The use of personal protective devices among this group of 100 chimney sweeps was not reported.

Chimney sweeps have also been reported to be exposed concurrently to sulfur dioxide and arsenic (Bagchi & Zimmerman, 1980).

Table 1.11. Concentrations of PAHs in the air and urine of workers in carbon electrode manufacturing other than for the aluminium industry

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^3)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Buchet *et al.* (1992), Belgium, NR	Conditioning	10	NR	7	Total of 13	2.8	1.0–9.3		
					Pyrene	0.10 NS; 0.04 S			
					1-Hydroxypyrene			0.55 NS; 0.55 S	
	Second thermal treatment	25	NR	17	Total of 13	4.1	0.2–50.9		
					Pyrene	0.05 NS; 0.05 S			
					1-Hydroxypyrene			0.57 NS; 0.79 S	
	Heating of raw electrodes	6	NR	4	Total of 13	17.4	100–117 [sic][a]		
					Pyrene	0.20 NS ; 0.39 S			
					1-Hydroxypyrene			2.56 NS; 3.13 S	
	Maintenance	17	NR	2	Total of 13	12.5	0.6–251		
					Pyrene	0.21 NS ; 0.13 S			
					1-Hydroxypyrene			1.21 NS; 3.76 S	
	Grinding and mixing raw materials	14	NR	9	Total of 13	96.0	17.7–551		
					Pyrene	10.75 NS ; 3.52 S			
					1-Hydroxypyrene			2.98 NS; 2.83 S	

Table 1.11 (Contd)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (μg/m^3)		Urinary levels (μmol/mol creatinine)	
						Mean	Range	Mean	Range
Buchet *et al*. (1992) (contd)	Electrode impregnation	8	NR	5	Total of 13	222.6	20.8–1212		
					Pyrene	27.27 NS ; 3.35 S			
					1-Hydroxypyrene			4.14 NS; 4.96 S	
Angerer *et al*. (1997), Germany, NR	Crushing	2	4	NR	Total of 8	5.19	0.37–10.0		
					Benzo[*a*]pyrene	0.09	0.01–0.17		
					Pyrene	0.72	0.04–1.40		
		2	NR		1-Hydroxypyrene			5.0	0.6–9.4
					Sum of OH-PHE			5.4	0.98–9.7
	Baking	5	10	NR	Total of 8	29.3	4.94–70.7		
					Benzo[*a*]pyrene	1.15	0.14–3.39		
					Pyrene	4.54	0.81–12.4		
		30	NR		1-Hydroxypyrene			12.1	0.9–169
					Sum of OH-PHE			12.0	1.7–56.0
	Impregnation	3	6	NR	Total of 8	23.4	16.9–31.1		
					Benzo[*a*]pyrene	1.09	0.47–1.46		
					Pyrene	3.12	2.19–4.55		
		9	NR		1-Hydroxypyrene			11.4	3.2–42.1
					Sum of OH-PHE			18.7	8.9–75.6
	Graphitization	4	8	NR	Total of 8	1.27	0.45–1.74		
					Benzo[*a*]pyrene	0.01	0.007–0.01		
					Pyrene	0.22	0.01–0.38		
		24	NR		1-Hydroxypyrene			0.93	0.1–3.3
					Sum of OH-PHE			2.4	0.77–8.5

Table 1.11 (Contd)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels ($\mu g/m^3$)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Angerer *et al.* (1997) (contd)	Conditioning	2	4	NR	Total of 8	0.37	0.11–0.63		
					Benzo[*a*]pyrene	0.01	0.003–0.02		
					Pyrene	0.03	0.01–0.05		
		2	NR		1-Hydroxypyrene			1.2	0.9–1.5
					Sum of OH-PHE			3.9	2.1–5.8

NR, not reported; NS, nonsmoker; OH-PHE, monohydrated metabolites of phenanthrene; PAH, polycyclic aromatic hydrocarbon; S, smoker

[a] [The lower value of 100 is inconsistent with a mean of 17.4.]

Table 1.12. Concentrations of PAHs in the air and urine of chimney sweeps

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH measured	Air levels (µg/m^3)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Knecht *et al.* (1989), Germany, NR		NR		NR					
	Oil fuel		37		Benzo[*a*]pyrene	0.36			
	Oil/solid fuel		34			0.83			
	Solid fuel		44			0.82			
								Median	
Letzel *et al.* (1999), Germany, Poland, 1995		100	100	42	1-Hydroxypyrene[a]			NR	0.04–4.5
	Apprentices, journeymen	79	79	NR				0.28	
	District master	21	21	NR				0.1	
	Workers from Germany	93	93	38				0.14–0.32	
	Workers from Poland	7	7	4				1.2	
	Smokers	42	42	42				0.39	
	Nonsmokers	58	58	0				0.19	
Pavanello *et al.* (2000), Italy, NR		27	27	0	1-Hydroxypyrene			0.56	0.04–2.34

NR, not reported; PAH, polycyclic aromatic hydrocarbon

[a] Originally reported in µg/L. Conversion factor: 1 µmol/mol creatinine = 1.93 µg/g creatinine = 0.013 µmol/L = 2.84 µg/L

(l) Thermoelectric power plants

Thermal power plants use the energy of heat to make electricity. Coal is burned to heat water in a boiler and convert it to high-pressure steam. The high-pressure steam is directed into a steam turbine which turns the turbine shaft. This shaft is connected to an electrical generator which produces electricity. A condenser converts the exhausted steam from the turbine back into water which is re-used in the boiler. The condenser contains tubes that have water circulating through them to cool the steam. The water is supplied by a nearby reservoir or river. This condensing process increases the efficiency of electricity generation (ATCO Power, 2008).

Coal for the generating stations may be extracted from a nearby coal mine or brought in by rail or ship. At the generating station, the coal is crushed and stockpiled. A conveyor belt carries the crushed coal from the stockpile to bunkers within the power station. The coal is fed as required into pulverizers, where it is ground to a fine dust, the consistency of talcum powder. A fan blows the coal into the boiler's furnace. Water flows through tubes that form the walls of the furnace and the intense heat of the burning coal causes the water inside the tubes to boil. The boiling water rises into the steam drum at the top of the boiler where the steam is separated from the water. The steam, at high pressure, is super-heated to still higher temperatures and then used to turn the steam turbine and an electricity generator. After leaving the turbine, the steam — now at a lower temperature and lower pressure — passes through the condenser, which condenses the steam back into water that is pumped back to the boiler to repeat the cycle. The fine, powdery ash produced when coal is burned is called fly-ash. The hot gases and fly-ash move out of the boiler's furnace and into electrostatic precipitators, which are a series of electrically charged metal plates that attract and hold the fly-ash particles. The collected fly-ash is either sold for use as an additive to concrete or transported to the mine site to be used for fill (ATCO Power, 2008).

Few studies have focused on the exposure to PAHs of workers in power plants that transform coal into electricity. A recent study by the Health and Safety Executive (Price *et al.*, 2000) evaluated exposures to PAHs of workers employed in a coal-fired power station (Table 1.13 and Figure 1.1). Twelve individuals (including drivers of bulldozers and other equipment, operators and fitters and welders) were monitored. The overall mean exposure was low (1.4 $\mu g/m^3$) and none of the end-of-shift urine samples contained levels of 1-hydroxypyrene above the detection limit (0.5 µmol/mol creatinine).

Other potential exposures present in the environment of workers in thermoelectric power plants are to residual coal or oil fly-ash, trace metals such as chromium, vanadium, nickel and mercury, and combustion gases such as sulfur dioxide and nitrogen oxides. Depending on the fuel that is used to drive vehicles such as bulldozers and other heavy equipment, there is also potential exposure to diesel exhaust emissions. Since the majority of workers in a power plant are involved in maintenance work, exposure to solvents, greases and oils, asbestos and welding fumes should also be taken into account (Price *et al.*, 2000).

Table 1.13. Concentrations of PAHs in the air and urine of workers in thermoelectric power plants (utility industry)

Reference, country, year of study	Job/task	No. of subjects	No. of samples	No. of smokers	PAH	Air levels ($\mu g/m^3$)		Urinary levels (µmol/mol creatinine)	
						Mean	Range	Mean	Range
Price *et al*. (2000), United Kingdom, 1998	Several	12	12	6	Sum of 19 PAHs	1.42	0.46–2.15		
					HSE11[a]	0.14	0.04–0.49		
					Benzo[*a*]pyrene	0.02	0.007–0.11		
					Pyrene	0.025	0.006–0.055		
					1-Hydroxypyrene			0.25	0.25–0.25

PAH, polycyclic aromatic hydrocarbon

[a] Benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, dibenzo[*a,h*]anthracene, anthanthrene, cyclopenta[*cd*]pyrene

(m) Overall ranking of industries by level of PAHs

To rank exposure to PAHs by industry, the Working Group compared the measurements of the analytes most frequently reported in air samples collected throughout the 10 industrial sectors. Relatively few of the studies conducted a detailed analysis to identify six or more of the component PAHs that comprised the overall exposure. Therefore, airbone concentrations of benzo[*a*]pyrene and urinary levels of 1-hydroxypyrene were compared across industries. Urinary levels of 1-hydroxypyrene also reflect dermal uptake and therefore should be interpreted as a measure of uptake via both inhalation and the skin. Ranges of personal measurements of benzo[*a*]pyrene and urinary levels of 1-hydroxypyrene were plotted by year and study (Figure 1.1). The relative ranking of the industries for 1-hydroxypyrene in urine and benzo[*a*]pyrene in air is summarized in Figure 1.3.

In the case of inhalation exposures to benzo[*a*]pyrene, reported levels were highest in the aluminium production industry (operating the Søderberg process), with values of up to 100 μg/m^3. These levels were substantially higher than those measured in the pre-bake aluminium production process. Levels in electrode manufacturing for aluminium reduction or manufacture of graphite electrodes for the metal industry were also considerably lower (up to 10 μg/m^3).

The levels of benzo[*a*]pyrene observed in studies of coke ovens were somewhat lower than those observed in aluminium production, and there was some evidence of a trend towards lower exposures over time within the studies conducted in western Europe and the USA; a study from Sweden documented substantial reductions by comparing exposures before and after a major plant renovation in 1990 (Levin *et al.*, 1995). A distinct reduction in exposures to PAHs was also evident from the analysis of longitudinal data from two Norwegian Søderberg plants that covered three decades (Romundstad *et al.*, 1999).

Studies conducted after 1995 do not support the downward trend in exposure, although this may be because more recent studies were performed in coke manufacture in Asian and eastern European countries. This coincides with a shift in coke production away from Europe and the USA. The extent to which controls of coke-oven emissions and associated exposure are in place in these facilities has not been reported. Given the reported (sometimes extreme) concentrations, it is unlikely that the control measures in place meet modern standards.

Comparison of the urinary levels of 1-hydroxypyrene between aluminium production and coke-oven workers shows a pattern of higher exposures among the coke-oven workers (up to 3261 μmol/mol creatinine), which is probably a result of the higher levels of exposure to pyrene in coke-oven environments than those in aluminium reduction plants.

Concentrations of benzo[*a*]pyrene measured during roofing and paving with coal tar were relatively similar, with ranges generally up to 10–20 μg/m^3. One exception was a study in the USA, in which exposure to benzo[*a*]pyrene ranged up to 64.5 μg/m^3 during

Figure 1.3. Relative ranking of industries by levels of exposure to (by inhalation only) and by urinary levels of 1-hydroxypyrene (inhalation and dermal exposure)

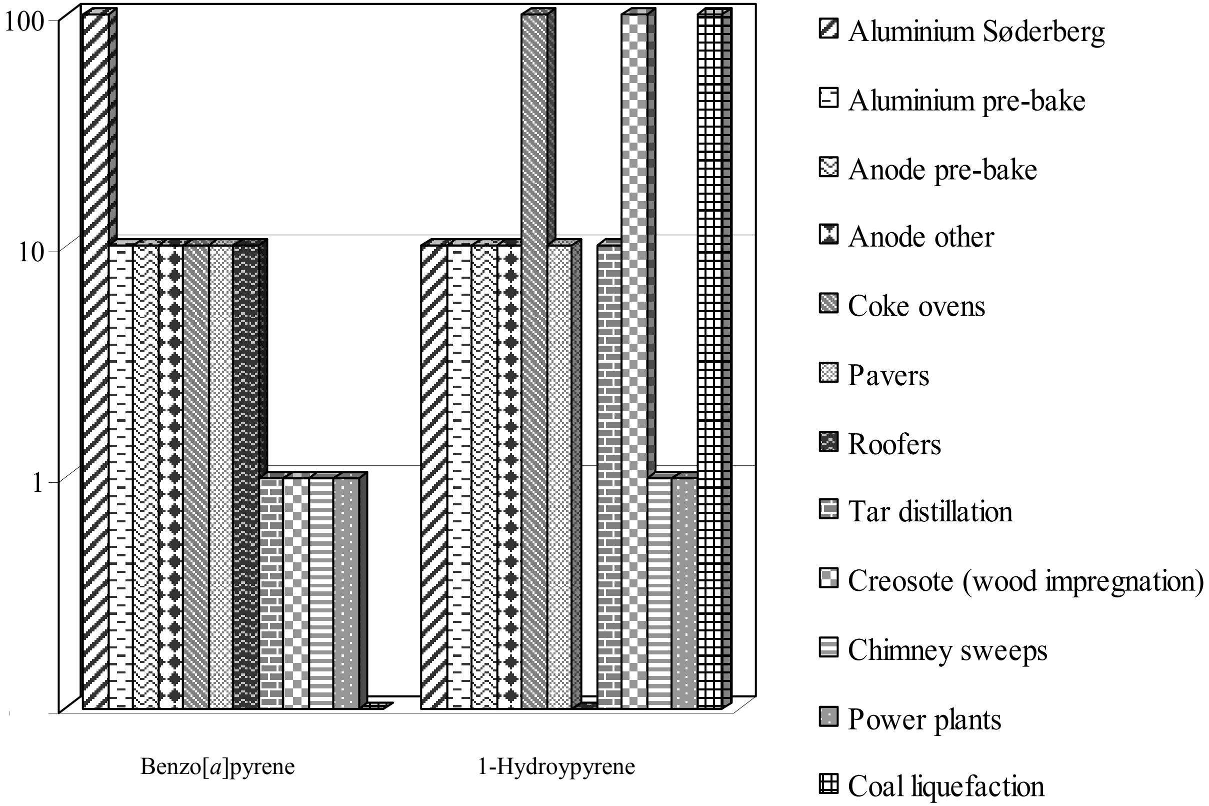


Figure compiled by the Working Group

tear-off of coal-tar roofing; however, no measures of 1-hydroxypyrene were reported among roofers. One study that measured 1-hydroxypyrene among pavers found levels of up to 3.2 µmol/mol creatinine, which are much lower than urinary levels seen in workers in aluminium production plants, electrode manufacturing plants, coke ovens and tar distillation plants. No trends in exposure to PAHs were apparent for roofers and pavers in the studies reviewed for the period 1982–89. The fact that coal tar had stopped being used in these applications would have resulted in greatly reduced exposures to PAHs. However, during tear-off in roofing and recycling in paving, exposure to coal tar can still occur.

The lowest tier of exposure to benzo[*a*]pyrene (at or below 1 µg/m^3) included workers in coal-tar distillation, coal liquefaction, power plants, chimney sweeping and wood impregnation (Figure 1.3). The pattern of urinary 1-hydroxypyrene among these industrial groups did not parallel airborne levels of benzo[*a*]pyrene; workers in coal liquefaction and wood impregnation with coal-tar creosote had levels of 1-hydroxypyrene of 10–100 µmol/mol. This may reflect the poor correspondence between exposure to PAHs by inhalation and urinary excretion of 1-hydroxypyrene, since dermal absorption may be a very significant route of exposure to PAHs. For wood impregnation, the high urinary levels of 1-hydroxypyrene may reflect a predominance of low-molecular-weight PAHs in this environment.

Substantial differences in exposures have been reported within industries and time periods. In Figure 1.1, more detailed temporal and geographical information is given. Differences between job/task within industries are shown in the tables.

(n) PAH profiles

A comparison of industries by composition of the PAH profiles is to some extent limited by the differences in the sets of PAH compounds that were measured in the individual studies. The set of PAHs measured also changed over time, as sampling and analytical methods evolved, making it possible to identify and quantify more components of these complex mixtures. Since the mid-1980s, benzo[*a*]pyrene and pyrene were measured more frequently. The heavier PAHs (heavier than coronene) have not been measured in these industries to date, largely because of the lack of SRMs in the past and difficulties in analytical techniques.

Studies that reported at least six individual PAHs are presented in Table 1.14. Some patterns are apparent in the profiles by industry, which are strongly influenced by the source material in the particular process and the temperature at which the operations were conducted. For example, coke ovens operate at high temperatures (up to 1300 °C), at which extensive pyrolysis of coal constituents occurs very readily. As a result, the studies showed higher levels of exposure over the entire range of PAH compounds and the greatest prevalence of high-molecular-weight PAH compounds (molecular weight > 252). At the other extreme, wood impregnation with creosote reflects a lower-temperature process that uses a distillate fraction of coal tar as a preservative. The resulting PAH exposure profile for this process is rich in low-molecular-weight PAH compounds (such as naphthalene, acenaphthylene, acenaphthene and fluorene), while very low to non-detectable levels of PAHs with a molecular weight of > 216 (benzo[*a*]fluorene) are reported. Some industries present intermediate profiles; for example, carbon electrode manufacture uses coal-tar pitch as the process material but does not raise the pitch to temperatures that promote the volatilization of the higher-molecular-weight compounds (molecular weight, 252 and above). The profiles for these operations reflect this, as the highest exposures in these industries are to pyrene (molecular weight, 202) and lower-molecular-weight PAHs. No profiles were available for the aluminum pre-bake process, coal gasification or chimney sweeps.

1.2.3 *Dietary exposure to PAHs*

The general population can be exposed to PAHs via grilled and smoked foods, foods grown in polluted environments, polluted air, drinking-water and tobacco smoking. Due to the ubiquitous nature of PAHs in foods, the estimation of their dietary consumption is challenging; thus, etiological studies of cancer must rely on exposure measures of dietary intake from questionnaires as well as on biological markers, such as urinary metabolites (Roth *et al*., 2001; Strickland *et al*., 2002) and DNA adducts (see Ramesh *et al*., 2004 for a comprehensive review of dietary PAHs).

Two general approaches have been used to measure PAH levels in the diet. The first approach is to measure a large number of PAHs (see Guillén, 1994; Phillips, 1999), while the second method measures benzo[*a*]pyrene as a surrogate marker for all PAHs (Kazerouni *et al*., 2001). The first approach provides a more realistic notion of the total burden from diet but individual PAHs in any particular foods may vary widely. Measurement of many of the PAHs was previously found to be difficult, and many studies have measured only benzo[*a*]pyrene as a marker of total PAHs in foods because of its carcinogenic potency in experimental animals.

To verify that benzo[*a*]pyrene is a representative marker of total PAHs in food, Kazerouni *et al*. (2001) calculated the correlation coefficients (*r*) between values of benzo[*a*]pyrene and the concentrations of individual and total PAHs in a selection of food items. Selected samples from each major food group were analysed for acenaphthene, anthracene, benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]-perylene, benzo[*a*]pyrene, chrysene, cyclopenta[*cd*]pyrene, fluoranthene, fluorene, indeno-[1,2,3-*cd*]pyrene, naphthalene, phenanthrene and pyrene by HPLC. The correlation coefficient between concentrations of total PAHs (the sum of all those measured in this study) and benzo[*a*]pyrene was 0.87 (*p*-value = 0.0001). The correlation value between PAHs that are known to have carcinogenic potential in experimental animals (i.e. benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, chrysene, cyclopenta[*cd*]pyrene and indeno[1,2,3-*cd*]pyrene) and benzo[*a*]pyrene was 0.98 (*p*-value = 0.0001).

A large body of international data on PAHs in food has recently been reviewed (http://epic-spain.com/libro.html) (Jakszyn *et al*., 2004). The data consist of information

Table 1.14. PAH profiles of the industries reviewed in this monograph[a]

No. of rings	PAH	MW	Coke ovens					Coke production		Coal-tar distillation	
			(top)					High temp.	Low temp.	High temp.	Low temp.
	Reference:		**A**	**B**	**C**	**D**	**E**	**F**	**F**	**F**	**F**
2/3	Naphthalene	128	5				5	4	4	5	3
	Acenaphthylene	152		4		3	5	3	3	2	1
	Acenaphthene	154		3		3	0	3	2	4	3
	Fluorene	166	5	4		3	4	3	3	3	2
	Anthracene	178	5	4	4	2	3	2	3	2	1
	Phenanthrene	178	5	4	5	3	4	3	3	4	2
4	Fluoranthene	202	5	4	4	3	4	3	2	2	1
	Pyrene	202		4	4	3	3	2	2	2	1
	Benzo[*a*]fluorene	216	5	3	3						
	Benzo[*ghi*]fluoranthene	226		2	3						
	Cyclopenta[*c,d*]pyrene	226		3	3						
	Benzo[*a*]anthracene	228	5	3	4	2	3	2	2	1	0
	Benzo[*c*]phenanthrene	228		2	3						
	Chrysene	228	5	3	4	2	3	2	2	1	0
5	Benzo[*a*]pyrene	252	4	3	4	3	3	2	2	2	0
	Benzo[*b*]fluoranthene	252	4	2	3	4	3	2	2	1	0
	Benzo[*e*]pyrene	252		3	4	3					
	Benzo[*j*]fluoranthene	252		2	3						
	Benzo[*k*]fluoranthene	252	4	2	2	3	3	2	2	1	0
	Perylene	252		2	3						
6	Anthanthrene	276		3	3			2	0	0	0
	Benzo[*g,h,i*]perylene	276		3	3	3	3	2	1	1	0
	Indeno[1,2,3-*c,d*]pyrene	276		3	3	4	3	2	0	0	0
	Benzo[*b*]chrysene	278									
	Dibenzo[*a,c*]anthracene	278		2		2					
	Dibenzo[*a,h*]anthracene	278			3		1	2	0	0	0
	Picene	278									
	Coronene	300		3	3						

[a] No profiles were available to the Working Group for coal liquefaction, coal gasification, aluminium production by the prebake process or chimney sweeps.

MW, molecular weight; PAH, polycyclic aromatic hydrocarbon; temp., temperature

A, Andersson *et al.* (1983); **B**, Haughen *et al.* (1986); **C**, Grimmer *et al.* (1993); **D**, Winker *et al.* (1996); **E**, Strunk *et al.* (2002); **F**, Price *et al.* (2000); **G**, Reed (1982); **H**, Zey (1983); **I**, Behrens & Liss (1984); **J**, Wolff *et al.* (1989); **K**, Darby *et al.* (1986); **L**, Knecht & Woitowitz (1989); **M**, Heikkilä *et al.* (1987); **N**, Tjoe Ny *et al.* (1993); **O**, Carstensen *et al.* (1999); **P**, Petry *et al.* (1996)

Categorised levels of exposure to selected PAHs: **0**: < detection limit; **1**: < 0.1 μg/m^3; **2**: 0.1–2 μg/m^3; **3**: 2–10 μg/m^3; **4**: 10–50 μg/m^3; **5**: > 50 μg/m^3

Table 1.14 (contd)

Coal-tar roofing				Paving		Creosote		Aluminium production			Carbon electrode manufacturing	Thermo-electric power plants
		Tear off only		Coal tar	Tar bitumen blend			Søderberg		Anode manufac-turing		
G	**H**	**I**	**J**	**K**	**L**	**M**	**F**	**N**	**O**	**P**	**F**	**F**
						5	5	5		3	4	2
							2	3		2	2	1
	0					5	5	4		4	3	1
	0		3			2	4	4		3	3	1
3	0		2				2	3	1	2	2	1
3	2	5				3	4	4	2	3	3	1
4	3	5			5		2	5	2	3	2	1
4	3	5	3		5	2	2	3	2	3	2	1
					4	1			2			
				3	3					1		
3	2	5	2	3	4		1	3	2	2	1	1
	0				1					1		
3	2	5		3	4	2	1	4	3	2	2	1
3	2	5	2	3	3	1	2	4	2	2	1	1
	3		2		2		0	4	3	2	1	1
	0	5		3	3	1			2	2		
		5			2				2	2		
			2		2	1	0	4	2	2	1	1
					1				2	2		
					1		0			2	0	1
		5	2		1	1	0	3	2	2	1	0
				2	1		0	4	2	2	1	0
										2		
										2		
				2	1	1	0	4		2	0	0
									2			
					1					1		

on food type, methods of cooking and preservation, benzo[*a*]pyrene and total PAH content, analytical technique, sampling method, authors and year of the study and the country where the food was obtained (see Table 1.15 as an example).

PAHs can contaminate foods by two major routes. They are generated through pyrolysis during the grilling/barbecueing of meat products when fat drips from the meat onto hot coals or a heated surface and produces smoke that coats the food with the compounds (Larsson *et al.*, 1983; Lijinsky, 1991). They are also introduced by certain methods of preserving meat and other food products. The other major source of PAH contamination of food is from environmental sources such as petroleum or coal-tar combustion by-products (Lijinsky, 1991).

Grilled foods of any type that are exposed to smoke are likely to have a high content of PAHs. The benzo[*a*]pyrene content of meat items depends on the method, temperature and duration of cooking (Larsson *et al.*, 1983; Larsson, 1986; Lodovici *et al.*, 1995).

Smoke curing of foods is commonly used for preservation and to add flavour. Although the methods differ, they all expose the food to potentially carcinogenic compounds such as PAHs. The level of contamination with PAHs can vary substantially depending on the procedure used in the smoking (Gomaa *et al.*, 1993; García Falcón *et al.*, 1999; Anastasio *et al.*, 2004). Currently, traditional smoking techniques are being partially replaced by liquid smoke flavour. The advantage is a more uniform flavour, which is easier to reproduce and allows greater control of the levels of toxic compounds. However, the level of benzo[*a*]pyrene in liquid smoke flavour samples can vary substantially, from not detected to 336.6 μg/kg (Gomaa *et al.*, 1993; Yabiku *et al.*, 1993).

Unprocessed foods such as vegetables, fruits, vegetable oils, dairy products and seafood can be contaminated with PAHs from the atmosphere, and by deposition and uptake from soil, water and sediment. The higher content in green leafy vegetables such as kale and collards compared with other vegetables is probably due to greater surface contact with ambient air and consequently deposition of airborne contaminants (Kazerouni *et al.*, 2001; Ramesh *et al.*, 2004). Vegetables can be highly contaminated when grown close to highways or on contaminated soils. As a result of stricter air emission regulations and improved environmental conditions in several developed countries, levels of PAHs in vegetables and fruits are now lower than those reported in the 1970s. Oils from different vegetable sources, such as rapeseed, olive oil, sunflower, soya bean and maize, contain considerable levels of PAHs (Ramesh *et al.*, 2004), which are probably formed during processing rather than as a result of airborne contamination. Similarly, PAH levels are low in cereals and beans, but drying techniques used for preservation, such as combustion-gas heating and smoking, increases concentrations of PAHs (Roth *et al.*, 1998; Ramesh *et al.*, 2004).

In addition to grilling and smoking processes, the accumulation of PAHs in foods of animal origin, especially livestock, is also due to the consumption of contaminated feed. Consumption of seafoods, in particular bottom-feeding shellfish and finfish, may contribute considerably to the amount of PAHs in the diet (Ramesh *et al.*, 2004). [High trophic-

Table 1.15. Examples of PAH concentrations in selected fruit and vegetables

Food	Cooking method	Preservation method	Mean BaP μ/kg	Total PAH	Analytical method	Reference	Country of study
Fruit							
Apple	Raw	Fresh	0.10		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Apple	Raw	NA	0.53	8.27	HPLC	Lodovici *et al*. (1995)	Italy
Apple (peeled)	Raw	NA	0.06	2.35	HPLC	Lodovici *et al*. (1995)	Italy
Banana	Raw	Fresh	0.16		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Fruits (citrus)	Raw	NA	0.03	1.67	HPLC	Lodovici *et al*. (1995)	Italy
Grapefruit	Raw	Fresh	0.02		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Orange	Raw	Fresh	0.16		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Peach	Raw	Fresh	0.17		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Peanuts	Toasted	NA	0.01		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Strawberry	Raw	Fresh	0.01		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Walnuts	Toasted	NA	0.03		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Vegetables							
Beans (greens)	NA	Canned	0.14		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Beets (greens)	Raw	NA	0.096	14.0	HPLC	Lodovici *et al*. (1995)	Italy
Broccoli	Raw	Fresh/frozen	0.17		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Carrot	Raw	Fresh/frozen	0.15		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Cauliflower	Raw	Fresh/frozen	0.12		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Cauliflower	Raw	NA	0.006	2.79	HPLC	Lodovici *et al*. (1995)	Italy
Cole slaw	Raw	NA	0.02		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Collars greens	Raw	Fresh/frozen	0.48		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Corn	NA	Canned	0.17		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Corn	NA	NA	0.022	0.85	HPLC	Lodovici *et al*. (1995)	Italy
Greens (mixed)	NA	Frozen	0.14		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Kale	Raw	Fresh/frozen	0.47		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Kale	NA	Frozen	0.15		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Lettuce	Raw	NA	0.007	2.61	HPLC	Lodovici *et al*. (1995)	Italy

Table 1.15 (Contd)

Food	Cooking method	Preservation method	Mean BaP μ/kg	Total PAH	Analytical method	Reference	Country of study
Peas	NA	Canned	0.09		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Spinach	NA	Frozen/fresh	0.10		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Spinach	NA	Frozen	0.12		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Squash	Raw	NA	0.45	8.90	HPLC	Lodovici *et al*. (1995)	Italy
Tomato	NA	Fresh/canned	0.19		HPLC + TLC	Kazerouni *et al*. (2001)	USA
Tomato	Raw	NA	0.003	0.64	HPLC	Lodovici *et al*. (1995)	Italy

BaP; benzo[*a*]pyrene; HPLC, high-performance liquid chromatography;NA, not available; PAH, polycyclic aromatic hydrocarbon; TLC, thin-layer chromatography

Adapted from http://epic-Spain.com/libro.html level consumers, such as humans, do not bioaccumulate due to a higher capacity to metabolize PAHs.]

A comparison of daily intakes of PAHs across studies requires the consideration of various issues, such as selection of food items, methodology used for extraction, identification and quantification. Estimated daily dietary intake of PAHs in selected countries has been summarized (Ramesh *et al*., 2004) (Table 1.16).

Table 1.16. Dietary intakes of PAHs in various countries

Country	Intake (µg/person/day)	Reference
USA	0.16–1.6 0.04–0.06[a] 0.12–2.8[a]	Santodonato *et al.* (1981) Kazerouni *et al.* (2001) Hattemer-Frey & Travis (1991)
United Kingdom	3.7	Dennis *et al.* (1991)
Germany	0.02–0.04	State Committee for Air Pollution Control (1992)
Austria	3.4 (0.7–15.6)[b]	Pfannhauser (1991)
Italy	3.0	Lodovici *et al.* (1995)
Spain	6.3–8.4	Falćo *et al.* (2003)
Greece	1.6–4.5	Voutsa & Samara (1998)
Netherlands	5–17	de Vos *et al.* (1990)
Sweden	0.08	Beckman Sundh *et al.* (1998)

PAH, polycyclic aromatic hydrocarbon
From Ramesh *et al.* (2004)
[a] Values reported were for benzo[*a*]pyrene concentrations only.
[b] Median and range for the sum of 16 PAHs

The FAO/WHO Joint Expert Committee on Food Additives and Contaminants (JECFA) recently selected a representative mean intake of 4 ng/kg bw benzo[*a*]pyrene per day and a high-level intake of 10 ng/kg bw per day for their evaluation of PAHs (JECFA, 2005). It also noted that some population groups who regularly consume food cooked over open fires or barbecues, or people who habitually consume foods from areas of higher contamination, may have higher intakes.

In spite of the differences observed in international studies, it is clear that dietary intake is the major route of exposure to PAHs for a large proportion of the nonsmoking, non-occupationally exposed population (Ramesh *et al*., 2004). In a study in the USA, Phillips (1999) estimated that, for nonsmokers who are not exposed occupationally, about 70% of exposure to PAHs typically comes from dietary sources. For a nonsmoking man aged between 19 and 50 years, total PAH intake was estimated at 3.12 µg per day, of which 96.2% was from food, 1.6% from air, 0.2% from water and 1.9% from soil

(Menzie *et al.*, 1992). However, in a study in which the relative contributions of dietary and inhalation exposures were compared directly, weekly intakes of benzo[*a*]pyrene by inhalation (mainly from indoor air) were greater than those from the diet in half of the subjects mostly because the range of dietary exposure to benzo[*a*]pyrene (1–500 ng/day) was wider than that of inhalation exposure (10–50 ng/day) (Lioy *et al.*, 1988; Lioy & Greenberg, 1990).

In a study conducted in the USA on the distribution of dietary intake of benzo[*a*]pyrene in 228 subjects, approximatively 31% of the subjects had an intake in the range of 40.1–60 ng/day (Kazerouni *et al.*, 2001).

Figure 1.4 presents the percentage contribution of various food groups to the mean daily intake of benzo[*a*]pyrene. The dietary information was collected using a food-frequency questionnaire that included detailed questions on the cooking methods of meat combined with a newly developed benzo[*a*]pyrene database (Sinha *et al.*, 2005). Bread and other cereal products (29%) followed by grilled/barbecued meat (21%) contributed most to the total daily intake of benzo[*a*]pyrene. In contrast, fat, sweets and dairy food groups contributed the least. Taking into account the concentration of benzo[*a*]pyrene in individual items in the cereal, fruit and vegetable food groups, the large contribution of each group is due to the size of the portion consumed. In terms of the percentage contribution to total dietary intake of benzo[*a*]pyrene, this result is consistent with the study by Lodovici *et al.* (1995) with regard to cereal products, vegetables and fruit groups, but not to grilled/barbecued meats. The studies by Larsson (1986) and by de Vos *et al.* (1990) reported a much higher contribution from fat/oil and from sugar and sweets, respectively.

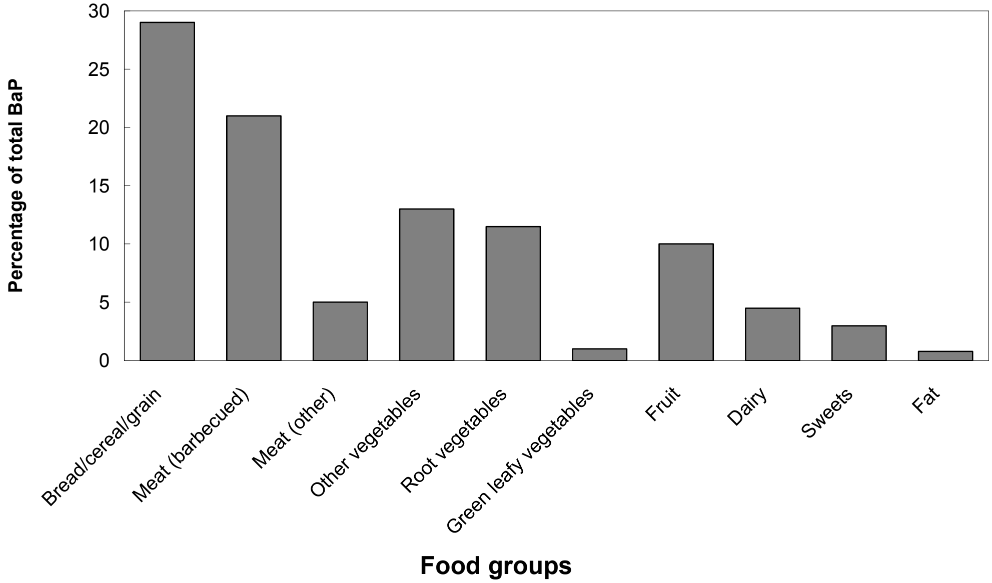
A database has been developed that can be used in conjunction with a food-frequency questionnaire to estimate the intake of PAHs (Kazerouni *et al.*, 2001; Sinha *et al.*, 2005). Multiple meat samples were cooked by different methods and to varying degrees, and additional foods were sampled and measured for benzo[*a*]pyrene as a marker for PAHs. The software application, CHARRED, which was developed to compute PAH values from meat intake, is now available (www.charred.cancer.gov).

1.3 Regulations and guidelines

Several countries have set occupational exposure limits for coal-tar pitch volatiles (CTPVs) or particulate PAHs. The values are typically based on the benzene- or cyclohexane-soluble matter of the particulates present in air. Some countries have exposure limits for individual PAHs, notably for benzo[*a*]pyrene.

For CTPVs, Belgium, Canada (Alberta, British Columbia, Ontario [short-term exposure limit (STEL)], Quebec), China, Malaysia, New Zealand, Spain and the USA have set the occupational exposure limit at a 0.2-mg/m^3 time-weighted average (TWA) for the benzene-soluble fraction (which includes acridine, anthracene, benzo[*a*]pyrene, chrysene, phenanthrene and pyrene). This value has also been suggested as the threshold limit value (TLV) by the American Conference of Governmental Industrial Hygienists (ACGIH) in the USA. China has set a STEL of 0.6 mg/m^3 for this parameter. Also in the

Figure 1.4. Percentage of total daily benzo[*a*]pyrene (BaP) intake from selected food groups among 228 subjects in Maryland, USA[a]



From Kazerouni *et al.* (2001)
[a] Data read from graph

USA, the National Institute of Occupational Safety and Hygiene (NIOSH) has suggested a recommended exposure limit of a 0.1-mg/m^3 TWA for the cyclohexane-extractable fraction of CTPVs; this value also is applied in Hong Kong, Ireland and South Africa. The Netherlands report a value of 0.2 mg/m^3, but without a designation of soluble fraction. Mexico has set a limit for CTPVs at 0.002 mg/m^3, without a designation of soluble fraction.

Mexico has set the limit for PAH particulates at a 0.2-mg/m^3 TWA and a 0.3-mg/m^3 STEL; the corresponding values for Canada (Alberta) are a 0.2-mg/m^3 TWA and a 0.6-mg/m^3 STEL as benzene solubles; Norway has set a limit of 0.04 mg/m^3 for total PAHs (ACGIH, 2005; OSHA, 2005a).

In Germany, benzo[*a*]pyrene is the indicator for external exposure to PAHs. The German technical guiding concentration for benzo[*a*]pyrene in the air is 0.005 mg/m^3 for the production, loading and unloading of pencil pitch and in the area near the ovens in coking plants and 0.002 mg/m^3 for all other workplaces (Bundesministerium für Arbeit und Sozialordnung, 2000; ACGIH, 2005). The Czech Republic has set the limit for benzo[*a*]pyrene at a 0.005-mg/m^3 TWA (with a skin irritation notation) and a 0.025-mg/m^3 STEL; Canada (Quebec) has set a limit of 0.005 mg/m^3; Poland, Sweden and Switzerland have set a limit of 0.002 mg/m^3; and Finland has set a limit of 0.01 mg/m^3 (ACGIH, 2005; Suva, 2005).

The US Occupational Safety and Hygiene Administration (OSHA) has established a permissible exposure limit for workers exposed to coke oven emissions; the concentration cannot exceed 0.15 mg CTPV/m^3 of air, averaged over any 8-h period (ACGIH, 2005; OSHA, 2005b,c,d). China has set the limit for coke-oven emissions at a 0.1-mg/m^3 TWA and a 0.3-mg/m^3 STEL (ACGIH, 2005).

While not determining an actual biological exposure index value, the US ACGIH® recommends that a benchmark value of 1 µg/L 1-hydroxypyrene/L (0.49 µmol/mol creatinine) in urine be considered as a postshift level that indicates occupational exposure to PAHs. The benchmark level is based on exposures to PAHs that result in urinary levels of 1-hydroxypyrene that are greater than those of at least 99% of the population with no occupational or significant environmental exposure. The biological exposure index is applicable to all exposures that involve PAHs, and is designed to assist industrial hygienists and other occupational health professionals to control occupational exposure to PAHs from all routes (ACGIH, 2005).

On the basis of the measured levels of 1-hydroxypyrene in the urine of workers exposed in the various industries surveyed, the Health and Safety Executive adopted a biological monitoring guidance value of 4 µmol/mol creatinine (Health and Safety Executive, 2005). This value represents the 90th percentile of measurements taken from industries that are deemed to have good controls, which includes the CTPV industries but excludes data from one timber impregnation site. This value was also approved by WATCH (Pedersen, 2003).

PAH mixtures are very variable qualitatively and quantitatively. The relative amounts of pyrene and benzo[*a*]pyrene in the applicable exposure matrix (air and/or dermal/surface contamination) should be determined; the benchmark level of 1 µg/L can then be adjusted to take into account different pyrene:benzo[*a*]pyrene ratios in the specific exposure matrix. The adjustment should be based on data collected from air, surface or skin samples, as follows:

$$\text{adjusted recommended level} =$$

$$1\ \mu\text{g 1-hydroxypyrene/L} \times \left(\frac{(\text{pyrene measured/benzo}[a]\text{pyrene measured})}{2.5}\right)$$

The ratio of 2.5 (pyrene:benzo[*a*]pyrene) was selected as the default ratio to provide a realistic, although in some cases conservative, estimate of the proportion of carcinogens in the mixture. Some reports of the relative amounts of pyrene:benzo[*a*]pyrene are summarized in Table 1.17 (ACGIH, 2005).

The 1993 WHO *Guidelines for Drinking-water Quality* concluded that there were insufficient data available to derive drinking-water guidelines for PAHs other than benzo[*a*]pyrene, for which the guideline value was calculated to be 0.7 µg/L and remains the current guideline value (WHO, 2004).

The European Union has set the drinking-water guideline for PAHs at 0.1 µg/L for the sum of four compounds (benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene

Table 1.17. Reported ratios of pyrene:benzo[*a*]pyrene

Mixture	Pyrene: benzo[*a*]-pyrene ratio	Reference
Aluminum workers: Anode factory (air)	3.7	van Schooten *et al.* (1995)
Aluminum workers: Bake oven (air)	4.3	van Schooten *et al.* (1995)
Aluminum workers: Electrolysis (air)	4.0	van Schooten *et al.* (1995)
Aluminum workers: Foundry (air)	2.0	van Schooten *et al.* (1995)
Aluminum workers: Pot relining (air)	30.8	van Schooten *et al.* (1995)
Bitumens (bulk) average of 8 samples	1.5	IARC (1985)
Chisellers of creosoted rails (air)	1.3	Heikkila *et al.* (1995)
Coal tar asphalt pavers (air)	9	Jongeneelen *et al.* (1988b)
Coal tar asphalt pavers (bulk)	4.0	Jongeneelen *et al.* (1988b)
Coal tar asphalt pavers (hand skin)	6	Jongeneelen *et al.* (1988b)
Coal tar asphalt pavers (wrist pad contamination)	8	Jongeneelen *et al.* (1988b)
Coke oven (air samples)	2.4	IARC (1985)
Creosote	7.2	Elovaara *et al.* (1995)
Creosote (bulk)	38	Elovaara *et al.* (1995)
Electrode manufacturing high exposure (air)	2.0	van Delft *et al.* (1998)
Electrode manufacturing intermediate exposure (air)	1.4	van Delft *et al.* (1998)
Electrode paste plant: all workers (air)	1.9	Bentsen *et al.* (1998)
Electrode paste plant: mixing (air)	11.5	Bentsen *et al.* (1998)
Electrode paste plant: mold filling (air)	2.5	Bentsen *et al.* (1998)
Electrode paste plant: truck drivers (air)	1.3	Bentsen *et al.* (1998)
Graphite electrode production (air)	4.0	IARC (1985)
Medicinal coal tar (bulk)	1.2	Godschalk *et al.* (1998)
Medicinal coal tar (bulk)	1.1	VanRooij *et al.* (1993c)
Protective paints (bulk)	3.6	IARC (1985)
Range of bulk samples in petrochemical industries	0.4–220	Boogaard & van Sittert (1994)
Road tars (bulk) average of 2 samples	3.4	IARC (1985)
Roofers (air)	3.2	Wolff *et al.* (1989)
Roofers (skin wipes)	2.1	Wolff *et al.* (1989)
Shale oils (bulk) average of 5 samples	3.8	IARC (1985)
Soots (bulk) average of 3 sites hardwood fireplace	2.2	IARC (1985)
Tobacco smoke	5	Guérin (1980)

From ACGIH (2005)

and indeno[1,2,3-*cd*]pyrene), and at 0.01 μg/L for benzo[*a*]pyrene (European Union, 1998).

Canada has set a guideline for the maximum acceptable concentration of benzo[*a*]pyrene in drinking-water at 0.01 μg/L (Health Canada, 1986, 2004).

The Environmental Protection Agency of the USA (2004) has set a drinking-water standard (maximum contaminant level) for benzo[*a*]pyrene at 0.2 μg/L.

In the USA, coal tar may be used as an active ingredient in external drug products at a concentration of 0.5–5% for control of dandruff, seborrheic dermatitis and psoriasis (Food and Drug Administration, 2005). When a coal-tar solution, derivative or fraction is used as the source of the coal tar, the labelling must specify the identity and concentration of the source of the coal tar used and the concentration of coal tar present in the final product.

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