The occupational exposure of polycyclic aromatic hydrocarbons (PAHs)

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Polycyclic aromatic hydrocarbons (PAHs) are a class of diverse organic compounds containing two or more fused aromatic rings of carbon and hydrogen atoms. The term PAH refers specifically to those polycyclic aromatic compounds that consist only of hydrogen and carbon, either unsubstituted or substituted by alkyl- (mostly methyl-) side chains. PAHs are formed during the incomplete combustion of fossil fuels and oil products and as a result are widely distributed in the workplace and the environment. The main sources of non-occupational exposure to airborne PAHs are from the exposure to combustion processes; these include motor vehicles, petroleum refineries, power plants using fossil fuels, coking plants, bitumen and asphalt production plants, aluminium refineries, iron and steel foundries, crop residue and forest burning, bushfires, smoke from open fireplaces, environmental tobacco smoke and cooking food. Exposure also occurs through ingestion of PAH containing foods. Raw food does not normally contain high levels of PAHs, but they are formed by roasting, baking, frying or processing. The major source of occupational exposure to PAHs include coke ovens and coal tar use, iron and steel works, aluminium works, foundries, carbon electrodes and carbon black manufacture, asphalt manufacture and use, and many others.

Table 1. Industry types and airborne PAHs of interest

Compound	Industry type
Naphthalene	High temperature coke oven
Acenaphthalene	Low temperature coke oven
Acenaphthene	High temperature tar distillation
Phenanthrene	Aluminium smelting
Anthracene	Clay targets
Fluoranthene	Pipeline coating and wraps
Pyrene	Coal fires power station
Benzo(a)fluoranthene	Timber impregnation
Chrusene	Electrical carbon
Benzo(b)fluoranthene	Integrated oil refinery
Benzo(k)fluoranthene	Petroleum tar distillation
Benzo(j)fluoranthene	Petroleum coking
Benzo(a)pyrene	Bitumen refinery
Indeno(1,2,3-c,d)pyrene	Asphalt roofing
Benzo(g,h,i)pyrene	Asphalt road dressing (surfacing)
Dibenz(a,h)anthracene	Road construction (base)
Anthanthrene	Carbon black manufacture
Cyclopenta(c,d)pyrene	Motor tyre manufacture
	Iron foundry
	Fish smokehouse

PAHs are colourless to yellow solids at ambient temperatures. High melting- and boiling-points, low vapour pressures, and low water solubility are common characteristics to this class. The low water solubility tends to decrease with increasing molecular mass. PAHs are also highly lipophilic and have the tendency to accumulate in fatty tissue.

Only a small number of PAHs are commercially produced. Fluoranthene is mainly used as intermediates in the production of fluorescent dyes and pyrene in the production of perinon pigments. PAHs are also found in coal and mineral oil products such as coke, bitumen, coal tar, heating oils, vehicle fuels, lubricating and cutting oils, and printing colour oils.

Sediments and soils are the main sinks for PAHs in the environment and PAHs with four or more aromatic rings are persistent in the environment.

In the occupational environment that includes the major industries, inhalation of volatile compounds or of particles with adsorbed PAHs and dermal absorption of mixtures containing PAHs are the most important routes of exposure. PAHs can enter the body by inhalation, absorption through the skin and through the intestinal tract. The intestinal absorption of the PAHs is highly dependent on their solubility, their limpidity, the presence of bile, and the limpidity of the various PAH-containing foods ingested. In laboratory animals, PAHs become widely distributed in the body following administration by any one of the absorption routes and are found in almost all internal organs, particularly the organs that are rich in lipid. There is also evidence that the PAHs administered orally cross the placental barrier and have been detected in the foetal tissues. Differences in concentrations in the foetus among the various PAHs appeared to be highly dependent on the gastrointestinal absorption of the compound.

The metabolism of PAHs in humans is very complex (Figure 1). The process involves epoxidation of double bonds, catalysed by the cytochrome P-450-dependent mono-oxygenase, the rearrangement or hydration of the epoxides to yield phenols or diols, respectively, and the conjugation of the hydroxylated derivatives. The metabolism leads generally to detoxification, but some PAHs in some situations become activated to produce DNA-binding species, principally diol-epoxides that can initiate tumors. Evidence that mixtures of PAHs are carcinogenic in humans comes primarily from occupational studies of workers. High lung cancer mortality has also been linked to PAH exposure from unvented coal combustion. The fact that in all the occupations where exposure to PAHs is relevant, workers are also

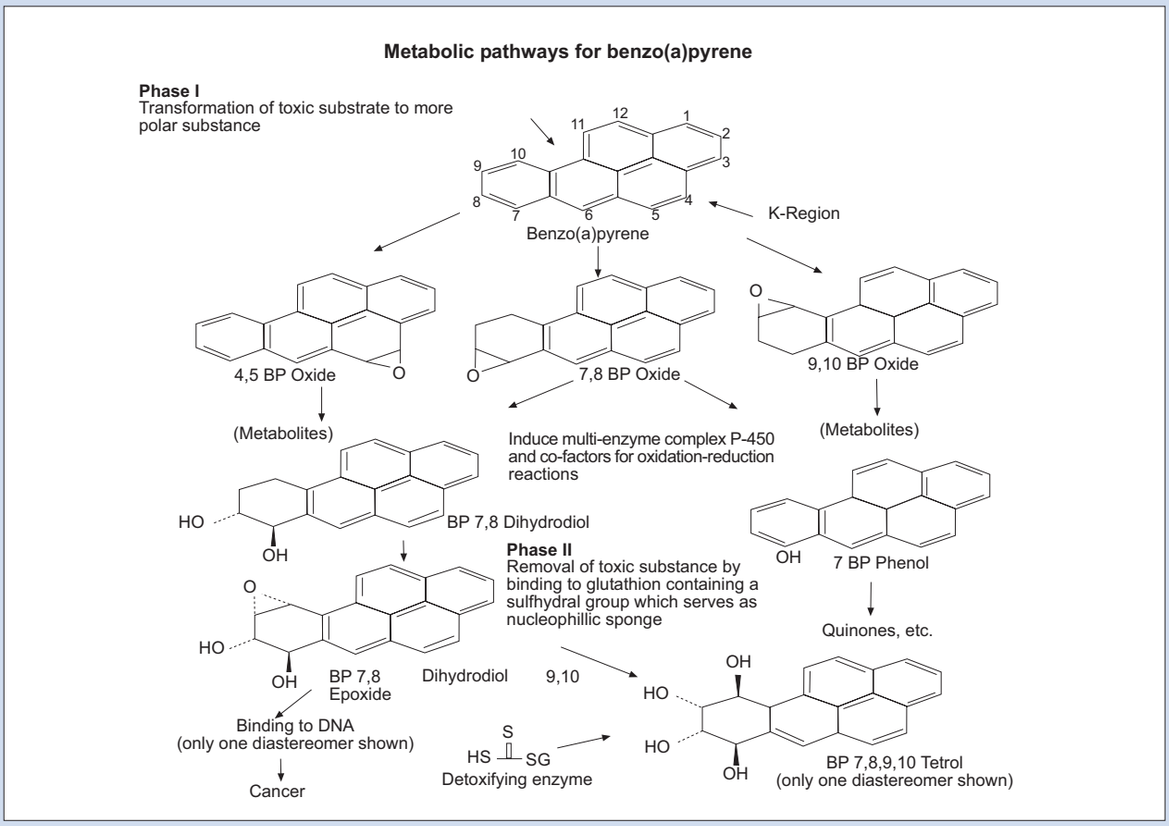

Figure 1. The metabolic pathway for benzo(a)pyrene represented in two phases. Phase I: the transformation and Phase II: the removing of toxic metabolites

exposed to other chemicals, makes a direct correlation between increased PAH levels with lung cancer more problematic. Dermal exposure of PAHs is also directly associated with skin cancer. There is additionally the confounding factor of smoking. PAHs present in tobacco smoke (mainstream and side stream) are implicated as contributing to lung and other cancers.

PAH metabolites and their conjugates are predominantly excreted via the faeces and to a lesser extent in the urine. Conjugates excreted in the bile can be hydrolised by enzymes of the gut flora and reabsorbed. Other PAH moieties that become covalently bound to tissue constituents, in particular to nucleic acids, are not removed. The excretion of urinary metabolites is a method used to assess internal human exposure of PAHs. One of the major components of many PAH mixtures is pyrene, and although it is not one of the carcinogenic compounds, its metabolite 1-hydroxypyrene is stable, relatively easy to detect in urine and has been proposed as a biomarker of exposure to PAHs. Statistical analysis revealed that only 1-hydroxypyrene and possibly chromosome aberrations show a correlation with PAH exposure. In addition to cancer, long term exposure to PAH compounds may lead to excessive deaths from respiratory diseases, Hodgkin's disease, and other hypertensive disease.

Exposure assessment: A non-specific approach was adopted in the past where a potential for high exposure due to the release of coal tar pitch volatiles (CTPV) from coke ovens existed. The measurement method was based on the mass of benzene or cyclohexane soluble material extracted from total aerosol collected on a filter. This method exhibited poor accuracy and precision and was not linked to a specific toxicological hazard. Extensive work (Figure 2) showed that the measurement of individual PAHs was the way forward to assess exposure to CTPV, but there are few occupational exposure limits for individual PAHs. The assessment of airborne exposure alone may not always give a complete picture of exposure. In such cases, biological monitoring has an important role to play but the complexity of the PAH mixtures, their low concentrations in biological media and their metabolism makes biological monitoring of the components of the mixture very difficult. The options for biological monitoring of PAH exposure include measurement of PAH adducts to DNA. The overall preference for biological monitoring is that it should be based on non-invasive sample collection if possible (i.e. urine).

Conclusion

It is general knowledge that PAH mixtures are highly toxic and long term exposure to these compounds may lead to excessive deaths from a number of diseases. Mortality from malignant neoplasms of the bladder and lung was found to be related to the number of tar-years and to the years of exposure. Biological monitoring for PAHs may be particularly useful where control relies on protective wear alone. However, a combination of biological and airborne measurements will be required to determine the effectiveness of the control system in place. Efforts to educate industry of the dangers involved when working with hazardous chemicals have been underway since the early nineties. However, PAH exposure seems to be a greater problem than was anticipated. Apart from the background exposure to PAH there is still an alarming amount of workers exposed to high levels of these compounds.

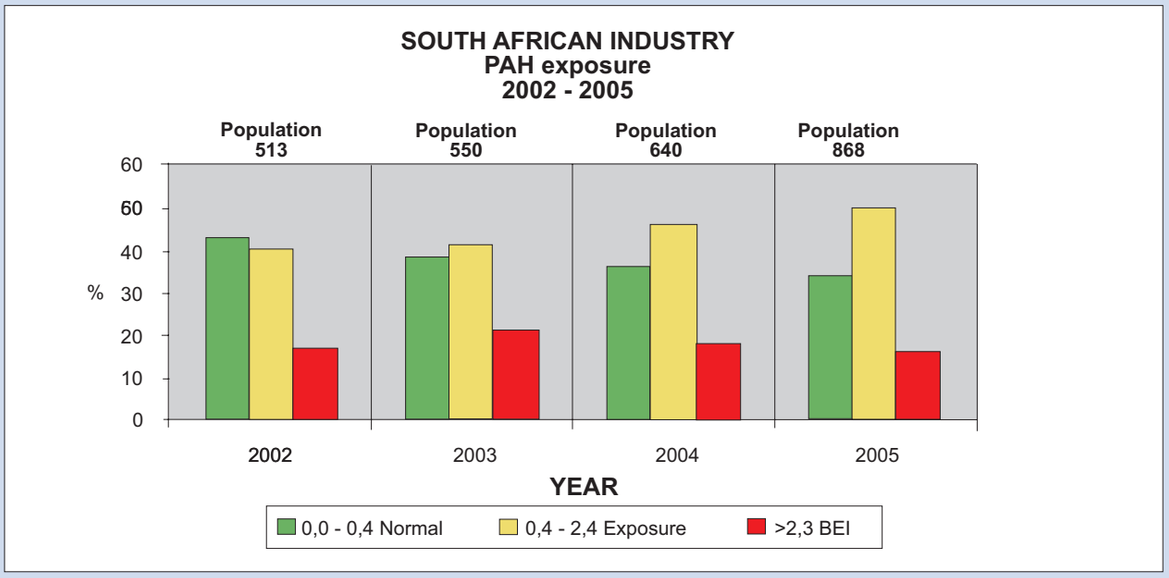

Figure 2. The statistical representation of the three different categories (non-exposed, exposed and above BEI) of PAH exposure by measuring 1-hydroxypyrene in urine

Table 2. Benzo(a)pyrene exposure levels for different workplaces

Degree of exposure	Different workplace
Very high exposure (>10 µg/m³)	• Gas and coke works (topside work). • Aluminium works (e.g. pin setters, pot-men, crane drivers, etc.). • Manufacture of carbon electrodes (pitch bin workers, etc.). • Handling of molten tar or pitch (roofing, paving, insulation, coating, etc.). • Chimney sweeping (from the top). • Asphalting if asphalt is mixed with tar (some jobs). • Timber impregnation.
Fairly high exposure (1–10 µg/m³)	• Gas and coke work in general (excluding topside work). • Blast furnaces. • Steel works (some jobs). • Manufacture of carbon electrodes (in general). • Aluminium works (in general). • Asphalting if asphalt is mixed with tar (in general).
Moderate exposure (0,1–1 µg/m³)	• Steel works (in general). • Foundries (some jobs). • Welding of rails on the railway track. • Manufacture of Söderberg electrode paste.
Low exposure (0,01–0,1 µg/m³)	• Automobile repair workshops. • Asphalt manufacture (from petroleum). • Foundries (in general). • Construction of tunnels and rock chambers. • Aluminium electrolysis with pre-baked electrodes.
Very low exposure (<0,01 µg/m³)	• Iron mines. • Garages.

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