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# **Ambient air pollution by Polycyclic Aromatic Hydrocarbons (PAH). Position Paper**



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# **Ambient Air Pollution by Polycyclic Aromatic Hydrocarbons (PAH)**

## **Position Paper**

July 27<sup>th</sup> 2001

**Prepared by the Working Group  
On Polycyclic Aromatic Hydrocarbons**

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# **1. Introduction, Characterisation and Current Regulation**

## **Scope of the PAH Working Group**

1. In 1999 the European Commission, created a Working Group to review the knowledge on polycyclic aromatic hydrocarbons (PAH) in ambient air and to consider the need and implications of regulations on the concentrations of PAH under the Air Quality Framework Directive (96/62/EC). Their work entailed:
  - examining the known sources of PAH emission;
  - assessing existing information on PAH concentrations in the ambient air;
  - assessing trends in emission and ambient levels;
  - reviewing currently available measurement and assessment techniques in relation to PAH;
  - the preparation of a review of the effects of PAH;
  - collating the experience of member states in the:
    - assessment and management of the risks associated with PAH;
    - setting air quality standards and guidelines;
  - making recommendations to the Commission for air quality standards and associated monitoring and assessment strategies.
2. The experts serving on the Working Group, whilst reflecting the concerns of member states, industry and non-governmental organisations, formulated an independent view based on scientific and technical consensus. A distinction was drawn between preferred air quality objectives based on an objective risk assessment and practically achievable ambient air concentration standards now and in the future.
3. PAH is a term encompassing a wide range of compounds that are emitted from a number of sources. Airborne PAH include substances which, when inhaled, are believed to produce lung cancer in humans. The attention of the Working Group focused on ambient air and the limited number of PAH compounds that showed the highest evidence of human carcinogenicity. Particular emphasis was given to lung cancer as an effect demonstrated by epidemiological and experimental studies using PAH mixtures typical of environmental exposure. The working group agreed therefore not to consider in detail:
  - exposure to PAH other than from breathing ambient air,
  - PAH compounds with no evidence of human carcinogenic activity, or which are not evaluable as human carcinogens
  - carcinogenic risk from transformation products or derivatives of PAH due to interaction with other pollutants such as oxides of nitrogen.Ingestion is an important exposure pathway, consequently eating food contaminated with PAH from the cooking process or deposited from the air may be a health risk but was judged to be outside the current remit of the working group. Exposure to airborne PAH occurs both indoors and outdoors. Indoor exposure to tobacco smoke, cooking and open fire places etc is beyond the scope of this report – as is exposure in the work place which is covered by regulations concerned with occupational health and safety.



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**Definition of PAH and their Properties**

4. PAH are a large group of compounds, they consist of two or more fused aromatic rings made entirely from carbon and hydrogen. The physical and chemical properties of the individual PAH vary. Some physical properties and structures are shown in **Table 1: Physical Properties and Structures of Selected PAH.**
5. Whilst the physico-chemical properties of PAH vary considerably the semi-volatile property of some PAH makes them highly mobile throughout the environment, deposition and re-volatilisation distributing them between air, soil and water bodies. A proportion of PAH is subject to long range atmospheric transport making them a transboundary environmental problem.
6. PAH are reported in many different ways. Different subsets of individual compounds are considered for different purposes. Some currently used lists of PAH together with the classification according to IARC, are shown in **Table 2: Details of carcinogenic groups and measurement lists of PAH.**

**Current Regulations in Member States**

7. There are currently no EU Directives or other guidance to member states which bear directly on either emissions or air quality objectives of PAH. PAH are, however, covered by the Persistent Organic Pollutant (POP's) -Protocol under the United Nations Economic Commission for Europe's Convention on Long Range Transboundary Air Pollution [UN ECE CLRTAP]; under the Protocol, emissions of four PAH compounds have to be reported annually; in addition, emissions of PAH in 2010 may not exceed the levels of 1990 (or any other base year between 1985 and 1995). The Protocol will enter into force after 16 ratifications, which is expected between 2001 and 2002. The European Community is a party to the Convention and will therefore have to fulfil the obligations of the Protocol after ratification. Of the EU member states currently only Italy has legally enforceable ambient air standards for PAH but five others have sufficient concern that they have issued guidance for planning and policy purposes. All have used BaP as a marker for PAH and one (Sweden) has gone further and set a value for fluoranthene as well. See **Table 3: Review of Legislation or Guidance intended to limit ambient air concentrations of PAH.**
8. While not directly controlling PAH it is likely that a number of Directives do, nevertheless, indirectly influence their emission or concentration in ambient air. These include the directives: arising from the Auto Oil programme, on the incineration of wastes, the IPPC directive (96/61/EC), the air quality framework directive (96/62/EC) and its first daughter directive -1999/30/EC [Council Directive relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air, OJ L 163, 29.6.1999, p.41] which addresses particulate matter. The objectives of this legislation can not be met without the control of the emissions of particulate material from a very wide range of sources, many of which are sources of PAH. It is likely that measures to meet the objectives of the daughter directive will reduce PAH emissions also. New vehicle emissions

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regulation ('EURO IV') will, in time, further reduce particulate emissions too; this will result in further PAH reductions. The effect of these measures is hard to predict.

9. The World Health Organisation [WHO] has examined the issue of PAH health risk on a number of occasions and has published Air Quality Guidelines in 1987 and 2001.

## 2. Sources of Emission, Sinks and Ambient Concentrations

### Chapter Summary

#### General Points

- There are five major emission source components:
  - Domestic,
  - Mobile,
  - Industrial,
  - Agricultural,
  - Natural.

The relative importance of these sources is expected to change with time as a result of regulations and economic development

- Current inventories have a high uncertainty and are often not directly comparable; some address BaP only, whilst others comprise additional compounds which are not always specified,
- Despite current uncertainties, a continued significant reduction in total mass emission from 1990 to 2010 is anticipated, predominantly in the industrial and mobile sectors; only minor reductions are predicted for the domestic sources.

#### Industrial Sources

- Most important industrial sources include cokerries, primary aluminium production (in particular plants using the Soderberg process) and wood preservation,
- Industrial sources are being increasingly regulated (e.g. through IPPC); in addition improved energy management is leading to improved combustion.
- Total PAH emissions from industrial sources are therefore decreasing,
- BaP from industrial sources is largely associated with particles <2.5µm,
- Some industrial sources have considerable impact on local air quality, even after applying BAT.

#### Domestic Sources

- Emissions are predominantly associated with the combustion of solid fuels (as wood and coal),
- BaP from domestic sources is associated with a range of particle size including <2.5µm,
- Sources are numerous and widespread,
- There is no uniform European regulation,
- Improvements can be achieved using new combustion appliances and fuel switching.

#### Mobile Sources

- Emissions from new vehicles are regulated at a European level but not specifically for PAH,
- Emission is a function of engine type, emission control, load, age, fuel and driving mode, including cold starting,
- There is increasing control over particles emission,
- BaP from mobile sources is largely associated with particles <2.5µm,
- Emissions are at ground level, widespread and concentrated in urban environments.

#### Agricultural sources

- Agricultural burning is a source of PAH which is regulated at a local level but not at a European Level.

#### Natural Sources

- Natural sources such as fire, volcanoes and other PAH-producing events are stochastic; they have not been investigated in great detail, but may contribute significantly to local PAH levels.

#### Post-emission transformation

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#### Chapter Summary

- The mass and chemical speciation of PAH-in-air changes in a number of ways following emission. Physical and chemical removal processes, and wet and dry deposition are all important,
- PAH containing 5 or more rings (including BaP) are found predominantly in the particulate phase; those containing 2 or 3 rings are almost entirely present in the vapour phase. 4 ring compounds are particle-bound but have the greatest seasonal variability between phases,
- The majority of particle-bound PAH is found on small particles ( $< 2.5 \mu\text{m}$ ),
- PAH-in-air is deposited to other media where it is degraded by a variety of mechanisms. PAH degradation rates in other media are generally lower than those in air, with BaP retention being greatest in the sea.

#### Markers

- BaP is a suitable marker due to its stability and relatively constant contribution to the carcinogenic activity of particle-bound PAH

#### Ambient Information

- Comparable and consistent ambient PAH concentration data for the whole of the EU region are sparse and do not allow a detailed analysis of either total or species-specific concentrations,
- Such data which do exist, centre on concentrations of BaP
- In the 1990's, typical annual mean levels for BaP in rural background areas vary between 0.1 and 1  $\text{ng}/\text{m}^3$ ; for urban areas between 0.5 and 3  $\text{ng}/\text{m}^3$  (traffic sites are included at the upper part of this range); and up to 30  $\text{ng}/\text{m}^3$  within the immediate vicinity of certain industrial installations. Very few measurement data exist for rural communities burning coal and wood domestically; however, these measurements suggest levels similar to those found in cities,
- Concentrations can be high close to large industrial sites and busy roads.
- There appears to be a downward trend in concentrations as a result of regulatory measures already implemented.

#### Emission Inventories

10. Emission inventories are an important tool in the management of air quality. Parties to the UN ECE CLRTAP report their emissions to the European Monitoring and Evaluation Programme (EMEP) on a regular basis. This activity is providing a more self-consistent European-wide PAH inventory. Nevertheless, some further work is required to ensure full inter-comparability – see **Table 4: Emission estimates from European countries**. The European Environment Agency (EEA), via CORINAIR, its initiative for the collection and reporting of emissions on a wide range of pollutants, has encouraged a consistency of approach between contributing countries. More recently, guidance for the estimation and reporting of emissions of air pollutants, including PAH, has been provided by a joint UN ECE European Monitoring and Evaluation Programme (EMEP) and EEA Task Force (EMEP/CORINAIR 1999).
11. There are four major anthropogenic emission source components: Domestic, Mobile, Industrial, and Agricultural. In addition PAH can be formed naturally as a result of uncontrolled or accidental burning. The principle sources and their relative importance are indicated in **Figure 1: Current and projected emission of BaP** [Holland et al., 2001]. The levels of emission from these sources are changing with time as a result of regulation and economic development. Only limited information on changes occurring in chemical and physical composition over time is available.

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12. Other international organisations/groups carrying out activities requiring inventories include the Global Emission Inventories Activities (GEIA) project, GENEMIS (part of the EUROTRAC programme), OECD/Eurostat - which collects information in their joint questionnaire, the Auto-oil II consortium and the EU work on Environmental Cycling of Selected Persistent Organic Pollutants (POPs) in the Baltic Region [Pacyna et al., 1999].
13. Current inventories have a high uncertainty and further work is required to improve the reliability of the estimates. Nevertheless these PAH inventories have allowed the identification and prioritisation of the likely main emission sources. The picture is further complicated by the lack of consistent data for PAH species other than BaP.
14. Emission factors are used to calculate the degree to which particular sources contribute to the total emission of a pollutant. The largest collection of emission factors available for PAH have been published in the USA [US EPA 1998]. It is unclear as to whether these data can be utilised in a European context as they are often based on a limited number of samples. The factors often exhibit a wide range of values - consequently their use can lead to widely differing estimates of emissions from the same type of process. On the other hand it is often difficult to compare emission measurements. The emission measurements which are available are few in number and do not always adequately describe the measurement method, the process, or the abatement system to be able to extrapolate the data for other installations. Standardized procedures are not available for reporting emission data.

**Emission Sources**

15. This section outlines what is currently known of sources of PAH emission, trend information, and associated uncertainty. Individual sources of PAH are characterised by combustion processes and by particular industrial processes which utilise PAH-containing compounds, e.g. processing of coal, crude oil, creosote, coal-tar and bitumen. The sources considered are industrial, domestic, mobile, agricultural and natural.

**Industrial Sources**

16. In general industrial sources are comparatively well understood and are increasingly being regulated at European level (e.g. by Council Directive 96/61/EC - IPPC). Currently these include:
  - Primary aluminium production (in particular plants using Soderberg technology)
  - Coke production (e.g. as part of the iron and steel production)
  - Creosote and wood preservation
  - Waste incineration
  - Cement manufacture
  - Petrochemical and related industries
  - Bitumen and asphalt industries
  - Rubber tyre manufacturing
  - Commercial heat and power

More comprehensive information on sources and abatement is given in Annex 3 'Industrial Sources of PAH Emission'. Overall PAH emissions are believed

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to be decreasing; improved energy management is leading to improved combustion which, in turn, leads to lower emissions. Most of the particulate based PAH is to be found associated with particles less than 2.5 µm. There are unlikely to be PAH 'finger prints' which are source specific but some industrial sources are associated with other chemical indicators (metals, other pollutant etc). Some industrial sources will have a local impact.

#### **Domestic Sources**

17. The domestic sources of PAH which can influence ambient air quality are, in the main, heating and cooking. Domestic heating based on the combustion of fuels varies within Europe from the use of natural gas or liquified petroleum gas (LPG) through paraffin and heating oils to wood, coal, peat, and brown coal. Domestic sources of PAH are geographically widespread, and the PAH emissions are largely unregulated. Some Member States have regulations controlling the general emissions from some domestic heating systems (e.g. soot, carbon monoxide).
18. Modern gas and oil burners, used for circulatory heating systems and hot water systems, have relatively low PAH emissions. Similarly, solid fuel systems (wood, coal, peat), which are automatically controlled and fed, are thermally more efficient (and have lower PAH emissions) than those which are hand fed. Abatement measures can be adopted, such as catalytic devices which will lead to a reduction of PAH emissions.
19. PAH emissions due to the domestic combustion of solid fuels make a significant contribution to the total PAH emission. In Sweden wood burning has been estimated to contribute 430 kg BaP in 1994 whereas gasoline and diesel vehicles together were estimated to contribute maximum of 320 kg BaP [Boström et al., 1999]. There is a large geographic variation in the domestic emissions within Europe due to the climatic differences and to the domestic heating systems in use. In urban areas where coal, wood and peat burning is predominant, a high proportion of the PAH ambient air concentration is associated with these sources.
20. The burning of wood, coal and peat in open fireplaces is often for the decorative effect in addition to the heating provided. These systems are often hand fed, of a low thermal efficiency and potentially have high PAH emissions. BaP from these sources is associated with a range of particle size including the <2.5µm fraction.

#### **Mobile Sources**

21. Mobile sources are modes of transport reliant on a combustion engine. This includes aircraft, shipping, railways, automobiles and other motor vehicles including off-road vehicles and machinery.

Motor Vehicles (automobiles, lorries, motorcycles): Motor vehicle internal combustion engines are generally fuelled by gasoline (petrol) or diesel fuels. There is a relatively small proportion of vehicles which run on LPG or LNG. PAH emissions are distributed between the vapour and the particle phase.

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One of the major influences on the production of PAH from gasoline automobiles is the air-to-fuel ratio; it has been found that the amount of PAH in engine exhaust decreases with a leaner mixture. The use of catalytic converters has also been shown to have a significant effect on the reduction of the PAH concentration in the exhaust gases. All internal combustion engines have varying PAH emission characteristics dependent on engine temperature (particularly cold-start), load, fuel quality and speed. Urban areas with congested traffic conditions and with vehicles often only travelling short journeys promote the emission of PAH. Engine deterioration and high mileage also increase emissions. Catalytic converters for gasoline engines have a marked effect on the reduction of PAH. Studies have shown that for all PAH compounds studied the reduction achieved due to catalytic converters was between 80 and 90% (for BaP 94%). Catalytic converters for diesel engines also reduce total PAH emissions, however the reductions are not as high as for gasoline engines. [CONCAWE 1998]. An additional source for PAH in the exhaust of gasoline fuelled vehicles is PAH in the fuel [Westerholm et al., 1988]; consequently a reduction of exhaust gas PAH emissions can be achieved by reducing fuel PAH content.

22. Diesel fuelled vehicles have higher particulate emissions than gasoline fuelled vehicles. The particles consist of combustion-generated soot, a solvent extractable hydrocarbon fraction, and a mineral fraction. PAH are found within the solvent extractable fraction. The use of turbo-charging and intercooling for heavy-duty diesel engines reduces diesel particulate emissions, and catalytic converters are very efficient at reducing particle-bound organic emissions. Other control technologies are currently being developed and improved (trap oxidisers and filters for example) for heavy-duty diesel engines. Such devices will be necessary to meet emission limit values set within EU regulations ('EURO 4'). As for gasoline vehicles, an additional source of PAH in the exhaust of diesel fuelled vehicles is the PAH content in the fuel [Westerholm and Li, 1994], i.e. by reducing fuel PAH content a reduction of exhaust PAH was achieved. In Sweden fiscal measures have been used to encourage the use of low PAH diesel fuels since 1992 [SFS 1991].
23. The implementation of trap oxidisers and filters in automobiles is complex due to considerations of weight, fuel consumption, maintenance, operating cycles, etc. Fuel composition also influences the PAH emissions from a modern diesel motor. It has been reported that the aromatic content [van Borstel et al., 1999, World Fuel Charter 2000, CONCAWE 1998] has an influence on the PAH levels in the exhaust gases. Fuels with 7-11% m/m di-aromatic and 1-3% tri-aromatic content gave significantly higher PAH emissions than fuels containing virtually zero di-/tri-content. Within the EU, the PAH content of diesel fuels is regulated to 11 % (m/m) within the Directive 98/70/EC. In this context, PAH are defined as the total aromatic hydrocarbon content less the mono-aromatic hydrocarbon content. The maximum content of aromatic compounds for fuels to be used for vehicles equipped with positive ignition fuels is currently 42 % and will be reduced to 35 % in 2005. A reduction in

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the sulphur content has been reported to decrease PAH emissions [Tanaka S et al., 1988] by enabling the catalytic converter to function more efficiently.

24. Two-stroke engines are relevant in the motor scooter and motor cycle sector of transportation. Two-stroke fuel is a mixture of gasoline and oil. The engines are generally small and not equipped with additional emission control systems. Recent Italian research has estimated that unabated PAH emissions whilst performing the ECE R40 simulation are 1.6 mg/km for the sum of 29 PAHs with 2 to 6 rings and 20.8 µg/kg for six carcinogenic PAHs (BaP, B(b+j+k)FA, BaA, DBahA). The same test cycle carried out with a catalytic converter fitted led to tailpipe emissions of 0.89 mg/km (29 PAH) and 14.2 µg/kg of the carcinogenic PAH [Gambino et al., 2000]. The use of motor scooters may present a significant PAH emissions source in some southern European cities where they are used in large numbers. A directive setting stricter emissions standards for motorcycles is in preparation.
25. Due to the long operational lifetime of existing vehicles and the difficulties in upgrading them with new technology, any new technological abatement measures will have a considerable lead-in time before their effects are appreciable unless a retrofit programme is introduced. Nevertheless, indications are that in the near future (10 - 20 years) PAH emissions from road vehicles will have reduced as a result of the introduction of EURO 4 provisions [UBA 1998, Fraunhofer ITA FoBiG ifeu 1999].
26. Off-road vehicles and equipment: There have been few studies carried out on PAH emissions from off-road vehicles. These include a wide range of vehicle types, from garden/agricultural engines to military vehicles.
27. Railways: The main source of PAH emissions in rail transportation is the use of diesel and diesel-electric locomotives. Coal-fired steam locomotives no longer represent a large proportion of the rolling stock in operation in Europe. As some locomotives are old, and produce large amounts of black smoke, they may be a significant source of PAH but no measurement data are available.
28. Aircraft: There have been very few studies carried out on PAH emissions of aircraft, and of those carried out, most have been for military aircraft. However, the results show that PAH emissions are dependent on fuel composition (volatility). PAH emissions are dependent on the power setting of the engine and tend to decrease as the power setting increases. Average emission factors for an aircraft gas turbine engine have been given as 1.24 mg/LTO (Landing–Take Off Cycle) for BaP. As air travel increases within Europe the proportion of total PAH emissions which are attributable to air transport could increase, though it is unlikely that it will become a major contributor to total PAH emissions [EPA 1998].
29. Shipping: Particulate emissions from shipping are not currently regulated. There are a limited number of publications focusing on PAH emissions from shipping. Westerholm et al., [1991] measured PAH emissions from an on-board marine diesel engine (6600 kW, maximum continuous rating) burning marine diesel fuel with a sulphur content of 1.9 % (w/w). Emissions of PAH



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of 500 µg/kg fuel (sum of 25 PAH, fluorene to coronene), BaP <2.2 µg/kg fuel and sulphur PAH 93 µg/kg fuel were reported, respectively. Within the Lloyds Marine Exhaust Emissions Research programme, [Lloyds, 1995] individual PAH from several different ships using marine distillates and heavy bunkers were measured. Lloyds reported emissions of PAH (phenanthrene to six-ringed PAH) in the range 21 to 244 µg/ m<sup>3</sup>, and for BaP in the range of 0.02 to 0.65 µg/ m<sup>3</sup>, respectively. Furthermore, the genotoxic DBaP was reported to occur in the exhaust at concentrations ranging from <0.01 to as large 3.20 µg/m<sup>3</sup>; this determination, however, may be subject to analytical limitations due to matrix interference, and needs to be further investigated and confirmed. Cooper et al., [1996] reported emissions of PAH of 73 µg/Nm<sup>3</sup> (or 410 µg/kWh) (sum of 23 PAH, naphthalene to benzo(ghi)perylene), and BaP emissions of 0.2 µg/Nm<sup>3</sup> (or 0.9 µg/kWh), respectively. The engine investigated had a 6400 kW maximum continuous rating running on fuel oil containing 0.48 % sulphur.

Additional PAH emissions from shipping result from the generation of electrical power by smaller diesel engines that are not considered in the publications discussed above. It is assumed that PAH emissions from larger ships/ferries may contribute significantly to PAH-in-air concentrations depending on the local harbour/city geographical conditions and the route; however, further investigations are needed.

30. In addition to the combustion emissions related to transportation there are additional emissions of PAH due to abrasion of rubber tyres, asphalt road surfaces and brake linings. The magnitude of these emissions is hard to quantify. High PAH emissions from these sources have been estimated in a Swedish paper [Ahlbom J and Duus U 1994], but have been disputed [Baumann W and Ismeier M 1997]. Larnesjo [1999] has indicated that the dominant PAH in the tyre tread are fluoranthene, pyrene, benzo(ghi)perylene and coronene. The PAH content of tyres is dependent on the manufacturer and the year of manufacture.

#### Agricultural Sources

31. Agricultural sources include the following activities:

- Stubble burning
- Open burning of moorland heather for regeneration purposes
- Open burning of brushwood, straw, etc.

All of these activities involve the burning of organic materials under sub-optimum combustion conditions. Thus it can be expected that a significant amount of PAH are produced. In some countries there are regulations in place regulating these activities but this is not the case for the whole of Europe. Due to uncertainties in emission factors and the occurrence of these activities, the emissions of PAH from agricultural sources are difficult to quantify. Nevertheless, they may contribute significantly to PAH levels at certain locations.

#### Natural Sources

32. Natural sources of PAH include the accidental burning of forests, woodland, moorland etc. due to lightning strikes etc. Meteorological conditions (such as

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wind, temperature, humidity) and fuel type (moisture content, green vs. seasoned wood, etc.) may play an important role in the degree of PAH production.

33. Another natural source of PAH are volcanic eruptions. No data are available regarding these emissions and their contribution to the overall PAH profile.

**Post Emission Effects and the choice of PAH Markers**

34. The possibility of using single PAH compounds as source-specific markers has been investigated in several studies. However, it is not clear if such markers are applicable over the wide range of geographical conditions and technologies used within the EU Member States. Furthermore improvements in product quality (e.g. reduced S-content in liquid fuels), combustion technology and the introduction of innovative abatement techniques (catalytic converters for example) may already have changed the PAH mix since some of these studies were conducted.
35. The mass and chemical composition of PAH in air changes in a number of ways following emission. Physical (such as wet and dry deposition) and chemical (degradation and derivatisation) removal processes are all important. Monitoring and modelling can be used to estimate the relative importance of these sinks and of secondary sources such as re-suspension/re-volatilization. A summary of these processes, based on a recently published review of available information on the lifetimes of PAH with respect to physical and chemical breakdown in both the gaseous and particle phases [Coleman et al., 1999], is given in Annex 4: Post Emission Transformation. It is important to note that BaP, like other PAHs containing 5 or more rings, is found predominantly in the particulate phase.

**The impact of long range transmission on European environmental levels of PAH**

36. Modelling work at a European scale, carried out under the UN/ECE's co-operative programme for monitoring of the long-range transmission of air pollutants in Europe [EMEP] has demonstrated that PAH can be transported over long distances [EMEP Report 4/2000]. Within this programme the long-range transport of a number of heavy metals and persistent organic pollutants (POPs) (such as BaP as a marker for PAH) were modelled. The model results were validated using measured concentrations of POPs in air, soil and water bodies at various European locations. Modelling within the MSC-E of EMEP predicts that 30% of the total BaP emission is transported outside the EMEP geographical zone; the rest is partitioned through the environmental media where it is degraded. The rate of flux in each media depends upon the rate of accumulation relative to the degradation rate. Air degradation rates are high, resulting in a relatively low content being maintained. Sea, soil and vegetation degradation rates are lower leading to a higher content and slower rate of clearance from these media compared to air.

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#### Markers for PAH

37. Many research workers and several member states use BaP as a marker for carcinogenic PAH for air quality management purposes. BaP has been shown to make a consistent contribution to the total carcinogenic activity of predominantly particle-bound PAH based on measured annual average concentrations at a wide range of European sites, including the UK [EPAQS 1998], Italy [Menichini E. (ed.) (1992a)], Netherlands [RIVM] and Sweden. A factor analysis of a large number of PAH measurements (usually in the form of annual mean) gathered over the period 1990 - 1998 from a number of German Federal States also demonstrated a high correlation between BaP and PAH under a variety of circumstances [Fertmann and Tesseraux et al., 1999]. On the basis of precedent and current knowledge of physical/chemical removal processes, BaP appears to be a suitable marker compound for total PAH for most atmospheric conditions appropriate to Europe.

#### Ambient Air Levels in Europe

38. In general, the data on PAH levels in ambient air are sparse compared to that of classical pollutants like SO<sub>2</sub>. This can be explained by the fact that (a) a rather complex and expensive sampling and analytical procedure is needed to measure the ambient air concentration of PAH and (b) there are only few countries with a legal basis requiring the measurement of PAH. Since PAH can be found in ambient air in both the gaseous and the particulate phase, it is important when reviewing reported data to know how the sampling was done and whether gaseous and/or particle phase fractions were determined.
39. PAH are ubiquitous; concentrations are lower at remote background sites than at rural sites. Higher concentrations are found in urban areas, with peak concentrations measured at urban sites with both traffic and nearby industrial installations. In the 1990's, typical annual mean levels of BaP in rural background areas varied between 0,1 and 1 ng/m<sup>3</sup>; for urban areas levels were between 0,5 and 3 ng/m<sup>3</sup> (with traffic sites at the upper boundary of this range); levels up to 30 ng/m<sup>3</sup> have been measured within the immediate vicinity of a cokery. Few measurement data exist for rural communities burning coal and wood domestically; however, these measurements suggest levels similar to those found in cities. Substantial within-town differences (commonly, ca. 2- or 3-fold) in PAH levels have been observed [Menichini E 1992b] between regions with different prevailing sources (traffic vs. domestic coal burning, Berlin); different heating fuels (coal vs. oil, Essen, Germany); different position relative to an industrial zone (downwind vs. upwind, Linz). A difference of ca. 2-fold was also found between a trafficked city centre site and an urban background site in Birmingham [Lee et al., 1999]. An 8-fold difference in mean BaP concentration was found between an industrial site (located on a roof in an area ca. 300 m from a coke-oven) and a city centre site in Genoa [Valerio F et al., 1996], and a 14-fold difference between a traffic-oriented site and a city park in Florence [Bini G et al., 1998].
40. The data reported in the literature give concentration values for a selection of compounds depending on the type of measurement method used. In addition to BaP the 'total PAH' may be given separately but these values can not always

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be compared, since different PAH species may be included in the sum. See **Table 5: Summary of recent (not older than 1990) typical European PAH- and BaP concentrations in ng/m<sup>3</sup> as annual mean value.**

### Distribution within different particle sizes

41. The particulate phase consists of aerosols of different sizes. The distribution of PAH in atmospheric particles has been investigated in several studies [Cecinato 1999, Bomboi et al., 1999, Kaupp et al., 1999]. Generally, between 80% and almost 100 % of PAH with 5 rings or more (which are predominately particle-bound in the atmosphere) can be found associated with particles with an aerodynamic diameter of less than 2.5 µm.

### Intra-annual variations

42. In general PAH concentrations tend to be about one order of magnitude higher in winter than in summer [Menichini et al., 1999]. This concentration pattern can be found at nearly all sites. A typical example of inter-seasonal variations is shown for Vienna, Austria in **Figure 2: Inter-seasonal variation of PAH in Vienna, Austria** [UBA Wien 2001]. The main reason for these variations are:
- meteorological factors (like increased atmospheric stability in winter)
  - higher emissions in winter (e.g. from wood and coal burning in domestic heating systems)
  - reduced atmospheric reactivity of PAH compounds in winter (e.g., reduced degradation by photo-oxidation and reaction with OH-radicals).

### Trends in emissions and ambient air levels

43. There are several sites where long time series measurements of PAH have been performed; generally, a decrease in concentration since 1990 can be seen. The UK seems to be quite representative of the majority of the European countries and as an example, the trend of the sum of PAH and BaP from two sites in the UK is shown in **Figure 3: Trend of sum of selected PAH and BaP in the UK**. Similarly **Table 6: Summary of benzo[a]pyrene emissions in the UK 1990-2010** illustrates, again using UK data, the generally downward trend currently being observed within the European Union as a whole. The estimated BaP emissions for 1990 and 1995, and the forecast emissions for 2010, represent a 'business as usual' scenario<sup>1</sup>. Between 1990 and 1995, the estimated total emissions of BaP had decreased by over 50 %. The main reduction was in the emission from natural fires / open agricultural burning which decreased by 90% from 1990 levels because of the ban on stubble burning in England and Wales. The UK BaP emission is forecast to further decrease by 2010 to 16.4 tonnes. The emission from vehicles is forecast to decrease under the 'business as usual' scenario, due mainly to stricter emission regulations which require e.g., the use of catalytic converters, and improved maintenance and vehicle condition. The emissions from anode baking (within the process of primary aluminium production) are predicted to

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<sup>1</sup> In respect of emissions: Business as usual should be interpreted as:

1. Human activity (industry, transport, domestic consumption, etc.) continue forecasted growth,
2. There is no new legislation introduced that would affect emissions,
3. Existing legislation is fully implemented.

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decrease sharply as a result of improved abatement equipment which were brought on-stream in 1998. The emission from domestic coal combustion is forecast to decrease between 1990 and 2010 due to a decrease in the quantity of coal burned. However, these sources are still likely to be responsible for a significant proportion of the forecast 2010 emission, which is spread across several sectors: vehicles (24 %), industrial combustion (24 %), domestic combustion (18 %), and natural fires (18 %).

44. While there are data on ambient air concentration from a few countries, there appears to be no exposure data for the general population.

### 3. Measurement: Methodology, Associated Uncertainty and Future Requirements

#### Chapter Summary

##### **Data acquisition and monitoring network design**

- Most PAH monitoring in the EU is carried out for public health reasons and concentrates on a limited number of individual PAH species.
- National monitoring networks operate in a limited number of member states. Most of monitoring campaigns are directed to particle-bound PAH.
- The number, type of location and mode of operation of sampling stations should depend on the location category (urban, suburban, industrial or rural).
- The cost of sampling and analysis is a function of the number of monitoring stations, the sampling method used, the frequency and analytical methodology adopted. Opportunities exist to optimise measurement cost effectiveness.

##### **Measurement Methods**

- Different procedures are used across the EU to collect and analyse ambient air samples for PAH. There is no formal standardisation of the fraction of the PAH 'mix' collected or the compounds analysed but there are similarities of approach. In general all collect the particulate phase and analysis methods tend to be based on a limited number of tried and tested techniques.
- While some national methods and an international standard exist there is no EN standard.

##### **Modelling**

- Dispersion models are well established but their use for PAH is limited due to the poor quality of emissions data. Similarly, there is little experience of model validation.

##### **Quality Assurance and Control required for PAH determination in air**

- The principles of quality management are well understood but there is currently no suitable standardised system of quality control in use throughout Europe against which to judge the comparability of reported PAH measurements.

##### **Uncertainty of the Measurement method**

- An analysis of the sources of uncertainty in the determination of atmospheric PAH suggests that using currently available best techniques measurements can be expected to have an uncertainty of about +/- 50% .

##### **Future Monitoring Requirements**

- BaP is a suitable 'marker' for particle-bound PAH and consequently an EN method should be developed for its measurement.
- The PAH 'mix' can be expected to vary seasonally and geographically; it may also vary as a consequence of changes to emission sources resulting from regulatory and economic developments. Hence it would be desirable to periodically monitor a number of other PAH, including: BaA, BbFA, BjFA, BkFA, IP, DBahA and FA, at a limited number of sites, in both the particulate and vapour phases.
- Both the measurement and monitoring used to support any possible air quality management standard should be fit for purpose, cost effective and take account of current best practise.

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45. This section of the position paper examines the role of PAH measurement in the definition and implementation of air quality management. It describes currently used sampling and measurement methods for PAH in the ambient air, the critical requirements of methods, the conditions under which measurements are made and the extent to which they are subject to quality management processes. The relationship between observed air quality and known sources of emission can be predicted or compared using models, this section also examines what can be learned from this process. Finally, an attempt is made to assess the weight/confidence which can be placed on existing measurement data, what should be expected of measurement methods for assessing compliance with a possible air quality standard for PAH and other - more general - monitoring requirements.
46. The proceedings of the workshop “State of the art of the PAH’ analysis in ambient air” are a useful source of further information [Freising-Weihenstephan (ed) 1999]. In practice, the measurement procedures, and especially sampling, vary depending on the target PAH(s). Presently, in most investigations performed in EU member states for monitoring purposes, only particle-bound PAH are collected and BaP is usually among the list of analysed compounds.
47. There is limited EU experience of ambient PAH measurement monitoring. Networks for PAH are operative in Germany [Beck and Hailwood 1999], Italy [Menichini 1999], Netherlands [Buijsman 1999] and United Kingdom [Coleman et al., 1999] **Table 7: Current network design at national level (end 1999)**; the national networks are different in design and were established to meet the specific national requirements.

## Data acquisition and monitoring network design

### Network Design

48. Within the following paragraphs, the design of networks to monitor compliance with a potential BaP limit value is outlined. The macro-scale siting criteria described in Annex VI of Council Directive 1999/30/EC for the protection of human health are also applicable to PAH. Measurements should be carried out:
  - to provide data on areas within zones where the highest concentrations occur to which the population is likely to be directly or indirectly exposed for a period which is significant in relation to the averaging period of the limit value;
  - to provide data on levels in other areas within zones which are representative of the exposure of the general population.
  - to cover the areas with the highest concentrations, locations in the vicinity of emission sources have to be installed. These include industrial sites, traffic sites and sites in environments where solid fuels are used for heating.

### Such sites include

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- *Urban hot spots.* Such stations should be located in areas with high traffic density, unfavourable street conditions (e.g. canyon streets), and/or in areas with high usage of coal or wood for domestic heating. They should measure PAH concentrations where they are expected to be the highest. The site should be representative of the area directly surrounding the *measurement* station; while samplers may be positioned adjacent to busy streets very small micro-environments and the direct influence of minor sources, if any, should be avoided. As a guideline, the sampling point should be representative of an area of at least 200 m<sup>2</sup>.
- *urban background.* They should be representative of larger parts of towns (of several km<sup>2</sup>) and should not be directly impacted by traffic, chimney stacks of domestic heating (coal, wood or oil) or any other PAH source. Appropriate sites may be: residential areas, parks, pedestrian-reserved areas, recreational areas or squares, yards of public buildings (such as city halls, schools or hospitals).
- *Industrial.* Only few installations will cause ambient air concentrations in excess of the 'normal' ambient air concentrations. Such installations include certain plants, e.g. for the production of aluminium and coke, wood preservation, or the combustion of coal. The relevance of the impact of any emitter should be investigated before setting up the sampling station. Suitable preliminary assessment methods which may be used (possibly in combination) are emission inventories, PAH emissions measurements, indicative measurements, measurements using bio-indicators and modelling. Monitoring at an industrial site should be regarded as relevant in particular if the levels are expected to higher than the upper assessment threshold and if residential areas are affected. In cases where several residential areas are situated in different directions with respect to the emitter, or at different distances from the plant, modelling and/or objective estimation methods may be used to identify the area with the highest levels and the best location for the sampling station. In any event, the air quality at the monitoring site should be at least representative of an area of 250 m x 250 m. Consequently, sampling points should keep a minimum of 100 - 200 m form the fence-line of the installation.
- *Rural sites*
  - *rural hot spots.* Such stations should be located in areas where solid fuels are commonly used for heating. They should measure PAH concentrations where they are expected to be the highest. Sites should be representative of the area directly surrounding the *measurement* station, preferably in a residential area; as a guideline, the sampling point should be representative of an area of at least 200 m<sup>2</sup>.
  - *rural background sites.* They should be representative of larger areas (several tens of km<sup>2</sup>) and should not be directly impacted by traffic, chimney stacks of domestic heating (coal, wood or oil) or any other PAH source.

Micro-scale criteria:



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The criteria established for measurements of particles and benzene, Council Directive 1999/30/EC and Council Directive 2000/69/EC are applicable. They stipulate:

- A minimum distance of 2 m from buildings or any obstacle to airflow is suitable [US EPA 1997; ISO Ambient Air 1999] and meets the requirements for sampling of particles according to Council Directive 1999/30/EC.
  - The height of the sampling inlet should be between 1.5 m and 4 m, reported in Council Directives 1999/30/EC and 2000/69/EC. A height of 1.5 m is preferred for assessment of potential human exposure near heavy traffic situations but for practical reasons (e.g., prevention of vandalism), a higher height may be used: ca. 2.5m. A height of ca. 4m may be necessary when a mobile laboratory is used for sampling. In the case of urban background sites, a higher position still may be considered, but the site should not be directly impacted by the exhausts of domestic heating (e.g. coal, wood or oil).
  - The sampling inlet should be away from where vehicles stop or wait with engines running (such as traffic lights or parking): a minimum acceptable distance could be 10m.
49. The Air Quality Framework Directive 96/62/EC [Council directive on ambient air quality assessment and management, OJ L 296, 21.11.96, p.55] requires member states to set up networks for various pollutants: the use of the same networks, as well as the collocation of sampling points or the use of the same samplers, would make it possible to reduce monitoring costs, especially for background measurements. Collocated samplers should not interfere with one another.

#### Number of sampling sites

50. The determination of individual PAHs is manual, relatively complex, time-consuming and expensive; furthermore analytical facilities and capability is not equally developed throughout Europe. Consequently it is unlikely, in the short term, that we will be able to collect data representative of the outdoor pollution to which the whole population is exposed. A first priority is to control PAH pollution (and check legal compliance) principally at sites where it is expected to be the highest; implicitly, this should reasonably protect all of the population. Relatively few installations would be required in urban background sites to assess the exposure of the general population.
51. The overall number of monitoring stations will depend *inter alia* on the spatial variability of the pollutant. Few data are available about the horizontal gradient of PAH concentrations with increasing distance from an urban street with heavy traffic; it is expected, however, to be marked. The urban background concentration, as opposed to roadside levels is expected to be quite uniform within a town and could be assessed by one or very few measurements sites.

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52. In zones with a single monitoring station, this station should be located where the highest concentrations occur to which the population is likely to be directly or indirectly exposed for a period which is significant in relation to the averaging period of the limit value. Such a location might be within an area where solid fuels are predominantly used for domestic heating and/or traffic related sites. The identification of such a location shall be done within the preliminary assessment and the rationale for selection shall be documented. In zones with two or more monitoring sites, at least one site should be located where the highest concentrations occur to which the population is likely to be directly or indirectly exposed for a period which is significant in relation to the averaging period of the limit value. Such a location might be within an area where solid fuels are predominantly used for domestic heating and/or traffic related sites. One additional site should be located in an urban background area. The identification of the locations of the sites should be done within the preliminary assessment. The site selection procedure shall be documented
- *BaP Point Sources*: For the assessment of pollution in the vicinity of point sources, the number of sampling sites for fixed measurement should be calculated taking into account emission densities, the likely distribution patterns of ambient air pollution and the potential exposure of the population.
  - Measurements should be done for those plants where the preliminary assessment has indicated that the limit value is exceeded
  - Measurements should be mandatory in the vicinity of those plants which are likely (even though operating to Best Available Technology according to IPPC) to fail to meet the proposed the limit value in 2010.
- The sites for these measurements should
- take account of residential areas in the vicinity of the plants
  - be located downwind of the prevailing wind direction
  - be representative of an area of at least 250 m x 250 m.
53. Sites collecting broad spectrum PAH information, i.e. BaP, BaA, BbFA, BjFA, BkFA, IP, DBahA and FA using ISO 12884, should be located at representative locations. The minimum number of sites is
- |   |                                                 |
|---|-------------------------------------------------|
| 1 | area < 50.000 km <sup>2</sup>                   |
| 2 | area between 50.000 and 100.000 km <sup>2</sup> |
| 3 | area > 100.000 km <sup>2</sup>                  |

Sampling duration and frequency

54. Long averaging times are required to assess long-term exposure to PAH levels. For this reason peak values or real time values need not be assessed and a reference measurement period of a year should be adopted.
55. Twenty four hour sampling is advisable, for analytical reasons, to avoid sample degradation, interference, and losses. With a long reference period, however, it is not necessary to collect samples continuously (i.e. every day) nor to analyse each sample individually. The number of collected samples being equal, discontinuous measurement could allow for more sampling sites,

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thus giving a better resolution in space at the expense of an additional uncertainty in time resolution.

56. Directive 96/62/EC makes provision for assessment thresholds as well as limit values. The existing Daughter Directives have set upper assessment thresholds (UAT) and lower assessment thresholds (LAT) which define three air quality assessment regimes. Above the UAT measurement is mandatory in all zones. Between the UAT and the LAT measurement can be combined with modelling. Below the LAT model calculations or objective estimations are sufficient. The UAT and LAT values are based on the inter-annual variability of time series data obtained from representative measurement sites as shown in Annex 5. An (upper) assessment threshold of 50% of the limit value would ensure a relatively low probability (i.e. less than 5%) of the limit value being exceeded as a result of inter annual variation. A (lower) assessment threshold, at a level where measurement adds relatively little value and objective estimations and modelling are the most cost effective course of action, could be set at 25% of a limit value – provided the limit value is set in the range 0.5 – 1.0 ng/m<sup>3</sup>.
57. An acceptable sampling strategy, for compliance measurement i.e. above the UAT, may be based on discontinuous but systematic sampling depending on data capture requirements – see Annex 5 - a practical way of doing this is to take a twenty four hour sample every three days. With care, up to five individual samples can be combined and analysed as a composite sample to minimise the time and cost of the analysis. For indicative measurements between the UAT and LAT the sampling frequency may be reduced to a single 24 hour sample every six days. Below the LAT objective estimation methods and modelling are acceptable indicators of air quality.
58. Higher frequency measurements of a wide range of PAH compounds are needed to understand the processes contributing to current PAH levels, follow trends in changing composition of ambient PAH and to detect any unrecognised significant sources. We recommend monitoring, in addition to BaP, at least the following: BaA, BbFA, BkFA, IP, DbahA and FA. This selection is based on both the evidence of their carcinogenicity and their occurrence in the atmosphere. These ‘monitoring’ stations need be relatively small in number, are not required to achieve the high levels of data capture nor the low level of measurement uncertainty that is required for compliance measurements.

## Measurement Methods

59. The principal stages of PAH determination involve sampling, extraction, clean-up and analysis. A number of different methods are currently used, and these are summarised in **Table 8: PAH sampling and analysis methods used in several European countries**. Sampling may be performed using either high or low-volume samplers, which may collect TSP or PM<sub>10</sub> fraction. Whilst the particulate phase is always collected, the vapour phase is only collected if a sorbent material, such as polyurathane foam or amberlite resin, is also located in the sampling train. Extraction and clean-up methods vary widely, with subsequent analysis performed by GC (with a flame ionization

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detector (FID) or mass spectrometric (MS) detector) or high pressure liquid chromatography (HPLC) (with a fluorescence and/or UV-DAD or MS detector). Quantification may be carried out for a range of PAH species, although BaP is always included.

60. For a variety of measurement reasons, particulate based PAH are preferred as markers of PAH concentration. The somewhat limited European experience has demonstrated that in general, atmospheric BaP is almost completely adsorbed on particulate matter. If, under warmer summer conditions, part of BaP is present in the vapour phase, this is likely to contribute less than approximately 10% when averaged on a yearly basis. **Table 9: BaP collected as vapour phase in European investigations: percent relative to total (vapour + particles) BaP** shows the available European data on the BaP collected as vapour phase (i.e. trapped by polyurethane foam or XAD-2 resin, placed behind a filter for particulate phase); this includes BaP already present in atmosphere as vapour phase and BaP desorbed from filter during sampling. Substantially similar results were reported in USA: BaP was not detected in vapour phase in most investigations, even under summer conditions with daily mean temperatures up to 29 °C [Coutant et al., 1988] or 31 °C [Hart & Pankow 1994].
61. While in practice BaP is found predominantly in the particulate phase the phase distribution is related to ambient temperature [Yamasaki et al., 1982] and so exceptions can be found. Differences between the relative distributions found in Oslo at street level and on a roof along the same street were not completely explained by the authors [Thrane 1981]. Similarly, the reason for the reported enrichment of the vapour phase fraction during winter in Birmingham was unclear [Smith 1996].

### European National and International standard methods

62. Several standard methods exist and these are summarised in **Figure 4: European and National Standard Methods**. In view of the lack of comparable PAH data across the EU there is a need to develop a CEN measurement standard and to validate it under proposed conditions of use. The standard method should be robust, cost effective and suitable for routine indicative or compliance measurement purposes. BaP is considered a suitable marker for PAH for the purposes of air quality management. BaP is mostly particle based; the PM<sub>10</sub> fraction is conventionally collected for a number of other pollutants and is suitable for BaP (the PM<sub>10</sub> reference standard EN12341 would be applicable). The proposed standard method should operate within the range 0.02 – 20 ng/m<sup>3</sup> BaP (the daily range typically encountered across the European Union). The standard method should cover the whole measurement process and give guidance on: sampling, sample management (both during sampling, and subsequent transport and storage), analysis and reporting (including the reporting of concentrations below the detection limit). The method should include quality management criteria and have known performance characteristics, including measurement uncertainty. Samples should be collected over a 24 hour period but may be bulked for analysis provided that a minimum of one result is obtained every 15 days; the method should ensure that the samples are stable for that period.

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**Objective estimation methods**

63. Other techniques can provide an indicative measurement of PAH concentration levels, albeit with a higher uncertainty than the reference method. These include the following:
- Historically black smoke and benzene soluble matter have both been used as indicative measures of PAH content [Barbour 1994]. Such estimations should be calibrated for specific sites.
  - Photoelectric ionisation by ultraviolet light of aerosols have been used for indicative determinations of PAH. The electric signal induced is correlated to the amount of PAH (four-ring PAH and greater) adsorbed onto the surface of airborne particles. As alkyl PAH and PAH derivatives contribute to the signal also, it is not specific. Comparison tests between this method and manual techniques have been carried out [Tatry 1998; Agnesod et al., 1996]. Such comparisons need to be repeated for specific sites.
  - The possibility of the use of other air quality parameters as indicators of PAH levels in urban sites has been studied. A three year study was performed at an Italian roadside site where PAH pollution was traffic dominated [Menichini et al., 1999]. NO and NO<sub>x</sub> correlated ( $r=0.92$ ) with particle-bound PAH; the corresponding value for CO was  $r=0.86$ . A study carried out in a heavily trafficked centre site in Birmingham (UK) also found a correlation with CO and NO<sub>x</sub> [Lee et al., 1999]. It should be born in mind that different correlations may be expected for different types of site depending on the dominant sources.
64. Although these methods can not be used for compliance or indicative measurements, they may be used for screening, zoning and establishing of concentration trends after adequate validation. However, it must be stressed that relative PAH mixture profiles in air will probably change in the future depending on combustion technology developments, exhaust after-treatment technologies and improved fuels, all of which may affect the correlation coefficients.

**Modelling – General Considerations**

65. Dispersion models are used to predict how pollutants are transported in the atmosphere from the point of the pollutant release (the emission source) to a distant receptor location, where the pollutant concentration (usually expressed in terms of mass per unit volume) is calculated. More sophisticated models take account of pollutant transformations and reactions in the atmosphere during the period of transport (e.g. in the case of ozone).
66. Dispersion modelling offers a number of significant benefits to the process of air quality management:
- It is possible to predict pollutant concentrations at a very large number of ground level receptors. These predictions can be used to produce pollutant concentration isopleths, which effectively map concentration areas. It is

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therefore possible to predict pollutant concentrations over a much wider spatial area than it would ever be possible to achieve by monitoring alone.

- Dispersion models can be used to predict pollutant concentrations in future years e.g. scenario testing, taking into account different pollutant reduction measures. The impact of different control measures can be studied.

67. Dispersion models have been effectively used in many Member States to investigate pollutant concentrations at both a 'local' level (effectively within about 10-50 km of the emissions sources) and at a 'regional' level (effectively across hundreds or thousands of kilometres). Such model applications are frequently used to supplement data from monitoring networks, and to support policy decisions on likely exceedances of air quality standards and suitable control strategies.

#### **Input data to dispersion models and model accuracy**

68. All dispersion models require input data which describe how much pollutant is being released. Depending upon the type of model used, a variety of other inputs may also be required, such as the meteorological conditions, the release conditions (e.g. the height of chimney stacks) or local environmental conditions (e.g. topographical features such as hills and valleys).
69. Any dispersion model will have an associated degree of error in the predictions due to simplifications in the model algorithms which are used to describe complex (and inherently random) atmospheric dispersion processes. Predictions of annual average concentrations are at best  $\pm 50\%$  of the true value; this may be improved where extensive validation trials are carried out.
70. The accuracy of the emissions data which are input to the model also have a significant effect upon the accuracy of the predicted concentrations. Where the model assumes that the emissions are not chemically transformed in the atmosphere, then the predicted ground level concentration from a single source will be directly proportional to the emission rate i.e. if the emission rate is doubled, the predicted ground level concentration will also be doubled.

#### **Application of dispersion models to predicting PAH concentrations**

71. There are a number of obstacles to the application of dispersion models for predicting ground level concentrations of PAH:
- As discussed, PAH emissions estimates (even for [BaP] alone) have a high degree of uncertainty. This level of uncertainty will be transferred to any PAH concentration predictions;
  - Processes which may be important for long range transport modelling (e.g. on a regional or national scale) such as dry deposition and degradation are not well known for PAH;
  - Emissions estimates in future years are uncertain;
  - There are a paucity of high quality monitoring data against which validation studies can be carried out.

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72. All of these combine to cast doubt over the ability of dispersion modelling studies to accurately predict ground level PAH concentrations, particularly where the emissions arise from poorly defined sources (such as wood burning). Despite these limitations, it is expected that dispersion modelling will play an important role in providing broad estimates of potential area exceedances (where the model predictions can be validated against monitoring data) and in the investigation of future control scenarios.

**Quality Assurance and Control required for PAH determination in air**

73. Member states and their laboratories may use different analytical methods for determination of PAH in air across the European Union. Consequently, quality assurance (QA) and quality control (QC) requirements differ. Quality Management is vitally important in insuring sufficient precision (and accuracy) of the measurements used for the legal aspects of a limit value of PAH in air.
74. Important stages to be covered by QA and QC are:

Sampling of PAH in air

The management of the sampling filter during and after sampling is important. Weather conditions as well as mobile and stationary sources influence significantly the levels of PAH in air. Because of this, it is necessary to document why the sampling site was selected and describe its operation. Depending on geographical location, a large variation in ambient temperatures may be expected.

Transport and storage of PAH sample

The transport and storage of samples needs to be validated, as it is important to know the “history” of samples.

Pre cleaning of PAH

This step in the analytical procedure involves extraction of the collected sample followed by clean up of the extract to obtain a PAH fraction which is then separated and detected.

Separation and detection of PAH

In this step, specificity, selectivity, the linear range as well as detection and quantification limits must be determined using reference materials. The robustness of the method must be evaluated and the robustness criteria stated.

75. Blank samples must be included in the full validation of the methodology used for the determination of PAH. Also, as many laboratories will be involved in the determination of PAH across Europe, it is important to have access to PAH reference materials and to undertake regular inter-comparison exercises (such as round robin tests). Green J M [1996] discusses validation of analytical methods in more detail.

## Uncertainty of the Analytical Methods

76. PAH have differing physical-chemical properties; each compound contributing in different proportion to the overall uncertainty. Furthermore, each analytical methodology has its own particular uncertainties. Consequently, a very dispersed range of uncertainty values is found in the literature, depending on the matrix, method used, authors, design of experiment, etc. For a typical PAH analytical methodology, the following budgets or sources of uncertainties can be identified:
- *Storage*  
For some compounds, storage conditions are critical and their stability should be considered as contributing to the global uncertainty estimation.
  - *Analytical standard*  
This is the uncertainty linked to the purity of the solid standards, which are used to prepare a calibration solution.
  - *Gas primary standard*  
If a PAH standard atmosphere generation system is used for the more volatile PAH (i.e., naphthalene, phenanthrene, fluorene), then the uncertainty linked to gas measurement systems should be taken into account.
  - *PAH reference material*  
This is the uncertainty of a certified reference material taken from real air samples and determined by laboratory inter-comparison exercises.
  - *Sampling and Sampling efficiency*  
Flow variability, efficiency of the sampling collection and the stability of the samples during the collection step have associated uncertainties. Additionally, vapour-particle phase distribution of the PAH is dependent on the sampling temperature. This fact becomes more important for the more volatile PAH and particular attention should be given when only one phase is considered for quantification.
  - *Extraction, concentration and clean-up*  
There are uncertainties associated with the different steps of extractions, concentration, drying, change of solvent, clean-up, i.e. the reproducibility of the extraction efficiencies or clean-up, evaporative losses, etc. are included.
  - *Calibration and quantification*  
The uncertainty associated with the analysis and the calibration method.
77. The importance of each contributory factor is related to the compound under consideration. Furthermore, the importance is also connected to the concentration level. All of these factors, in addition to the lack of performance and validation studies for many currently used methodologies, makes an accurate evaluation of the overall uncertainty of the reported PAH analyses quite difficult to assess. Nevertheless, by taking into account the current available bibliographic data, approximate values for uncertainty contributions can be estimated and are displayed in **Table 10: Sources of uncertainties for PAH analysis**.



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78. Following standard procedures for the evaluation of uncertainty in measurement [ENV 13005], the combined uncertainty values range from 13 to 16.5 %, which implies an expanded uncertainty (at 95 % of its confidence value) ranging between 26 to 33 %. As a conservative approximation, a value of  $\pm 35$  % for the overall uncertainty can be claimed for the analytical measurements of these compounds. This value is in agreement with the uncertainty assigned in the analytical method of ISO 12884, which establishes an overall uncertainty of  $\pm 50$  % or better. The uncertainty value should be understood to be applicable at concentrations higher than the limit of quantification of the technique. Typical detection limits for the analysis of PAH fall within the range 0.02 to 0.05 ng/m<sup>3</sup>.
79. The estimated overall uncertainty is an assessment of the intrinsic uncertainty of the method. Effective quality management systems, including inter-comparison exercises, should also be adopted to keep the levels of uncertainty within this 'best possible' range.

## 4. Toxicological basis for limit value for PAH compounds

### Chapter Summary

- A number of comprehensive and up to date reports are available on the inhalation health impacts of PAH, the working group has adopted the recent work of Boström and co-workers [1999] as the most appropriate starting point for its work.
- Ambient PAH include substances which are probable or possible carcinogens. The relevant exposure route for the lung is via inhalation of PAH compounds associated with airborne particles.
- Occupational studies exist which can be used as the basis for estimating the risk to human health posed by ambient levels of PAH and on the balance of current evidence we have adopted BaP as an indicator compound for assessing the risk associated with ambient mixtures of PAH compounds.
- There are insufficient data on the effects on health of exposure to PAH compounds in vehicle exhausts for deriving the risk to human health posed by ambient levels of PAH.
- The unit risk (lifetime exposure to a mixture represented by 1 ng.m<sup>-3</sup> BaP), based on a number of occupational studies, is in the range 80 – 100 x 10<sup>-6</sup>. As a result of developing knowledge there is increasing uncertainty about the reliability of the unit risk estimate.
- Adopting the current WHO estimate of a unit risk of 87 x 10<sup>-6</sup> results in the increased risk associated with BaP concentrations of 0.01, 0.1 and 1.0 ng/m<sup>3</sup> being 1 x 10<sup>-6</sup>, 1 x 10<sup>-5</sup> and 1 x 10<sup>-4</sup> respectively.
- A number of EU member states have adopted AQ guidelines.

### The case for a limit value for PAH

80. Ambient air contains a mixture of PAH compounds, concentrations are higher in urban areas and close to industrial plants than in rural areas. PAH compounds include some of the best studied substances known to produce cancer in experimental animals. The importance of these compounds in establishing current views of links between exposure to chemicals and the development of cancer has been reviewed by many authors. Pott's observations in 1775 of scrotal cancer amongst chimney sweeps [Pott 1963]. Volkman's report in 1875 of increased skin cancer in workers exposed to coal tar [von Volkman 1875] and the isolation by Kennaway and colleagues of pure aromatic hydrocarbons from coal tar and the demonstration of their carcinogenicity in the 1920s and 1930's [Kennaway 1924; Kennaway 1925; Kennaway and Hieger 1930] are all landmarks in the development of understanding of chemical carcinogenesis.
81. Exposure to single PAH compounds does not occur in man and thus it has been impossible to classify individual PAH compounds as proven human carcinogens. The International Agency for Research in Cancer [IARC] has classified a number of individual PAH compounds as probable human

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carcinogens (category 2A) and a number of common mixtures of substances that include PAH compounds as carcinogenic to humans (category 1). Thus, the fumes to which workers have been exposed during coal gasification, coke production and aluminium production have been classified as category 1 carcinogens. It should be noted that diesel exhaust is classified as category 2A: a probable human carcinogen. It is known that diesel exhaust contains a number of PAH compounds, some of which also occur in the fumes generated, for example, during coking of coal. This is hardly unexpected as incomplete combustion of carbon-containing fuel takes place in the production of both diesel exhaust and coke. The mixtures differ in terms of their detailed composition. A list of 20 PAH compounds and their IARC categories of carcinogenicity is shown in **Table 11: The degree of evidence for carcinogenicity of alternant PAH in experimental animals and overall evaluations of carcinogenicity to humans evaluated by IARC 1983; 1987.**

82. A list of mixtures which include PAH compounds and their IARC classification of carcinogenicity is shown in **Table 12: IARC evaluations of certain complex mixtures and occupational exposures involving exposure to PAH compounds.**
83. In considering a Limit Value for PAH compounds found in ambient air a chain of reasoning has been developed. This takes us from established facts to what we believe are reasonable deductions and conclusions. The process is open to argument and a number of possible objections are discussed below.
84. Rationale for recommending a Limit Value for PAH compounds
  - i. Well studied mixtures of chemicals, that contain a number of PAH compounds, produced by a range of industrial processes are accepted to cause cancer in man.
  - ii. The carcinogenicity of these mixtures is believed to be due in large part to the carcinogenic activity of PAH compounds present in the mixtures.
  - iii. Ambient air contains many of the PAH compounds found in the mixtures shown in an industrial setting to cause cancer.
  - iv. Thus, the mixture of chemicals that makes up ambient air should be considered to be carcinogenic in the same way as the industrial mixtures discussed above. It is accepted that the risk of cancer associated with exposure to ambient air will be considerably lower than that associated with exposure to the industrial mixtures discussed above because of the much lower concentrations of PAH compounds found in ambient air.
  - v. It, therefore, seems reasonable to develop a Limit Value that will control exposure to PAH compounds in ambient air and reduce attendant risk of cancer to a low level which would be regarded as tolerable by regulators.

## **Toxicological Guidance**

85. The argument set out in preceding paragraph has been accepted in a number of countries and air quality standards for PAH compounds have been recommended and, in some cases, accepted (see paragraph 7).
86. The line of argument developed above can be challenged at several points. It may be sensible to deal with these now and then to turn to the procedure that we suggest for developing the Limit Value. The following points should be considered.
- (i) The above argument assumes that the PAH compounds to which people have been exposed in an industrial setting are similar to those present in ambient air, that they are present in the same state and that a similar pattern of exposure can occur. The composition, as regards PAH compounds, of some industrial mixtures and ambient air is shown in Tables 5, 13, 14 and 17. **(Table 5: Summary of recent (not older than 1990) typical European PAH- and BaP concentrations in ng/m<sup>3</sup> as annual mean value. Table 13: Levels of polynuclear aromatic compounds (µg/m<sup>3</sup>) in the atmosphere of areas of an aluminium production plant; Table 14: Concentrations of polynuclear aromatic compounds (PACs) (µg/m<sup>3</sup>) in the atmosphere of a coke plant; stationary sampling at the battery top, 1976. Table 17: The estimated contribution of selected PAHs (particulate and gaseous) to total carcinogenic activity of PAH mixtures from different sites of exposure).**

It will be seen that the key PAH compounds, ie, those categorised by IARC as 2A (probable human carcinogens) occur in both industrial mixtures and ambient air. PAH compounds vary in volatility - the less volatile compounds being associated with particulate matter. There are no studies which show the effects on health of vapour phase PAH compounds [WHO 2001]. However, the current body of opinion is that the bulk of the key carcinogenic PAH compounds found in ambient air would be associated with particles and thus it is likely that a similar pattern of exposure will occur. Particles bearing PAH compounds will be inhaled and deposited in the airways in accordance with well understood physical principles. The distribution of particle aerodynamic diameter in the ambient aerosol will control the pattern of deposition in the lung. This distribution is well understood. The distribution of particle size in the industrial mixtures has been less well studied and it could be argued that if this differed significantly from that of the ambient aerosol then different toxicological effects might occur. There are insufficient data to answer this question conclusively but we have assumed that a significant proportion of the particles in both the industrial mixtures and the ambient aerosol are likely to reach the intra-thoracic part of the respiratory system, ie, are likely to be of less than about 10 µm aerodynamic diameter. We also assume that the bio availability of PAH compounds associated with the ambient aerosol will not be significantly less than that of PAH compounds

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associated with particles in industrial mixtures. We thus regard the objections listed above as theoretical and unlikely to be of practical importance.

- (ii) It is accepted that a significant proportion of PAH compounds found in the ambient aerosol in roadside and urban situations are produced, along with particles, by diesel engines. Our assumption that the ambient mixture is carcinogenic would thus be considerably strengthened by the clear demonstration of the carcinogenicity to humans of diesel exhaust. It is, however, true that no such conclusive demonstration has been reported (IARC concluded there was limited evidence but diesel exhaust was probably carcinogenic in humans). This is worth further discussion. Diesel exhaust contains a range of PAH compounds that are accepted as carcinogens in experimental animals; it also contains broadly the same PAH compounds that are found in industrial mixtures that are accepted as carcinogenic to humans. Thus, it seems likely, on theoretical grounds, that diesel exhaust should be carcinogenic to both experimental animals and to humans. Effects in animals have been studied in detail and the results reviewed at length. Whilst exposure to high concentrations of diesel particulates (diesel soot) produced lung tumours in rats this did not occur in hamsters or in mice. Much discussion of the tumours, cystic squamous cell tumours not seen in man, and of the high doses needed to produce such tumours has followed. It is now generally accepted that the tumours reflect overload of the rat's particle clearance mechanisms and that the findings cannot be used as a basis for predicting effects in man either qualitatively or quantitatively. Overload may be a phenomenon specific to the rat, evidence in other rodents is less good, and may reflect a different pattern of handling of particles from that seen in primates. Studies in cynomolgous monkeys have shown a greater degree of interstitialisation of particles than seen in the rat [Nikula al 1997]. Mauderly has recently contributed a detailed review of this area [Mauderly 1997]. It might be asked why diesel exhaust is not carcinogenic in hamsters, mice and monkeys. That the mixture contains compounds that are accepted as animal carcinogens is clear, why prolonged exposure to high concentrations does not lead to lung cancer is unknown. It may be that the carcinogenic compounds are not biologically accessible to cells in the lung. Alternatively it could be that despite the accepted genotoxicity of some of the PAH compounds a threshold of effect does, in practice, occur. This could be a result of defence systems that prevent low levels of attack on genetic material leading on to cancer.
- (iii) The problem is further complicated by the fact that epidemiological studies of the effects on people of exposure to high concentrations of diesel exhaust have also not produced clear cut evidence of carcinogenicity. These studies have been reviewed in great detail [California Environmental Protection Agency 1998; Bhatia et al., 1998; Health Effects Institute 1995; Health Effects Institute 1999; US EPA 1998]. Without repeating this review here it can be said that

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problems of confounding by cigarette smoking and difficulties of exposure assessment have made many epidemiological studies in this area difficult to interpret. Mauderly concluded his critical review of these studies with a paragraph that is quoted in full below: it seems unlikely that much will be added to this judicious conclusion at least in the near future.

"The weight of epidemiological evidence (i.e. of the epidemiological studies of exposure to diesel exhaust) reviewed above suggests that long-term employment in jobs involving substantial exposure to diesel exhaust is statistically associated with a small increase in risk for lung cancer. However, the existing data do not allow confirmation of the increase, determination of the magnitude, or description of the exposure-response relationship with a high level of confidence. Many of the studies did not detect significant increases in risk because, although their central estimates of risk were positive, their 95% confidence limits included values indicating no increase or even reduced risk. The studies indicating statistically significant increases have estimates of increases ranging from approximately 20% (relative risk of 1.2) to twofold (relative risk of 2). Increases in risk of less than twofold are difficult to assess with confidence from epidemiological data under any circumstances. Thus, it is unlikely that the issue will ever be resolved with a high degree of certainty by epidemiology, even if new prospective studies are conducted with much better assessment of exposure."

It should also be noted that improved control of exposure to diesel exhaust in the occupational setting will make it more difficult to detect effects in future studies.

- vi. It is argued (see (ii) above), that studies of exposure to diesel exhaust in rats are confounded as there is clear evidence of overload of the animal's normal particle clearance mechanism. This risk assessment is based on extrapolating from human epidemiological studies of industrial exposure to PAH mixtures (exposures at comparatively high concentrations, including particle-bound PAH), to the ambient air (much lower concentrations). Overload is generally considered to be a phenomenon specific to the rat, with evidence in other rodents and primates is less good. Nevertheless, it is a key presumption that in the epidemiology studies, the occupational exposures were not at 'overload concentrations' - that is, that the results at high exposures may be extrapolated to lower ambient concentrations. In reviewing the available reports of the occupational epidemiology studies, there was no evidence of overload presented.
87. We conclude that some PAH compounds are probable human carcinogens and that though some industrial mixtures containing PAH compounds are accepted as carcinogenic to humans, other important sources of exposure to PAH, such

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as those encountered at urban roadsides and in residential areas with a high usage of wood and coal for domestic heating, may also be carcinogenic to humans. However, recent work [Romundstadt et al., 2000] has tended to weaken the link between BaP exposure and lung cancer. Resolution of these difficulties cannot currently be complete and application of the precautionary principle is necessary if progress is to be made towards limiting ambient exposure to PAH compounds. Thus, we recommend that the mixture of PAH compounds found in ambient air should be regarded as likely to be carcinogenic to humans and that a Limit Value for such compounds should be set. Derivation of this Limit Value presents formidable difficulties especially as data relating to the effects of diesel exhaust can not be used as a sound basis for such a Limit Value. This turns us back to two key sources of data:

- i. data produced by studies of the carcinogenic effects of PAH compounds in experimental animals;
- ii. data produced by epidemiological studies of the effects on humans of exposure to industrial mixtures that contain PAH compounds.

We have chosen to base our recommendations on the latter, our reasons are given below.

**Key Sources of Information**

88. In developing our thinking about a Limit Value for PAH compounds we have identified a number of important and extensive reviews of the toxicity of PAH compounds. These deal with the evidence relating to the toxicology of PAH compounds in great detail and we see little purpose in repeating here the discussions provided in these reviews. The following have been particularly helpful:

- i. Environmental Health Criteria (EHC) report 202 "Selected Non-Heterocyclic Polycyclic Aromatic Hydrocarbons", [WHO2001].
- ii. Environmental Health Criteria (EHC) report 171 "Diesel Fuel and Exhaust Emissions", [WHO 1996].
- iii. Air Quality Guidelines for Europe: [WHO 2001].
- iv. Report on Polycyclic Aromatic Hydrocarbons published by the UK Expert Panel on Air Quality Standards [EPAQS 1999].
- v. Report by CONCAWE 98/55: "PAH's in Automotive Exhaust Emissions and Fuels" 1998.
- vi. IARC Monograph: Volume 34. Evaluation of the Carcinogenic Risk of Chemicals to Humans: PAH Compounds, Part 3. Industrial Exposure to Aluminium Production, Coal Gasification, Coke Production and Iron and Steel Founding, [International Agency for Research on Cancer 1998].

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- vii. US EPA. Toxicological Profile for PAH's, 1994. (Only available in draft form).
  - viii. Cancer Risk Assessment, Indicators and Guidelines for Polycyclic Aromatic Hydrocarbons (PAH) in the Ambient Air. [Boström et al., 1999].
89. It will be appreciated that this collection of reviews presents a great deal of detailed information on the toxicological effects of PAH compounds. The review of Boström and co-workers [1999] (viii above) is particularly focussed on standard setting for ambient air and we decided to request permission to adopt this report as a background document for developing a Limit Value for PAH compounds. In accordance with instructions regarding the development of EC Limit Values for air pollutants, we have also drawn extensively on the WHO Air Quality Guideline for PAH compounds. In accordance with WHO policy on genotoxic carcinogens the WHO Guideline for PAH compounds is presented as a Unit Risk estimate and not as a concentration, qualified by an averaging time, thought to be unlikely to be associated with significant adverse effects on health. We have been aware from the beginning of our work that recommending a Limit Value that would be generally accepted as being "safe" - in the sense of not being associated with increased risk - would be likely to be impossible and have aimed to produce an estimate of the risk likely to be associated with exposure to the ambient mixture of PAH compounds.

**Toxicological mechanism and effects**

90. A brief summary of the toxicology of PAH compounds is provided. Though exposure to high concentrations of PAH compounds can produce a range of toxicological effects the effect of greatest significance, on exposure to low and realistic concentrations, is the production of lung cancer. Extensive mechanistic studies have shown that many PAH compounds - including some that occur in ambient air - are complete carcinogens, i.e. they can both induce cancer by producing mutations in DNA and promote cancer by affecting the proliferative capacity of affected cells. These effects are referred to as genotoxic and epigenetic effects, respectively. Genotoxic effects depend on intracellular conversion of PAH compounds to diol-epoxides. This essential step is part of the process by which PAH compounds are converted to forms that can be conjugated with, for example, glucuronic acid and glutamic acid, rendered water soluble and excreted by the kidney. The epigenetic effects of PAH compounds involve binding to the aryl hydroxylase (Ah) receptor in the cytoplasm, translocation of the PAH-Ah complex into the nucleus, binding to a nuclear transcription factor and activation of genes that regulate the expression of factors that control cellular growth and differentiation. This epigenetic effect does not seem to be dependent on initial conversion to diol-epoxides. Details of the structural requirements of PAH compounds for binding to the Ah receptor have been worked out and may be found in the reports listed above. PAH compounds may also affect the production of cancer by triggering an inflammatory response and generating intracellular oxidative stress by free-radical production.



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91. Understanding of the mechanisms of action of PAH compounds has implications for the mathematical models used to predict the risks of cancer attendant upon exposure to these compounds. The risk associated with carcinogens that act solely as initiators is usually modelled linearly: the assumption being made that even at low doses some background level of promotion will be available to allow the effect of the initiator to be translated into cancer. The dose-response relationship of promotion is better described by an S-shaped curve - it being accepted that there is a threshold of effect below which promotion will not take place. Boström et al., [1999] summarise these points and conclude that, for carcinogens such as PAH compounds (capable of acting both as initiators and promoters), the probability of cancer occurring (Pcan) is represented by the product of the probability of initiation occurring (Pini) and the probability of promotion occurring (Ppro).

$$P_{can} = P_{ini} \times P_{pro}$$

92. If we can accept that Pini should be modelled linearly and Ppro according to an S-shaped curve, the possibility that a threshold of effect exists arises. In effect this is because though initiation can occur at very low doses this will not lead on to cancer unless promotion occurs and the promotion component is characterised by a threshold. The problem is complicated by the fact that the steps involved in the promotor activity of PAH compounds (beginning with binding to the Ah receptor) lead to up-regulation of the enzymes involved in production of the diol-epoxides from PAH compounds: these mediate the genotoxic effects of PAH compounds. The problem of the choice of the best model, for predicting risks attendant on exposure to low concentrations of PAH compounds remains. The WHO Air Quality Guidelines report recommends use of the US EPA default model: the linearised multistage model but acknowledges that this will be likely to produce a conservative (ie, safe, probable overestimation) of risk.
93. Given that we accept that at least some PAH compounds found in ambient air are genotoxic carcinogens before concluding that inhalation of such compounds may lead to lung cancer we need to be assured that activation (production of the diol-epoxides) can take place in lung tissue. For the purposes of this report we will consider the lung as the most important target organ: evidence relating to bladder and other cancers, being less well developed. This has been demonstrated, for a number of important PAH compounds, in animals by implantation studies [Deutsch-Wenzel et al., 1983; Wenzel-Hartung et al., 1990]. It is also known that PAH compounds are rapidly absorbed in the lung. It has been suggested that the association of PAH compounds with particles might prolong the retention of the PAH compounds in the lung - ie, delay clearance and increase effective dose - "dose" here being regarded as a complex term involving both mass of compound and how long the compound remains in contact with the target tissue [Henry and Port 1975]. More recent studies [Gerde et al., 1993], have shown that PAH compounds desorb rapidly from particles and cross the epithelial barrier in the lung to reach the blood. This process is less rapid in the airways than in the alveoli. Gerde pointed out that the slow passage of lipophilic PAH compounds, such as benzo[a]pyrene, across the bronchial

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epithelium, would lead to high dose levels in these target cells [Gerde et al., 1997]. It is likely that metabolism to active forms in airway epithelial cells is more important as a source of active carcinogenic forms that act in the lung than metabolism in the liver [Wiersma et al., 1983, Wall et al., 1991]. This may not be true at high levels of exposure.

**Risk assessment**

94. A number of studies of the effects of benzo[a]pyrene and other PAH compounds involving inhalation and implantation have been undertaken in animals. These are summarised in detail in Boström et al., [1999]. These studies have been used to generate models linking exposure to PAH compounds and risk of lung cancer. We have not summarised these studies here as we have not used them in developing a Limit Value. Our reasons for not using the animal studies are:

- i. all quantitative extrapolations from animals to man involve assumptions about comparative, ie, inter-species, sensitivity.
- ii. adequate human epidemiological studies are available.

We turned back, however, to the animal data in developing our case for recommending that benzo[a]pyrene should be used as an indicator of the ambient PAH mixture.

95. A number of epidemiological studies of the risk of lung cancer associated with exposure to mixtures of PAH compounds have been reported. These studies all involve estimating, often retrospectively, exposure to PAH compounds, and analysis of mortality data to calculate the increased risk of lung cancer associated with such exposure. Exposure estimates are often categorical rather than quantitative and this makes derivation of a satisfactory exposure-response relationship difficult or impossible. It is interesting to note that in some studies, eg, of workers at coal gasification plants in the UK [Doll et al., 1965; Doll et al., 1972; Lawther et al., 1965], despite high levels of exposure, the risk of lung cancer was only moderately increased: by a factor of about 2. This is encouraging in the sense that if such data can be used to predict the likely effects of exposure to ambient concentrations of PAH the increased risks at such ambient levels are likely to be small. It is also encouraging that the increased risks of lung cancer, expressed as increase in life-time risk per  $\text{ng/m}^3$  BaP, predicted from the various studies available, are rather similar. It will be noted that increased risks are presented per life-time exposure to unit concentrations of BaP. BaP is in fact used as an indicator of exposure to the mixture of PAH compounds encountered in the various industrial settings. In some studies only BaP concentrations were measured - in others, "benzene-soluble compounds" were measured. The interconversion of these indices has been discussed in the WHO Air Quality Guidelines for Europe (1987) and, for example, for coke ovens a value of 0.71% BaP in benzene-soluble compounds has been reported [Lindstedt and Sollenberg 1982]. Conversion of risk estimates expressed as per  $\mu\text{g/m}^3$  benzene-soluble compounds to per  $\text{ng/m}^3$  BaP is thus possible. It should be noted that the increased risks related in the standard expressions to unit concentration BaP are not assumed to be all due

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to exposure to BaP. On the contrary, the increased risks are assumed to be associated with exposure to the mixture, that mixture being characterised by its concentration of BaP. We shall return to this point when we argue for the use of concentrations of BaP as a basis for a Limit Value.

96. **Table 15: Summary of Unit Risk Estimates for BaP and for PAH with BaP as indicator substance (life-time risk per ng/m<sup>3</sup> of BaP)** summarises Unit Risk Estimates derived from both animal and epidemiological studies. It will be seen that though the Unit Risks derived from animal studies vary widely, by a factor of more than 1400, the Unit Risks derived from the epidemiological studies are remarkably consistent: the range is described by a factor of 18.7. We have taken this as another point in favour of using the epidemiological studies rather than the animal studies as a basis for a Limit Value.
97. Of the Unit Risk estimates shown in the epidemiology part of **Table 15**, three are remarkably similar: the US coke oven workers study ( $87 \times 10^{-6}$ ), the aluminium smelters study ( $90 \times 10^{-6}$ ) and the RIVM "most appropriate" estimate of  $100 \times 10^{-6}$ . The latter is, of course, not an epidemiological study as such, but a best estimate produced by the RIVM as a contribution to a Dutch Criteria Document on PAH compounds. This review [ RIVM 1989] examined a range of studies then available and recommended a Unit Risk estimate of  $100 \times 10^{-6}$ , expressed as above, as the most appropriate estimate that the authors could produce. The other studies listed in **Table 15** produce Unit Risk estimates to either side of these control figures of  $80\text{-}100 \times 10^{-6}$ , and as a result of developing knowledge there is increasing uncertainty about the reliability of the unit risk estimate. We acknowledge that we know of no means of identifying which of the epidemiological studies listed is the most suitable for use as a basis for developing a Limit Value for PAH compounds. We recommend, nevertheless, that the Unit Risk estimate adopted by WHO [WHO 1987; WHO 2001] from the US coke oven workers study, ie,  $87 \times 10^{-6}$ , be taken as a starting point for developing a Limit Value. This study has been considered in detail by a number of authors and the Unit Risk estimate produced is towards the centre of the Unit Risk estimates produced by the range of epidemiological studies listed above. To us this seems a reasonable choice.
98. It has already been noted that most epidemiological studies of the effects of exposure to mixtures of PAH compounds express their results in terms of the concentration of BaP present in the mixture studied. Older studies used "benzene-soluble compounds" as an index but, again as discussed, this can be converted into an equivalent BaP concentration. We note that the quantitative nature of this conversion will vary from study to study. In deriving a Limit Value for PAH compounds we seek to derive a risk estimate for exposure to PAH compounds in ambient air. This we can do by adopting BaP as an indicator compound, determining the concentration of BaP in ambient air and estimating the increased risk likely to be associated with the life-time exposure from a Unit Risk estimate derived from the studies of occupational exposures. Thus, if the ambient BaP concentration were to be  $10 \text{ ng/m}^3$  the increased risk produced by life-time exposure would be calculated as  $10 \times 87 \times 10^{-6}$  ie, 0.87

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$\times 10^{-3}$ . Such an increased risk would generally be considered unacceptably high and to obtain a more acceptable increased risk of, perhaps,  $1 \times 10^{-5}$  an ambient concentration of  $0.1 \text{ ng/m}^3$  would be sought. This was, in fact, the target concentration set by the Swedish Governmental Commission on Environmental Health in 1996, in an action plan to reduce environmental health risks.

99. It will be understood that the calculations shown in preceding paragraph are based on an important and, as yet, unsupported assertion: that BaP can be used as an indicator to calculate the increased risks likely to be associated with exposure to the ambient mixture of PAH compounds given that BaP was adopted as an indicator compound in the epidemiological studies upon which the calculation is based. In using BaP in this way we are assuming that BaP makes a similar contribution to the carcinogenicity of the ambient mixture of PAH compounds as it does to the mixtures of PAH compounds encountered in the occupational settings of the epidemiological studies. This is a cardinal point. It should be noted that use of BaP as an indicator does not at all require that the mixture of PAH compounds met with in ambient air should be identical with, or even similar to, that met with in the occupational setting, but only that BaP should make a similar contribution to the total carcinogenicity of both.
100. This requirement has been addressed by a number of reviews and is considered, at length, in the review of Boström et al., 1999. In principle, it is not difficult to test the similarity of the contribution made by BaP to the total carcinogenicity of both the ambient and industrial mixtures of PAH compounds. The procedure requires the following steps:
- i. determination of the concentrations of key PAH compounds in the different mixtures;
  - ii. scaling the contribution made by each PAH compound to the carcinogenicity of the mixture against that made by BaP;
  - iii. calculating the contribution made by BaP to the carcinogenicity of the different mixtures.
101. It will be appreciated that step (ii) requires a knowledge of the relative carcinogenic potency of different PAH compounds. This cannot be determined from the results of epidemiological studies and we need to turn again to animal studies.
102. Boström et al., [1999] described the results of a number of studies designed to compare the carcinogenic potency of a number of PAH compounds - see **Table 16: Relative potency of individual PAH compared to BaP (TEF-values), according to different authors**. When the UK Expert Panel on Air Quality Standards 1999 considered the use of BaP as an indicator compound they focussed on six PAH compounds in addition to BaP [DETR 1999]. These compounds were chosen because they have been classified as either probable (2A) or possible (2B) carcinogens by either IARC or the UK's own

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Committee on the Carcinogenicity of Chemicals in Food, Consumer Products and the Environment and were being measured in ambient by the UK's Toxic Organic Micropollutants (TOMPS) measurement network. It is likely that the seven PAH compounds considered make the major contribution to the PAH-attributable carcinogenicity of ambient air. The calculations done by EPAQS and by Menichini [1998] are shown in **Table 17: The estimated contribution of selected PAH (particulate and gaseous) to total carcinogenic activity of PAH mixtures from different sites of exposure**. It will be seen that the contribution made by BaP to the total carcinogenicity of the four mixtures (ambient air in London, ambient air in Middlesbrough, air at an aluminium smelter and in coke-oven fumes) was similar. Other authors have produced other figures. Petry et al., [1996] estimated the relative contribution made by BaP in mixtures encountered in coke plants, aluminium plants, graphite, silicon carbide and metal recycling plants and bitumen paving as between 27 and 67%. The Canadian risk assessment of PAH compounds reported that BaP contributed 70-100% of the total PAH-attributable carcinogenic activity in different localities in Canada [Meek et al., 1994]. In Sweden equivalent figures of 50-58% were produced and it was estimated that fluoranthene contributed 21-26% of total carcinogenic activity [Larsen et al., 1998]. In the Italian risk assessment, the excess risk globally associated with the seven carcinogenic PAH (see Table 2) was estimated to be approximately 75% due to BaP [Menichini 1992a]. These estimates, which though similar are by no means identical, have persuaded us that BaP can be used as an indicator compound in developing a Limit Value for PAH compounds.

103. Much, of course, depends on the choice of Toxic Equivalency Factors (TEFs) to describe the relative carcinogenic potency of the PAH compounds considered. The individual compounds considered by the UK Panel on Air Quality Standards 1999 are highlighted in **Table 16: Relative potency of individual PAH compared to BaP (TEF-values), according to different authors**. It will be seen that significantly different figures for the relative potency of these compounds could have been chosen - compared with those used by the UK Panel on Air Quality Standards 1999. This explains, in part, the range of estimates for the contribution of BaP to the total carcinogenicity of various mixtures produced by other authorities.
104. Fluoranthene has been considered in some detail in the report the Swedish EPA [Boström et al., 1999]. The authors point out that fluoranthene is mutagenic, though not classed as a carcinogen by IARC, and high concentrations occur in ambient air. It is particularly relevant that emissions from domestic oil heating plants contain more than 50 times as much fluoranthene as BaP and that the equivalent ratio for diesel exhaust is more than 100. The authors argued that fluoranthene was probably carcinogenic, animal studies support this and that there was a case for using fluoranthene as an additional indicator for the ambient mixture of PAH compounds. We have not pursued this here, though we include (below) a recommendation that fluoranthene concentration in air should be monitored.

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**Limit value options**

105. The case for adopting BaP as an indicator compound is strong. Given the argument outlined above it seems to us eccentric to suggest that some PAH compound other than BaP should be chosen at least as the primary indicator compound for the ambient PAH mixture.
106. This being so, and adopting the WHO Unit Risk estimate for PAH compounds we calculated the following values:

Possible Limit Value Value ng/m <sup>3</sup> BaP	Increased risk (life-time exposure to Limit Value)
0.01	1 x 10 <sup>-6</sup>
0.1	1 x 10 <sup>-5</sup>
1.0	1 x 10 <sup>-4</sup>

As is usual for carcinogens, an annual average concentration, would be supportable from a toxicological standpoint.

107. It is interesting to note that the UK Expert Panel on Air Quality Standards 1999 recommended a standard of 0.25 ng/m<sup>3</sup> expressed in terms of the concentration of BaP. This figure was derived without the use of Quantitative Risk Assessment (QRA). The details of the method adopted which involved the use of uncertainty factors, are spelled out in the EPAQS report [DETR Expert Panel on Air Quality Standards 1999].
108. The most up to date version of guidance from member states is given in Table 3.
109. We have mentioned above the importance of accepting, in deriving our proposed Limit Value, that BaP makes a similar contribution to the total PAH-attributable carcinogenicity of the ambient air as it does in various industrial settings. To ensure that any variations in this contribution are recognised it is important that a range of PAH compounds be monitored in ambient air. In the UK, emphasis has been placed on the seven PAH compounds that were compared with BaP in terms of their contribution to the total carcinogenicity of the ambient mixture. In Sweden a longer list has been recommended (See **Table 18: Summary of PAH and related substances recommended to be included in ambient air monitoring**). Other Member States may also have views on which PAH compounds - in addition to BaP - should be routinely monitored.
110. PM<sub>10</sub> represents those particles (the thoracic fraction) that can pass beyond the larynx and deposit in the airways and in the deep lung. PM<sub>2.5</sub> represents respirable particles, ie, particles capable of being deposited in the deep lung. Because lung cancer is the main risk associated with inhaled PAH compounds

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and this disease occurs both in the large airways and in the deep lung PM10 is a more appropriate measurement basis than PM2.5.

### **Toxicity to Environmental Organisms**

111. The Working Group was unable to provide information on eco-toxicity. Most available data on the effects of PAH on organisms in the environment relate to exposures via water or sediments. However, there are few data included in the recent WHO Environmental Health Criteria document on the direct toxic effects to terrestrial organisms exposed to PAH via soil, though none relating to exposure of plants or animals to vapour or particulate-bound PAH in the air [WHO 1998].

#### Plants

The effects of anthracene on seed emergence was reported in three species of native Australian plants and three crop species; sensitivity ranged from 30 mg/kg to greater than 1000 mg/kg dry weight of soil [WHO 1998].

#### Invertebrate animals

Growth of the terrestrial isopod Porcellio (woodlouse) was reduced at soil concentrations of BaP of 100 mg/kg dry weight and greater [WHO 1998]. Fourteen day LC50 values for fluorene in various earthworm species were in the range 17-210 mg/kg dry weight in soil. No effects were recorded following exposure to chrysene for a similar period at a concentration of 1000mg/kg dry weight soil. The 28 day LC50 value for phenanthrene was 150 mg/kg/dry weight of soil, whilst the No Observed Effect Concentration for reproduction was in the range 75 to 240 mg/kg dry weight of soil. No effects on reproduction were seen after 28 days exposure to chrysene, benzo(k)fluoranthene or benzo(a)pyrene at concentrations of 180 mg/kg dry weight of soil [WHO 1998].

#### Vertebrate animals

72 hour LD50 values for chick embryos were determined by applying PAH dissolved in oil to the surface of duck eggs [WHO 1998]. The significance of these data to the establishment of an air quality standard is uncertain.

## **5. WG Findings, Conclusions and Recommendations**

### **Working Group Findings**

112. The Working Group defined the scope of European PAH air pollution, in particular:
- examining the known sources of PAH emission;
  - assessing existing information on PAH concentrations in the ambient air (this comes from direct measurement, informed estimations and assumptions, and modelling work. Linked with this we examined the issues of data quality/quantity, uncertainty, and comparability);
  - reviewing measurement methods for PAH, in particular those which are suitable within regular monitoring networks;
  - assessing trends in emission and ambient levels;
  - preparing a review of the effects of PAH;
  - collating the experience of member states (i.e. the precedent) in the:
  - assessment and management of the risks associated with ambient PAH,
  - setting air quality standards and guidelines
  - making recommendations to the Commission for an air quality standard and associated monitoring and assessment strategies as appropriate.
113. The Working Group focused on the limited number of PAH compounds that are probable or possible human carcinogens. Particular emphasis was given to effects linked to direct exposure via inhalation and those substances that health studies have associated with lung cancer. As a result the Working Group did not consider in detail:
- exposure to PAH other than from breathing ambient air,
  - PAH compounds with little evidence of human carcinogenic activity,
  - carcinogenic risk as a result of possible transformations of PAH due to interaction with other pollutants such as oxides of nitrogen.
114. Assessment of any health risks associated with exposure via ingestion of food contaminated with PAH which has been deposited from the air or arising from cooking processes - together with 'indoor' exposure as a result of occupational exposure to tobacco smoke, cooking or heating - was judged to be outside the current remit of the Working Group.
115. On the basis of WHO guidance a number of Member States have set guidelines or mandatory limits for ambient PAH. The UN ECE CLRTAP, furthermore, in a protocol designed to control and reduce the emissions of POPs, specifically refers to PAH. Many countries also have PAH emission control regulation but there are no direct controls on PAH emissions at European Union level; nevertheless a number of EU initiatives are likely to lead to reduced emissions and hence to reduced ambient PAH concentrations in the period up to 2010.
116. Emission inventories for PAH, while improving, are relatively poor. There are no standardised procedures for: reporting the process conditions characterised in direct measurements, compiling emission factors, selecting



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and reporting the compounds determined. Consequently emission estimates vary widely between member states.

117. There are four major anthropogenic emission source components: Domestic, Mobile, Industrial, and Agricultural. The levels of emission from these sources and their relative importance have different uncertainties; there is evidence that they are changing with time as a result of regulation and economic development. In addition PAH can be created naturally as a result of uncontrolled or accidental burning:
- Domestic sources** are often numerous, widespread, individually small sources which can, under unfavourable conditions, lead to widespread population exposure sometimes at elevated levels. Emission data are poor and the sources are not well characterised. There is no uniform European regulations on emission control and the net size of the source is likely to remain relatively constant over the period to 2010. Factors such as the type of fuel used and the design of the 'stove' are important - increased combustion efficiency in modern stoves and the use of 'cleaner' fuels have the potential to reduce emissions considerably. PAH is associated with a large range of particulate matter including PM<sub>2.5</sub>.
- Industrial Sources** are increasingly being regulated at European level. Improved energy management is leading to improved combustion which, together with the application of more advanced abatement techniques introduced to reduce other pollutants like PM, leads to lower PAH emissions. Consequently total PAH emissions are decreasing. Particulate PAH are largely associated with the fine fraction (particles <2.5µm).
- Mobile Sources** too are becoming more stringently regulated but not specifically for PAH. The emission is a function of engine type, emission control, load, age, fuel and driving mode, in particular "cold start". As with industrial sources there is increasing control over emissions and particulate PAH are associated with the fine fraction (particles <2.5µm). Emissions are at ground level, widespread and concentrated in urban environments, where they have the potential to create elevated levels.
- Agricultural** burning can be a source of PAH and while often regulated at a local level is not uniformly controlled at a European level.
- Natural sources** such as fires, volcanoes and other PAH producing events are stochastic, they are not well characterised and are not considered in detail by the report. While natural events cannot be controlled they do contribute to the background and can have an important local impact. They may therefore effect the ability of a member state to meet any emission limit. It is not anticipated that the contribution to background PAH concentration from these sources will change by 2010.
118. Significant reductions in total mass emission from 1990 to 2010 may be anticipated with a shift, in some countries, in the relative importance in the inventory components from mobile and industrial to domestic sources.
119. PAH in air is deposited to other media where it is degraded by a variety of mechanisms; degradation rates in air are generally higher than those for other media and retention is greatest in the sea. BaP is frequently used as a marker of PAH carcinogenic activity and there is a consistent contribution of BaP

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from a variety of sources, under a range of conditions, across Europe; like other PAH containing 5 or more rings it is found predominantly in the particulate phase. Other components, DBaP for instance, may have a high carcinogenic potency compared to BaP, such compounds are usually present in very low concentrations and can not be unambiguously identified in atmospheric samples.

120. At a EU level ambient PAH concentration data are sparse and not always directly comparable. Because sampling is both costly and technically challenging, no Community-wide and consistent set of data is available at present. In the nineties, typical levels for BaP (as annual mean) in rural background areas varied between 0,1 and 1 ng/m<sup>3</sup>, for urban areas between 0,5 and 3 ng/m<sup>3</sup> (traffic sites at the upper boundary of this range) and up to 30 ng/m<sup>3</sup> within the immediate vicinity of a cokery. Few measurement data exist for rural communities burning coal and wood domestically; however, these measurements suggest levels similar to those found in cities. The limited data available suggest a reducing trend of both total PAH and BaP, reinforcing the trend predicted in the emission inventory studies. There is a strong intra annual variation, particulate PAH concentrations, including BaP, can be an order of magnitude higher in winter than in summer. Most PAH monitoring in the EU is carried out for public health reasons and concentrates on a limited number of individual PAH species. National monitoring networks operate in a limited number of member states. Most monitoring campaigns are focussed towards particle-bound PAH. The cost of sampling and analysis is a function of the number of monitoring stations, the sampling method used, the frequency of sampling and the analytical methodology adopted. Opportunities exist to optimise measurement cost effectiveness if a predominantly particulate bound PAH is adopted as a marker as these could be linked with sites or equipment measuring other particulate pollutants such as metals or PM<sub>10</sub>.
121. Modelling and measurement has indicated that there are populated areas of elevated PAH concentration; consequently some people are subject to greater risk than the general population, not only near to industrial and urban sources but also in communities where domestic solid fuel burning is prevalent. On the basis of the cost benefit analysis study [Holland M 2001] it is likely that: ambient concentration levels currently exceed 1.0 ng/m<sup>3</sup> BaP in some locations and may continue to do so in the future; 0.5ng/m<sup>3</sup> is a suitable lower limit for the air quality limit based on practicality issues and control strategy availability; 2010 is a suitable time for the limit to be introduced.
122. At present different procedures are used throughout the EU to collect and analyse ambient air samples for PAH. There are several national measurement methods and ISO standards available which can determine individual PAH compounds, including BaP, at a detection limit of approximately 0.02 ng/m<sup>3</sup> (based on a 24hourly sample). There is no international standard method which is suitable for frequent, cost effective, BaP measurement. An analysis of the sources of uncertainty in the determination of PAH indicates that, using currently available best techniques, individual measurements can be expected to have an uncertainty of about +/-

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50% at the 95% confidence level. When used for generating time series of annual means, as would be required for testing compliance with an air quality limit, the likely expanded uncertainty arising from reducing daily to once in every 6th day sampling would be between 25 and 30% falling to ~10% when every third day is sampled.

123. The inter annual variance of annual mean BaP concentrations obtained from a variety of sites in the EU were used to calculate upper and lower assessment thresholds. The variance of the results were such that the UAT and LAT values, at 50% and 40% of the limit value respectively, were relatively close together.
124. The PAH 'mix' may vary geographically and temporally following changes to the emission sources as a result of regulatory and economic changes.

## **Conclusions**

### **Emissions, ambient air quality and control measures**

124. Quantifying emissions of PAH, assessing ambient concentrations, characterising speciation and determining trends has proved difficult due to a lack of commonly accepted and comparable data at an EU level. There is broad agreement on the main emission sources but harmonisation of emission estimation and reporting is still at an early stage of development. The relatively few ambient PAH measurements carried out in the past have not usually been conducted to common methods and criteria and so there remain questions regarding data coverage, quality, associated uncertainty and, consequently, inter-comparability. Knowledge of PAH speciation obtained as a result of direct measurement has tended to be study and site specific as have assessments of trends in emission, ambient levels and speciation. Control measures introduced under Community legislation for particulate and other pollutants have also reduced PAH emissions from a number of major sources. Further reductions in emissions are anticipated over the period 2000 – 2010 so a suitable margin of tolerance, as defined by in Council Directive 96/62/EC 1996, for a limit value to be obtained in 2010 would be 50%. Nevertheless it is likely that some important sources, especially the burning of solid fuels for domestic heating, will not decrease unless new measures are introduced. As a result of recent work inventories of emissions are now improving and PAH modelling and assessment has become more meaningful.

### **Health effects**

125. Data from a number of occupational health studies suggest that there is an association between lung cancer and exposure to PAH compounds. The most important exposure route for lung cancer would appear to be via inhalation. Several PAH have been accepted as probable or possible human carcinogens, most of them are known to be associated with airborne particles. BaP, a probable human carcinogen found in appreciable concentrations in the

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atmosphere, can be used as a marker of the carcinogenic risk of airborne PAH. The WHO considered BaP in their air quality guidelines when deriving a unit risk factor and a number of member states have, independently, adopted health guidelines or regulations for BaP; a common air quality criterion based on BaP would foster harmonisation across the EU.

126. WHO guidance suggests that the unit risk of lung cancer is  $87 * 10^{-6}$  per ng BaP /m<sup>3</sup> for lifetime exposure. Member States have variously set guideline or mandatory values of between 0.1 and 1.3 ng BaP/m<sup>3</sup>. Since the risk has been evaluated on a lifetime exposure basis these limits usually relate to a yearly average. A consideration of the health based evidence and acceptance that the upper limit of the additional lifetime risk should be less than  $1 * 10^{-4}$  ( $\sim 1 * 10^{-6}$ /year is generally accepted as the maximal risk level), would suggest a common air quality standard for BaP of less than 1.0 ng/m<sup>3</sup>, averaged over a yearly period. PM<sub>10</sub> is the most appropriate measurement fraction because lung cancer associated with inhaled PAH compounds occurs both in the large airways and in the deep lung. Provisions for 'alert thresholds' to protect against short term exposures are inappropriate since there is no evidence for acute effects at likely ambient concentrations.
127. There does not appear to be a body of data suggesting that there is a significant impact on non-human fauna, flora or the built/historic environment requiring the establishment of objectives for ambient air quality other than those designed for the protection of human health.
128. Atmospheric transformations of PAH, while known to occur, are complex and the products various. There are insufficient exposure data to assess their harmful effects and consequently insufficient information on which to assess the need for or, indeed, define additional objectives for ambient air quality.

**Practical considerations related to setting and implementing a PAH air quality objective for an ambient air quality objective**

129. Given the large number of compounds in the PAH family, together with their widely varying physical and chemical properties, the measurement of PAH is difficult and costly. Methodology for sampling, analysis and reporting will need to be harmonised across the EU in order to implement control measures, monitor their impact and refine any further action which may be required in the future. A standard, ISO 12884, exists which is adequate for the collection of information for quantitative inter-comparison of a broad spectrum of PAH components but it is not suitable for compliance purposes due to its cost and lack of validation under European conditions. To date most workers have focused on BaP as a marker for PAH or include it in their suite of analyses; consequently a reasonable body of information and experience has built up on its sampling and analysis. BaP is predominantly confined to the particulate phase throughout the EU. Even though it is possible to use available techniques to collect and analyse BaP further work is required within CEN to elaborate a robust and cost effective reference method. The performance of such a method will not be known until the method is tested but a likely estimate for the overall measurement uncertainty is +/- 50% or better.

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130. Sampling and analysis of PAH is costly and sample numbers should be reduced to the minimum consistent with the general requirements of the Directive (96/62/EC). To prevent sample degradation individual sampling times should not exceed 24 hours. A sample every third day throughout the year is regarded as a minimum requirement for compliance checking at sites with levels approaching a future limit value; this is in order to minimise the uncertainties taking into account source and seasonal variability. The number of samples taken could, however, be adjusted according to the variability and the proximity to any assessment threshold values of the BaP annual mean at the site in question.
131. Available monitoring data suggests that concentrations of BaP can be expected to be greatest near to particular industrial installations, busy roads, and in both urban and rural communities burning solid fuels. Ideally the network design and siting criteria, together with the rationale for determining numbers of sites per zone, should reflect the nature of the exposure pattern and the criteria used in the extant daughter Directives. Bearing in mind the difficulties of sampling BaP and the cost of chemicals analysis a pragmatic compromise should be struck between numbers of sites and population density.
132. The high level of inter-annual variance of BaP annual mean concentrations require an upper assessment threshold (UAT) to be set at about 50% of the limit value to ensure a low probability (<5%) that zones with yearly mean values at or below the UAT do not breach the limit value. Notwithstanding the relatively high level of BaP measurement uncertainty, zones with yearly mean values of about 25% of the limit value (provided the limit value is in the range 0.5 –1.0 ng/m<sup>3</sup>) are highly unlikely to breach the limit value. Furthermore measurements are not necessarily cost effective at concentration levels set purely to provide information for assessment according to Article 6 of Directive 96/62/EC. Consequently a lower assessment threshold (LAT) could be set at a level of 25% of the limit value. Above the UAT compliance measurement should be mandatory, below the LAT objective estimations and modelling could be used. In view of the shortage of BaP data measurement should also be undertaken between the UAT and the LAT but a reduced frequency of sampling would be acceptable.
133. On the balance of available evidence reductions below an annual mean level of 0.5 ng BaP/m<sup>3</sup> will be difficult to achieve at a large number of sites in the near future. A level of 1.0 ng BaP/m<sup>3</sup>, while likely to be technically feasible by 2010, is currently exceeded in some locations, especially those with heavy traffic and/or extensive wood or coal burning and may continue to be so in the future. Some industrial plant, such as cokerries, may also continue to give rise to local concentrations above 1.0 ng BaP/m<sup>3</sup> beyond 2010.
134. To provide information on PAH composition by region and to track possible changes in composition over time, a broad range of PAH should be monitored at a limited number of representative BaP measurement sites in each member state. To check that any variation in PAH mix does not affect significantly the representativity of BaP as a carcinogenicity marker the compounds to be

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determined should include at least: BaA, BbFA, BjFA, BkFA, IP, DBahA and FA. This choice is based on carcinogenicity and observed occurrence in the atmosphere. ISO 12884 is suitable for the measurement. The three congeners, BbFA, BjFA, and BkFA, are difficult to resolve analytically, for the purposes of this general monitoring task they can be reported as a sum.

135. On the balance of current evidence BaP can be used as a marker of the carcinogenic risk of airborne PAH compounds despite not necessarily being the most potent carcinogen present. Data exist from occupational health studies which can be used as the basis for estimating the risk to human health posed by ambient levels of PAH. Monitoring will be necessary to detect any significant changes in the PAH profile (and hence the carcinogenic impact) of the ambient PAH mixture in the future. The compounds to monitor should include those indicated in paragraph 134 above. The unit risk (lifetime exposure to a mixture represented by 1 ng/m<sup>3</sup> BaP), based on a number of occupational studies, is in the range 80 – 100 x 10<sup>-6</sup>. Working on the WHO estimate of a unit risk of 87 x 10<sup>-6</sup> the risk associated with standards of 0.01, 0.1 and 1.0 ng/m<sup>3</sup> would be 1x10<sup>-6</sup>, 1x10<sup>-5</sup> and 1x10<sup>-4</sup> respectively. As a result of developing knowledge there may be increasing uncertainty as to the reliability of the unit risk estimates.

**Recommendations**

The Working Group recommends that:

1. **The EU shall regulate PAH.** From a health perspective ambient concentrations should be below 1.0 ng BaP/m<sup>3</sup>, annual mean; this level is currently exceeded in some locations and may continue to be so in the future.
2. Taking into account the best available scientific evidence, in order to reduce the risk of harmful effects on human health arising from exposure to ambient levels of PAH, the EU should regulate PAH air quality. Bearing in mind the current uncertainty (in emissions estimation, assessment of ambient air concentrations, population exposures, and in the use of unit risk factors derived from occupational epidemiology studies), together with the difficulty in reducing emissions from some sources **the EU shall adopt an air quality limit of between 0.5 – 1.0 ng BaP /m<sup>3</sup>, annual mean, measured in the PM<sub>10</sub> fraction and expressed at ambient conditions. This limit should be reviewed in the light of improved knowledge after 5 years. A suitable margin of tolerance could be 50%, the limit should be attained by 2010.**
3. **The Working Group recommends upper and lower assessment thresholds at 50% and 25% of the limit value respectively. The measurement criteria are as follows:**

Criteria	Compliance measurement – for use above the upper assessment threshold	Indicative measurement – for use between the upper and lower assessment thresholds
Sampling Frequency	Every 3 days	Every 6 days
Data capture	90%	90%

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Uncertainty of individual measurements	50%	50%
Sampling duration	24 hours	24 hours

(N.B. below the lower assessment thresholds objective estimates and modelling may be used)

4. **The siting criteria shall correspond with those of Directive 1999/30/EC excluding provision 1(b) therein, special sites for the protection of ecosystems and vegetation not being required. For diffuse sources, including zones containing rural hotspots, the minimum number of BaP measurement sites per zone shall be as shown in the following table.**

<b>population of agglomeration or zone (in 1000's)</b>	<b>If concentrations exceed the upper assessment Threshold</b>	<b>If concentrations are between the upper and lower assessment Thresholds</b>
<250	1	1
<750	2	1
<1000	3	1
<1500	4	2
<2750	5	2
<4750	6	2
<6000	7	2
> 6 000	8	2

Measurements should also be made:

- in the vicinity of point sources where preliminary assessment has indicated that the limit value is exceeded,
  - at one rural background station per 100000 km<sup>2</sup>.
5. **To assess concentrations of BaP on a common basis and to monitor compliance with the recommended air quality limit CEN shall elaborate a standard reference method for BaP, suitable for use in the range 0.02 to 20 ng/m<sup>3</sup>, measured in the PM<sub>10</sub> fraction, with a known measurement uncertainty. The method shall include sampling, sample treatment and analysis.**
6. **To obtain adequate information for use at the 5 year review a broad spectrum of PAH shall be monitored at a limited number of representative BaP monitoring sites in each EU member state in order to build up a consistent and comparable body of data on the composition and trend of ambient PAH across the EU. The species to be determined shall include at least: BaA, \*BbFA, \*BjFA, \*BkFA, IP, DBahA and FA. ISO 12884 is suitable for the purpose. This information should be reported to the Commission on a**

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**regular basis.** Such ‘monitoring’ stations need be relatively few in number; they are not required to achieve the high levels of data capture and need not have the same level of measurement uncertainty as that required for compliance measurements.

( \* may be summed for reporting)

7. **The EU and member states shall encourage the development of knowledge of emissions from dominant sources and the impact on health of ambient PAH.**