

**COUNCIL DIRECTIVE ON
AMBIENT AIR QUALITY ASSESSMENT AND MANAGEMENT
WORKING GROUP ON BENZENE**

POSITION PAPER

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COMMISSION OF EUROPEAN COMMUNITIES

Council Directive on Ambient Air Quality Assessment and Management Working Group on Benzene

Benzene:

Preface

Preface

Scope

At the meeting of the Steering Group of National Experts on Air Quality in July 1995 it was agreed that working groups would be established to produce position papers in preparation for development of daughter legislation under the Council Directive 96/62/EC on Ambient Air Quality Assessment and Management. The present position paper is developed for Benzene by a working group with participants from Denmark, Germany, Italy, Joint Research Centre (Ispra), The Netherlands, Spain, Sweden, European Environmental Agency (Topic Centre for Air Quality), from Industry, from the European Environmental bureau and from the European Commission (DG XI). Italy is responsible for the chairmanship and co-ordination of the Working Group. The position paper must be prepared in accordance with the recommendations from the Commission (AAQ/95/1/2) with the amendments from the meeting on 5 July 1995. It will provide a technical basis for establishing limit values and air quality objectives over the EU territory for the protection of human health, ecosystems and the environment and for achieving an effective reduction of Benzene pollution taking into consideration costs and benefits. The position paper will be published as a stand alone technical paper to be used as a technical reference.

This paper addresses air quality objectives for the outdoor ambient atmosphere and it does not address indoor air pollution, deposition or synergistic effects between benzene and other pollutants. Even though parts of the population may be exposed to significant indoor and/or workplace benzene pollution, this is outside the scope of the Directive and will not be considered in the position paper. However, as with other common outdoor pollutants, benzene may be present at high concentration levels in indoor environments such as house interiors, inside cars and the working place. In addition, Benzene is a category one carcinogenic compound. It is not expected to present a potential risk of acute effects, and therefore only long term limits air quality objectives are planned.

Summary

Chapter 1 of the position paper describes the emission sources of Benzene in atmosphere giving some quantitative data for Europe and for other industrialised countries. Emphasis is given to the emission by vehicles, especially in urban locations where it is expected to reach the highest concentration. Emissions are resulting from direct emission from the exhausts and from the evaporation of fuels either by car or from fuel distribution and refuelling. Factors controlling the concentration levels, such as the emission rates and meteorological factors, e.g. mixing properties of the atmosphere, are also presented. The physico-chemical evolution of Benzene after the emission step is also presented. It includes atmospheric chemistry of aromatic compounds related to photooxidant formation and the main processes for transport and deposition. Current air concentrations in several locations are reviewed. They include mainly conurbation, but industrial sites and remote observations are also reported. In order to show a decreasing trend in benzene concentration, some data relevant to past years are included.

The impact of Benzene on the environment and especially on human health is reported in Chapter 2. Toxicological data are examined and epidemiological studies on population exposed to Benzene are presented and discussed to give the basis to assess the risk assessment as a function of exposition. Recommendations are made for a basis for developing limit values.

Chapter 3 of the position paper addresses methods and tools for the measurements and assessment of Benzene concentrations in environments where a risk of exposure is present. A detailed description of available instruments for the automatic monitoring as well as manual sampling and analytical methods are presented. A network design for Benzene is suggested and the inclusion of Benzene monitors in existing monitoring stations is reviewed. Quality assurance and quality control are presented in order to ensure data of sufficiently high reliability in terms of accuracy and sensitivity. Preliminary assessment techniques are also presented. They are mainly based on the use of proper models which take into account emission rates, traffic distribution and prevalent meteorological conditions. Accuracy and reliability of existing models for Benzene are reviewed.

Cost and benefit implications of Benzene reduction are considered in Chapter 4. Finally, Chapter 5 summarises the main points of the previous Chapters and makes final recommendations.

Chapter 1

Benzene:

Introduction

1. INTRODUCTION

1.1 - Benzene in the Atmosphere

Benzene is an aromatic hydrocarbon with molecular formula C_6H_6 (PM = 78.11). It is a colourless liquid at ambient temperature with a boiling point of 80.1 °C at atmospheric pressure, and a vapour pressure of 10 kPa at 20° C and about 12.27 kPa at 25 °C. Benzene vapour has an "aromatic" odour and an odour threshold of 1.5 ppm (v/v). It is slightly soluble in water (1,8 g/Kg at 25 °C). Benzene is a Volatile Organic Compound (VOC). This is a class of compound, which includes chemical species of organic nature such as alkanes, alkenes, aromatics, ketones, aldehydes, alcohols and others. They are characterised by a vapour pressure at ambient temperature higher than 100 Pa, so that most are found in gas phase. They are commonly present in air at concentrations ranging from a few micrograms to many hundreds of micrograms per cubic meter, depending basically upon the emission sources, meteorological factors, transport and photochemical phenomena.

Emissions of benzene to the atmosphere are due mainly combustion processes for energy production (including motor vehicles) and domestic heating. Since fuels are distributed from the producers to the user, evaporative processes are also responsible for the emission of large amounts of aromatic hydrocarbons in the atmosphere.

The world-wide industrial production of benzene is in the order of more than 15 million tons per year. In 1991-93 the European production of benzene, excluding benzene in petrol, was 5.5 million tons. The only significant natural sources of benzene are biomass burning, and brush and forest fires. However, these sources do not affect air quality in densely populated areas in the EU.

1.2 - Emissions of benzene

Benzene in the atmosphere is due mainly to anthropogenic sources. Natural sources are estimated in the order of 3-5% while more than 90% are estimated to come from anthropogenic sources. The anthropogenic sources in Europe are distributed according to Table 1-I, where an estimation of different contributions to the total emission of benzene is reported.

Tab. 1-I - Contribution of main anthropogenic sources of Benzene in Europe

Sources	(%)
Vehicular traffic	80-85
Petroleum Refineries	0.3-1.5
Fuel Distribution	2.6-6
Chemical Industry	1.3-13
Domestic Heating	3-7
Solvent Use	1-4

Source: Air Quality Report of the Auto Oil Programme (data for 1990)

The most important and significant anthropogenic sources are combustion sources, where benzene is emitted as unburned compound. However, benzene is also formed from the thermal degradation of other aromatic compounds. Main contributors are traffic and other mobile sources and energy production (including industrial combustion). Emissions from traffic are the largest source. Therefore, benzene pollution is highest in densely populated areas characterised by high traffic density. Industrial activity can contribute to ambient benzene levels, but its contribution to the total exposure is very low.

Unfortunately, national emission data based on emission inventories may not be very accurate, and data from different Member States may not be directly comparable owing to different classification systems and methods of calculation. The results reported here are therefore subject to uncertainty. Since benzene emissions from traffic are not directly regulated (though benzene emissions are reduced by catalytic converters), standard vehicle emission tests do not include benzene as such. In research experiments benzene emissions have been determined, and the results have been extrapolated to car fleets, based on an analogy with hydrocarbon emissions, which are measured in standard tests. The uncertainty of benzene emissions from industrial sources depends on the source type. Evaporative emissions from handling and storage of oil and benzene are uncertain and very difficult to measure. Often the benzene content of evaporated solvents is not known and a default percentage is used as an estimate. Clearly, better emission inventories are key elements for an effective benzene reduction program.

1.2.1 - National Emission data

Emission data from individual European countries have been gathered from national emission inventories and are reported in the following Tables.

1.2.1.1 - Sweden

In Sweden, the estimated total amount of emitted benzene in 1994 was about 23 KTonnes. The distribution of benzene emissions from different emission categories is given in the Table 1-II

Table 1-II - Sweden, benzene emissions from different source categories given as % of the total benzene emission

Source Category	%
Road traffic, including petrol Evaporation and asphalting	38
Other mobile sources	3
Working machinery	4
Energy production	<1
Small scale wood Combustion for heating	54
Industry	3
Domestic use	<1
Pesticides	<1

Source: Swedish Environmental Research Institute

1.2.1.2 - Germany

Benzene emissions in Germany were 32.4×10^3 tons per year in 1995. In the years 1990 and 1985 the benzene emissions were estimated to be more than twice as high, amounting to $77,8 \times 10^3$ tons and $73,5 \times 10^3$ tons per year, respectively. The emissions can be broken down to source categories as follows:

Table 1-III - Germany, benzene emissions from different source categories

source category	1985 t	1990 t	1995 t	1985 %	1990 %	1995 %	
Traffic	64314	70304	29420	88	91	91	
Exhaust-emissions:	60966	66932	27622				
Passenger cars	49982	56806	21881				
Light duty. Veh. $\leq 3,5$ t	4229	3910	1396				
Heavy duty veh., $> 3,5$ t	823	996	1124				
Buses	148	155	120				
Two-wheeled	3584	3365	1851				
Agriculture, Construction, Military	2200	1700	1250				x
Evaporative losses, Passenger cars, Petrol	3348	3372	1765				
Distribution of Petrol	1500	1700	600	2	2	2	
Combustion plants (mostly solid fuels)	5100	4300	1150	7	6	4	x
Industry without combustion plants	2590	1500	1275	4	2	4	x
Processes:	2340	1250	1025				x
Chemical industry	450	450	450				x
Refineries	170	170	170				x
Cokeries	1370	280	55				
Miscellaneous	350	350	350				x
Chemicals (laboratories)	250	250	250				x
Sum (of major categories)	73504	77804	32445				

Source: Umweltbundesamt, 1998

x = rough estimates

1.2.1.3 - The Netherlands

The 1995 total benzene emissions for The Netherlands were estimated to be about 8 KTonnes. Table 1-IV shows the different contributions of benzene emissions according to the different source groups.

Table 1-IV - The Netherlands, benzene emissions from different source categories given as % of the total emission

Sources	%
Vehicular traffic	50
Extraction of fossil fuels and power generation	23*
Industry (including refineries and Petrochemical plants)	8
Domestic use, small installations	13
Other	6

* This figure includes emissions from North Sea Oil and Natural Gas Platforms as well as direct emissions from generating stations

Source: RIVM

1.2.1.4 - United Kingdom

In United Kingdom, the estimated total amount of emitted benzene in 1995 was about 35 ktonnes.. The distribution of benzene emissions from different emission categories is given Table 1-V.

Table 1-V - UK, benzene emissions (1995)

Source	Emission (ktonnes)	%
Road transport (DERV)	0.44	1.3
Road transport (gasoline)	22.84	65.3
Petrol evaporation	2.02	5.8
Other transport (1)	0.20	0.6
Off road (2)	2.50	7.1
Stationary combustion	2.40	6.9
Extraction/distribution of fossil fuels	1.29	3.7
Processes	2.89	8.3
Solvent use	0.26	0.7
Waste treatment	0.16	0.5
Total	35	

Source: Salway *et al.*, 1997.

(1) Other transport includes shipping, railways and civil aircraft

(2) Off road includes naval shipping and military aircraft

1.2.1.5 - Italy

The total benzene emissions in Italy in 1994 were estimated in 23.800 Tons. Table 1-VI presents the different source groups.

Table 1-VI - Italy, benzene emissions from different source categories given as % of the total emission in 1995

Source Category	%
Petrol production Distribution	2.9
Evaporative emissions	2.6
Vehicular evaporation	12.1
Vehicular traffic	76.9
Other sources	5.5

Source: Unione Petrolifera, 1997

Emissions for 1995 were estimated to be in the order of 20,000 tons (Air Quality Report of the Auto Oil Programme).

1.2.1.6 – Emissions in different Member States

The reported data are very similar and consistent in all countries (except for Sweden and Austria where wood burning appears to be a very significant contributor to the total emission of benzene). They are also consistent with data available from countries outside Europe characterised by similar social and economical development.

Table 1-VII shows a summary of different information gathered from several European Countries where a direct comparison between different benzene sources can be made.

Table 1-VII - Benzene emissions of individual Countries from different source categories given as a % of total emission

Source Category	SE	D	NL	I	A	UK
Vehicular Traffic	38	93	50	89	41	79
Industry	6	5	8	5.5	3	13
Domestic use	54	2	13		52	7
Energy Production	1		23			
Other	1		6	5.5	4	1

Source: Swedish Environmental Research Institute; Landesumweltamt; RIVM; Department of environment, The United Kingdom National Air Quality Strategy, March (1997).

1.2.2 - Emission Trends

Emissions of benzene have declined in recent years. Tab. 1-VIII the situation in Italy, with the decline expected to continue to the year 2000.

Table 1-VIII - Emission estimates for Italy (Tons of benzene)

Emission Sources	1991	1995	1997	2000#
Fuels production and distribution	945	709	236	-
Refuelling	472	472	236	*
Vehicles	3780	2598	1890	1181
Exhausts	19422	16535	13743	8031
Others	1181	1181	945	718
Total	25800	21500	17050	9930

Existing and proposed legislation on vehicle emissions, automotive fuel standards, solvent use, etc. will lead to substantial reductions in benzene emissions across the whole EU by 2010. Furthermore, the European Council has adopted a first daughter Directive relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air. The Directive sets limit values to protect human health for sulphur dioxide, particulate matter and lead to be met by 2005, and for nitrogen oxide to be met by 2010. Measures taken to attain these limit values, and

to reduce congestion and other transport-sector problems will also reduce benzene emissions. Some of these measures will be enacted throughout the EU, others only locally.

The Air Quality Report of the first Auto-Oil Programme (AOP1) estimated a 56% reduction in urban emissions of benzene between 1990 and 2010, though this did not include the effects of legislation following AOP1 and work on other Air Quality Directives (EC DGXI, 1996). Estimates for Italy suggest a 62% reduction in emissions from 1990 to 2000 with major reductions made by all of the most significant source types.

1.3 - Atmospheric Chemistry and transport

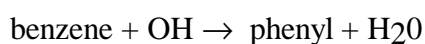
The concentration of benzene in the atmosphere is a complex function of emission rates, meteorological conditions and chemical removal. In the atmosphere benzene is only removed by the reaction with OH radicals. The reaction rate of this process is $1.2 \cdot 10^{12} \text{ cm}^{-3} \text{ molec}^{-1} \text{ sec}^{-1}$ (Atkinson, 1985) and with a 24 hour average concentration of OH equal to $10^6 \text{ mole cm}^{-3}$ representative for the troposphere, the lifetime of benzene is 9 days (in highly polluted air the lifetime is 1 day).

The residential time of an air mass in a street canyon is in the order of minutes and in an urban area in the order of a few hours even in high pressure situations with stagnant wind velocities. Therefore, chemical removal on a local scale (within an urban area) is negligible, but on a regional scale chemical removal of benzene can be important, (see below).

On a local scale the concentration of benzene is controlled by the source intensity and the degree of dispersion. In a street canyon the main source is traffic and thus the emission depends on the traffic density. The dispersion of benzene is dependent on wind speed and wind direction, solar radiation, and temperature, where the lowest dispersion is found during stable meteorological conditions with high pressure, stagnant wind velocity, low inversion layer etc. Such conditions occur in southern and central Europe and special meteorological conditions can exist where air masses are recirculated, although residence time as long as 9 days in an urban area is rare.

On a regional scale the chemical removal of benzene is more important than at local scale but the lifetime of 9 days is more than sufficient for benzene to be transported over long distances. In fact, elevated concentrations in remote European sites have been observed when they received air masses from central and southern Europe. For example on the west coast of Sweden a monthly average concentration of $2 \mu\text{g m}^{-3}$ is observed when air masses arrive from south compared to a monthly average concentration of $0.7 \mu\text{g m}^{-3}$ when air masses come from the Atlantic sector, representing an atmospheric background concentration of benzene (Svanberg *et al.*, 1994). Similar observations are reported from other European countries (Beck *et al.*, 1996).

Eventually benzene is removed from the atmosphere by OH hydrogen abstraction:



followed by a series of complex reactions leading to the formation of e.g. phenol, glyoxal, 2,4-hexadienal, butenedial and recently also benzene oxide and oxepin have been identified (Klotz *et al.*, 1997).

As with other VOCs, the photo-oxidation of benzene contributes to the formation of ozone in the troposphere (see Table 1-IX). The contribution to ozone formation depends on the reactivity of the compound with the OH radical, the carbon number, the chemical environment and the time scale considered. Different concepts can be used for classing the contribution. One commonly used concept is photochemical Ozone Creation Potentials (POCP). This refers to the amount of ozone formed, during a pre-defined period, following the release of a given mass of the organic compound into the atmosphere. POCP is often given relative to ethene (POCP = 100), defined for a given hydrocarbon as: $\text{POCP} = (\text{ozone increment with the HC} / \text{ozone increment with ethene}) \times 100$.

Table 1-IX POCP values calculated with the IVL model (1) and with a trajectory model using a master chemical mechanism (2)

Compound	As max. diff. in conc. (1)	As average ozone contribution during:		
		0-2 days (1)	0-4 days (1)	0-5 days (2)
Ethene	100	100	100	100
Benzene	31.7	28.0	40.2	21.8
Toluene	44.6	32.3	47.0	63.7

o-xylene	42.4	-5.6	16.7	105.3
m- xylene	58.3	27.3	47.4	110.8

Source: (1)Andersson-Sköld et al. 1992; (2) Derwent et al. 1998

The reactivity of benzene, compared to that of other aromatic components is therefore not so high. It is therefore not expected that benzene is depleted to the same extent as other VOCs in photochemical pollution. In fact, the ratio of Toluene to benzene is used as an important parameter to estimate ageing of air masses resulting from photochemical pollution. A typical example is shown in *Figure 1.1* where it is clearly seen that the value of the ratio T/B is about 3 when the emission sources dominate the concentration trend (Mornings and Evenings). This ratio is lower in the afternoons when photochemical pollution is dominating, and removing Toluene more efficiently than benzene.

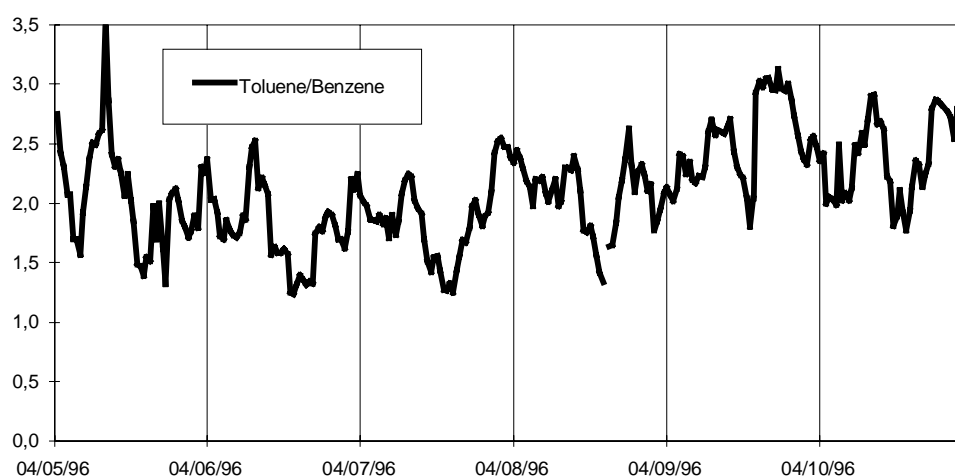


Figure 1-1 - Ratio of Toluene/Benzene for the sampling site of Villa Ada (Urban Background station, Rome, Italy)

There are some minor sinks in addition to photochemical pollution which may contribute to the atmospheric depletion of benzene. They include surface adsorption on soil and particles and the solution in water (surfaces and rain). Probably the latter is the second important depletion path from the atmosphere and it causes the transfer of airborne benzene from atmosphere to surface water and also to the food chain.

1.4 Benzene ambient air concentrations

1.4.1 Data

Measurements of benzene are not as systematic as those available for pollutants on which there is existing EC legislation. Monitoring networks were often established with the main purpose of gathering data related to the exceedances of air quality standards in the area where monitoring was carried out. For several years the available data for the EU as a whole dealt almost exclusively with regulated pollutants and were limited to the documentation of exceedances. Benzene is regulated in several Member States but regulations tend to be dated just a few years ago. Historical data are therefore not common and do not allow a precise and accurate evaluation of concentration trends. However, taking into account that the most effective control equipment was the extensive use of catalysts, it is expected that concentrations should have reduced significantly in the last ten years, as suggested by the emission scenario described in the previous subchapter.

Models applied to some European cities show a marked reduction in benzene concentration levels from 1990 through 2010. The models show that, although a significant reduction in the pollution level will be achieved, several cities will not reach a concentration below the most conservative target of $2.5 \mu\text{g}/\text{m}^3$ used in modelling Auto Oil 1. This is the case for cities in Southern Europe where the economic development will not allow a sufficiently rapid turnover of existing car fleets. In addition, as will be shown later, cities in Southern Europe suffer extensive atmospheric stability periods when accumulation of pollutants emitted at ground level occurs. In other words, similar emission rates in different cities might result into very different ambient concentration levels.

In order to give an approximate idea about the concentration levels and their variability, results from a series of measurements carried out in Germany is shown in Table 1-X (A through D). Data were obtained in urban background stations, in street canyons or hot spots, in industrial sites and in background sites. As expected, data shows values in the range of a few to several $\mu\text{g}/\text{m}^3$. Remote background data show concentration levels below or at about $1 \mu\text{g}/\text{m}^3$. It is important to observe that the ratio of hot spot to urban background concentration is about 5. Human exposure is dependent on the concentration levels but also on the habits of people. It is human activity that in general leads to the emission of benzene, and therefore humans are generally exposed to the maximum concentration at a given location. For this reason hot spots may be more important for exposure levels than actually seen by just looking at the average concentration levels.

**Table 1-X - Benzene concentration in ambient air
(annual means, $\mu\text{g}/\text{m}^3$) Germany**

A urban background

Station	annual mean 1997
Karlsruhe-Mitte	5.1
Karlsruhe-Nordwest	3.2
Heilbronn	2.9
Mannheim-Mitte	3.5
Mannheim-Süd	3.1
Pforzheim-Mitte	3.1
Leipzig-West	3.0
Magdeburg-West	2.7
Halle/Nord	2.5
Nürnberg	1.8
München (16 sites, range)	1.8 - 3.9
Duisburg-Meiderich	3.9
Neuss-Hafen	2.3
Gelsenkirchen	3.9
Bottrop	3.1
Bonn	2.2
Köln-Rodenkirchen	2.3
Dortmund-Hörde	5.7
Berlin (3 sites, range)	2.1 - 2.8

B traffic hot spots/street canyons

Station	annual mean 1997
München, Stachus	6.9

Düsseldorf-Mörsenbroich	12.1
Essen-Ost	5.7
Düsseldorf-Corneliusstr.	9.7
Magdeburg	7.7
Halle	11.2
Weißenfels	8.5
Bernburg	3.7
Frankfurt, Friedberger Landstr.	10.0
Wiesbaden – Ringkirche	11.0
Frankfurt/O. Leipziger Str.	7.3
Cottbus, Bahnhofstr.	6.3
Hannover-Linden	9.0
Braunschweig	16.0
Osnabrück	3.0
Hamburg-Stresemannstr.	7.0
Dresden-Nord	5.0
Mannheim-Friedrichsring	8.5
Karlsruhe	10.4
Stuttgart-Vaihingen	4.7
Berlin, 27 streets (range)	3.3 - 9.6
Berlin Motorway	6.3
Potsdam, Hans-Thoma Str.	6.3

C industrial hot spots

Station	annual mean 1997
Duisburg-Bruckhausen, Cokery	10.2

D rural, remote areas

Station	annual mean 1997
Eggegebirge	1.0
Eifel	0.8
Rothaargebirge	0.6
Schwarzwald-Süd	0.5
Welzheimer Wald	0.5
Wood near Berlin	0.5

Source: P Bruckmann

Table1-XI summarises benzene ambient air concentrations ($\mu\text{g}/\text{m}^3$) as measured in intensive field campaigns in the Basque country (Spain). Random sampling was performed with sorbent (TENAX) tubes, grab sampling and pre-concentration sampling.

Table 1-XI - Random sampling on sorbent (TENAX) tubes (GC/EM analysis), concentrations in $\mu\text{g}/\text{m}^3$

	24 h Mean	No of values
Urban background (Jun/Oct 1995)	7.5	14
Urban traffic (March/Oct 1995)	4.8	8
Industrial (Fenceline) (June 1997)	13.3	4

Grab sampling (instantaneous data) (portable GC/PID analysis) , concentrations in $\mu\text{g}/\text{m}^3$

	Mean	st. dev.	Maximum	No of values
Urban background (Jun/Oct 1995)	4.2	1.6	16.2	1479
Urban traffic (March/Oct 1995)	7.1	8.8	102.7	1383
Industrial (Fenceline) (June 1997)	21.45	50.7	448.1	464

Preconcentration sampling (hourly data) (auto GC/FID analysis), concentrations in $\mu\text{g}/\text{m}^3$

	1 h Means	st. dev.	Maximum	No of values
Urban traffic (Sept/Nov 1997)	4.6	4.2	32.8	1600

Table 1-XII below present half year average concentrations in the urban background in Sweden.

Table 1-XII - The 1995/96 winter half year averages of benzene in urban background in Sweden

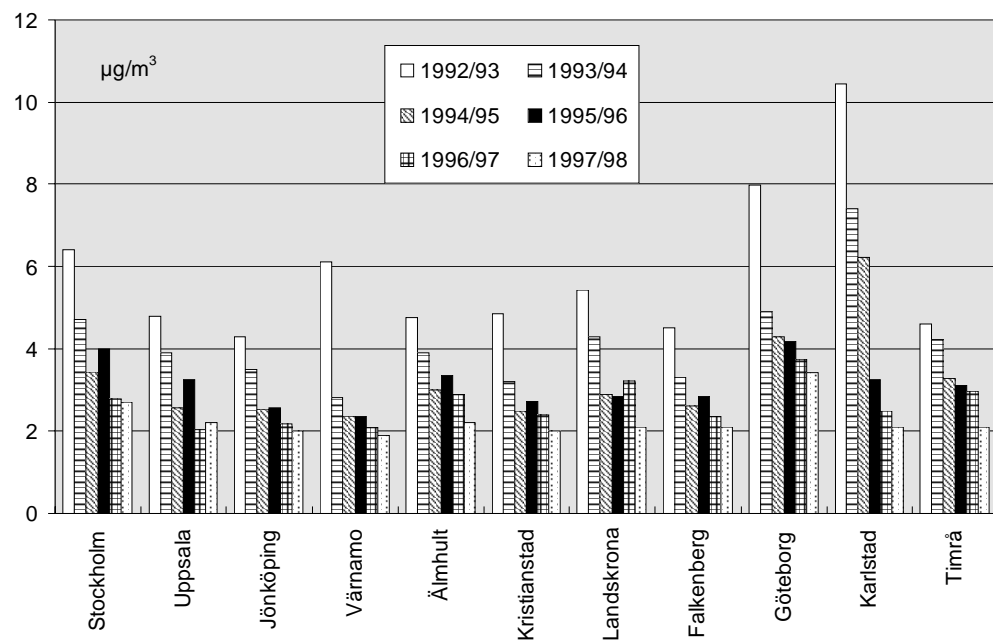
Site	$\mu\text{g}/\text{m}^3$	Site	$\mu\text{g}/\text{m}^3$
Stockholm	4.0	Sandviken	3.3
Uppsala	3.2	Hudiksvalls	5.0
Motala	2.1	Timra	3.1
Jonkoping	2.5	Ornskoldsvik	3.5
Varnamo	2.4	Ostersund	4.4
Eksjo	2.7	Lycksele	6.4
Almhult	3.4	Kalix	4.4
Vastervik	2.9	Gallivare	2.8
Kristianstad	2.7	Robertsfors	3.1
Landskrona	2.8	Mala	2.7
Falkenberg	2.8	Storuman	2.6
Goteborg	4.2	Norsjo	2.8
Kungalv	3.8	Skelleftea	3.4
Stenungsund	3.1	Bjurholm	2.2
Mariestad	3.7	Vilhelmina	3.1
Arjang	4.1	Umea	3.6
Karlstad	3.3	Vannas	4.8
Orebro	3.3	Vindeln	4.2

Karlskoga	4.6	Sorsele	3.8
Koping	3.7	Dorotea	3.7
Ljusdal	4.6	Nordmaling	3.1
		Asele	2.9

Source: Swedish Environmental Research Institute

Table 1-XII shows the concentration levels obtained from a series of measurements carried out in Swedish cities. The towns listed in the right column are located in the northern part of Sweden and in some cases experiencing emissions from small scale wood burning for heating. The national average based on these urban averages is $3.5 \mu\text{g}/\text{m}^3$. Street level measurements performed in other measurement campaigns have revealed concentrations of benzene which are 3-7 times higher than the corresponding urban background concentration.

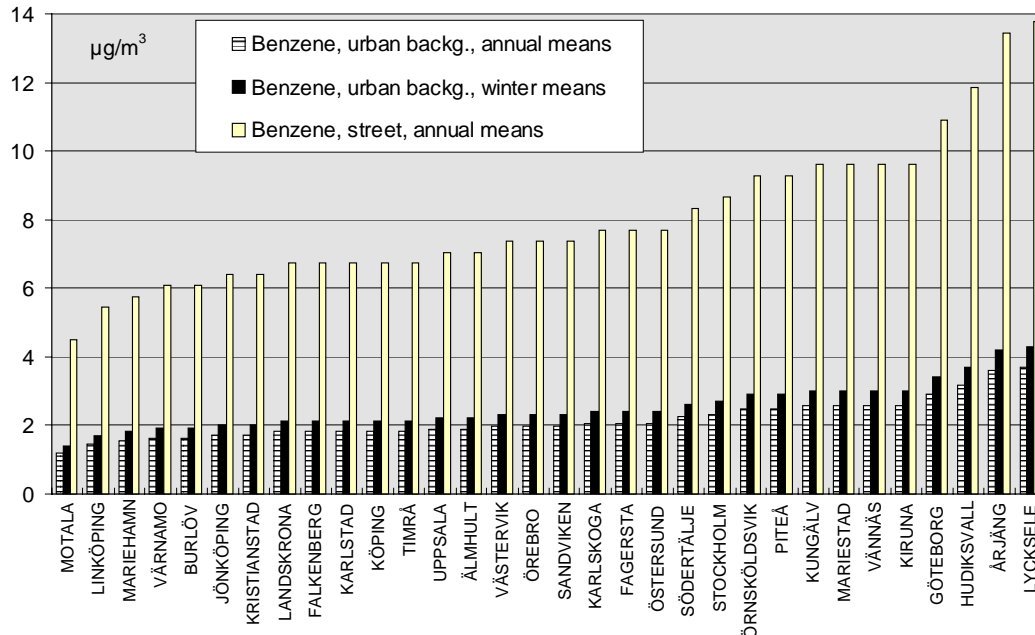
Figure 1-2 reports winter half year average concentrations of benzene in several Swedish towns. During the four first winter seasons the concentrations of benzene have decreased compared with the first year. This decrease is explained by the increasing number of catalyst cars, a reduction of the benzene concentration in fuels and measures taken by the local authorities in terms of traffic planning.



Source: Data from the Swedish Urban Air Quality Network

Fig. 1-2 - Winter half year averages of benzene ($\mu\text{g}/\text{m}^3$) in urban background in Sweden

Figure 1.3 shows estimated hotspot concentrations in Swedish urban areas extrapolating from the data shown in Figure 1.2 for 1997/98.



Source: Data from the Swedish Urban Air Quality Network

Fig. 1-3 – Estimated winter half year averages of benzene ($\mu\text{g}/\text{m}^3$) in hotspots in urban areas in Sweden

The black bars are the urban background winter half-year means 1997/98, calculated from weekly means obtained using diffusive samplers. The striped bars represents estimated urban background annual means based on the winter half-year means using a factor of 0.8. The white bars represents estimated street canyon concentrations as annual means, with the assumption that these are a factor 4 higher compared to urban background.

Results from a measurement campaign in Paris are reported in Table 1-XIII (Donati; 1994). Concentrations levels of a few $\mu\text{g}/\text{m}^3$ in urban background and higher level in high traffic roads are observed. In this case, the concentrations are approaching few tens of $\mu\text{g}/\text{m}^3$ with a ratio of concentration levels between hot spot to urban background of 7.4 to 10.3. This is another indication of strong dilution of benzene in the far field.

Table 1-XIII - Morning and evening concentrations of pollutants in three sites of Paris ($\mu\text{g}/\text{m}^3$)

	Site 1	Site 2	Site 3	Ratio	Ratio
	Carrefour	Place du	Jardin du	Site1/Site2	Site1/Site3
	Mendès- France	Pilori	çail		
Morning	37±17	5±2	4±1	7,4	9,2
Evening	31±11	4±1	3±1	7,7	10.3

Source: Donati, 1994

Another example which shows the concentration gradient of benzene is reported for Florence, Italy, as annual means for the year 1996 in three different sites. The sites have been chosen depending on the following criteria according to Italian regulation:

Site A which corresponds to Giardino di Boboli (Urban Background);

Site B which corresponds to Via U. Bassi (Residential area)

Site C which corresponds to V.le F.lli Rosselli (Intense traffic area).

Figure 1.4 shows the spatial gradient of benzene concentrations which moves from high values in urban traffic site to lower values in low density urban traffic site with a concentration ratio of about 6.

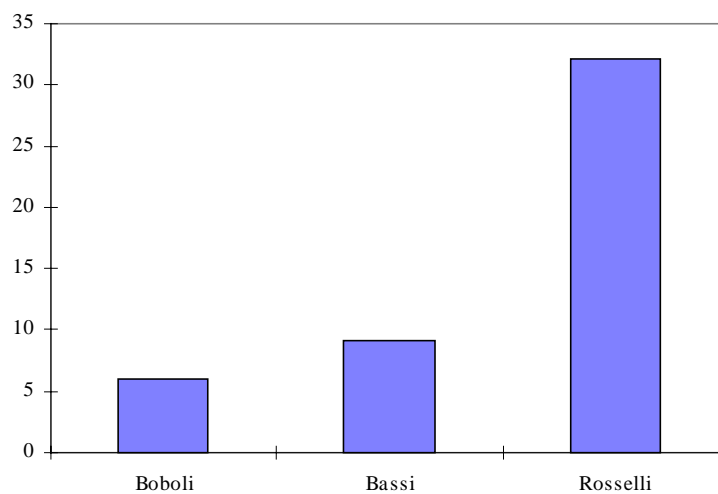


Figure 1-4 - Annual average of benzene concentrations ($\mu\text{g}/\text{m}^3$) in three different urban stations of Florence

As explained above, climate and in particular ventilation (air flow and mixing layer height) are as important in determining atmospheric concentrations as the emission values. Thus, the study of the structure of the wind fields and the dynamic evolution of the boundary layer is a key element in the evaluation of those processes responsible for urban atmospheric pollution.

The weather in northern Europe is mostly controlled by low pressure systems giving an unstable atmosphere without any thermal inversion whereas the southern Europe has a much larger probability of building up high pressure events with stagnant wind velocities and low inversion layers. During these events air pollution is concentrated in a relative small geographical area and in the street canyons the car induced turbulence is the major mechanism for dispersion.

It is interesting to observe how field data may be compared with results from model in order to obtain a distribution pattern over an extended territory. This is the case of a study carried out in the Netherlands. (NOTE: reference needed). Exceedance of the Dutch limit value of $10 \mu\text{g}/\text{m}^3$ was experienced along 30 Km of road in 1995. Compared to the 300 Km estimated in 1987, the decreasing trend in concentration appears to be quite clear. Although some exceedances are experienced, the mean benzene concentration in the Netherlands is estimated to be $1.2 \mu\text{g}/\text{m}^3$ with low values in the Northern part and higher values in the Southern part.

A summary of relatively recent indicative measurements in Member States has recently been published by the European Environmental Agency. According to the figures in Table 1-XIV below, it appears concentrations of benzene range from a few $\mu\text{g}/\text{m}^3$ to more than $50 \mu\text{g}/\text{m}^3$ with maximum values found near to high traffic streets. It is worth observing once again that measurements on urban background locations show atmospheric benzene concentrations of the same magnitude.

Table 1-XIV - Benzene concentration levels observed in European Cities; Units and Average time

Country	Site(s)	Urban bkgnd	Street
Austria	Several sites	4-7	3.7-17
Belgium	Brussel, 68 Sites, 1994	1.6-11	15
Denmark	Copenhagen, 1995- 96		16 (Winter)
Italy	Bari (8 Sites) 1993, Milan (2 Sites) 1994 Rome (1 Site)	8	20-50
Germany	13 cities (1993)	2-5	10-12
Sweden	28 cities (1995-96)	2-5	7-10
The Netherlands	3 cities (1993-94)	2-5	3-9
Norway	3 cities (1994)	10-40	
United Kingdom	6 cities (1994)	2-5	6

NB. As pointed out in section 1.4.1, benzene measurements are not always directly comparable. No data are available on the time periods over which measurement took place or the methods used.

As outlined before, benzene reactivity with respect to the species controlling atmospheric oxidising properties, is relatively low. Thus a relatively high lifetime in the atmosphere is expected and there may be considerable potential for long-distance transport of benzene. In fact, benzene ambient concentrations found in rural locations range from a few tenths to about 1 $\mu\text{g}/\text{m}^3$. It is difficult to prove whether benzene concentration levels in rural locations are due to far field dilution from emitting anthropogenic sources, or whether they result from natural emissions. However, it is worth stressing that the concentration levels observed in extremely remote locations are very similar to those found in European rural sites. For instance, data gathered in Polar sites show that the benzene concentration at Ny-Alesund, Svalbard Islands (80° N), is ranging from 0.3 to 1.5 $\mu\text{g}/\text{m}^3$ (P. Ciccioli *et al.*; 1993), while observations at Terranova Bay, Antarctica, (75° S) confirmed concentration levels ranging from 0.15 to 1.5 $\mu\text{g}/\text{m}^3$ (P. Ciccioli *et al.*; 1996). Although these sites may be considered as remote, the observed levels might be influenced by the presence of scientific settlements. Thus some local contamination is always possible.

1.4.2 Factors governing benzene concentrations

The description of the temporal evolution of the concentration of a pollutant in the atmosphere is a very difficult task because of the contemporary presence of emissive processes, diffusion, transport and chemical reactions.

In the case of benzene, its atmospheric concentration depends on two factors: the emissions (from exhausts, industries, evaporation fuels, etc) and meteorological phenomena such as advection, breeze circulation and the height of the mixing layer (H_e).

For pollutants emitted at ground level, and, in this case, for benzene, it can be demonstrated that the concentration follows a relatively simple relationship that directly comes from the continuity equation:

$$\frac{\partial C}{\partial t} = \alpha[\Phi_s(t) + \Phi_e(t)] - \beta \{C\} - Adv \quad [1]$$

where:

- $\Phi_s(t)$ is the emission intensity due to traffic.
- $\Phi_e(t)$ is the emission intensity due to evaporation.
- α is a parameter related to atmospheric stability.
- $\beta \{C\}$ is a diffusion term.
- Adv is the advection term

1.4.2.1 Concentrations on the Urban Scale

For surface sources the parameters can be estimated from meteorological measurements and by means of the measurement of ground concentration of Radon and daughters. Knowledge of the independent temporal evolution of Radon concentrations makes it possible to decouple the meteorological contribution from that of emissions to ambient concentrations of benzene.

Radon is also emitted at ground level and the temporal evolution of its concentration can be expressed by an equation similar to the previous one:

$$\frac{\partial C_R}{\partial t} = K\alpha - \beta C_R - Adv \quad [2]$$

where the ground emission of radon can be considered nearly constant, i.e.

$$\beta C_R \cong K$$

Figure 1-5 shows data gathered from the main station of Rome (Villa Ada) where several analysers intended for benzene measurement are operating. The data were obtained through the use of a DOAS coupled with a novel radioactivity monitor (Stability monitor) intended for the evaluation of the mixing properties of the atmosphere. From the figure, it can be seen that the highest levels of benzene are typical of periods characterised by maximum atmospheric stability (i.e. highest radioactivity count). Similar behaviour is shown in *Figure 1-6* which has been derived from data obtained in Milan in 1993 where the association between benzene and atmospheric stability evaluated through Radon measurements is quite straightforward.

Figure1.5

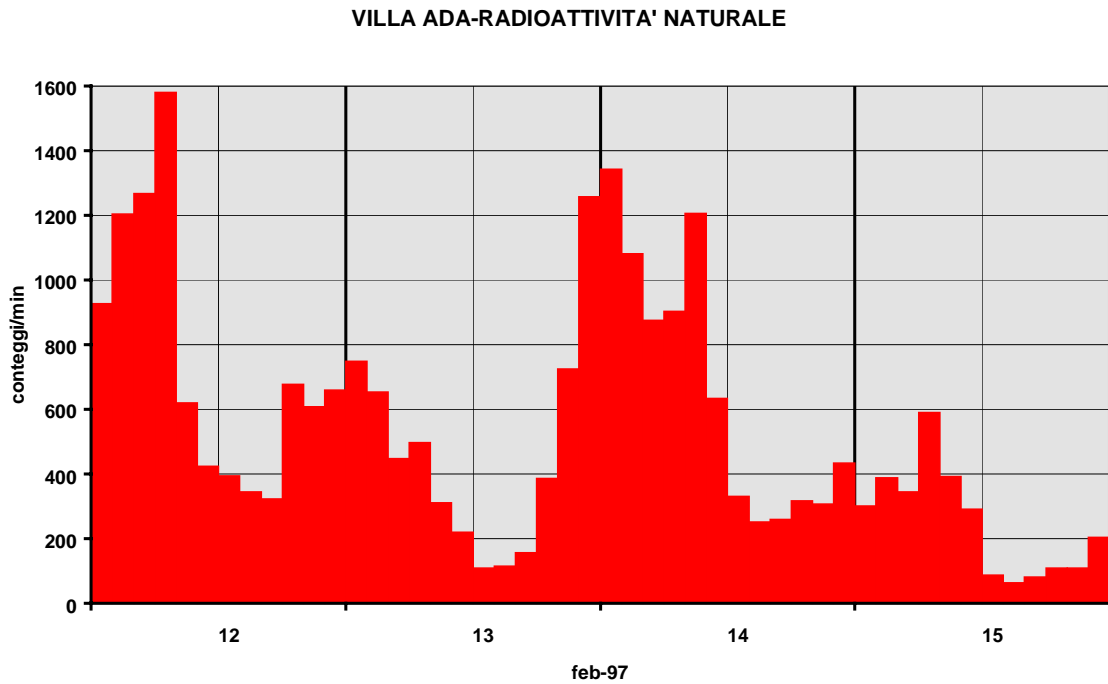


Figure 1.6

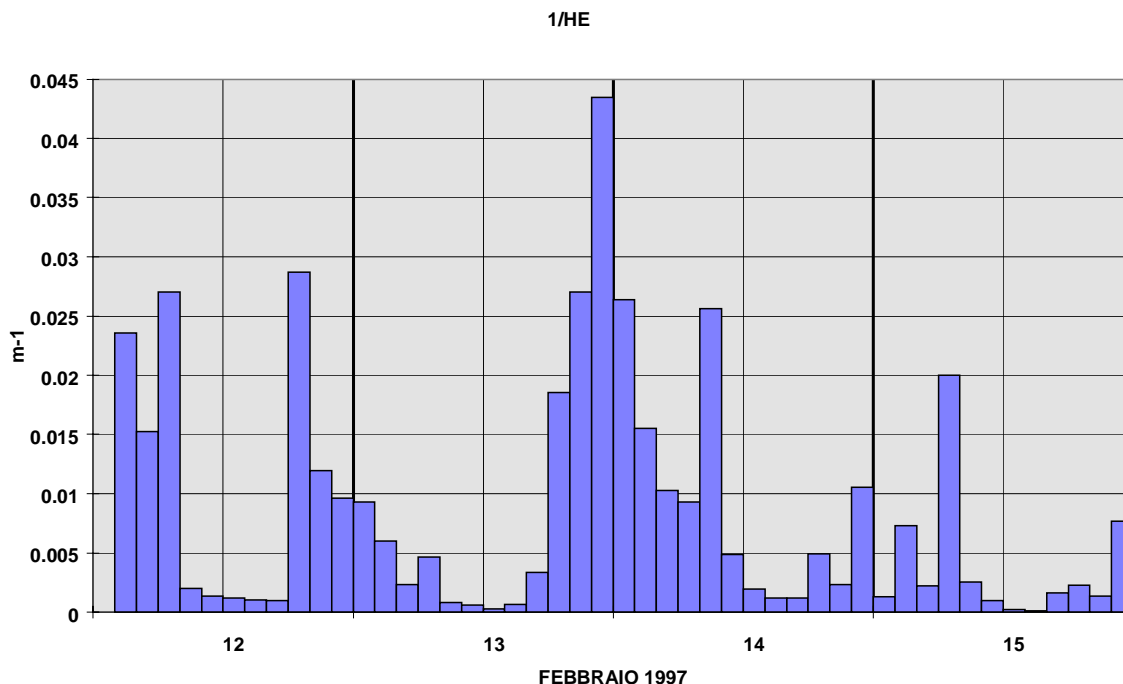


Figure 16 - Monitoring benzene (Concentration in parts per billions) in Villa Ada Station, Rome and natural radioactivity. Atmospheric stability ($1/Heq$ [m^{-1}]) is derived from radioactivity measurement.

Since the maximum stability conditions are occurring overnight, even the maximum concentration of benzene are observed in the period late afternoon-early morning. Even though the traffic intensity in this period is very low, the concentration levels are high as an additional proof that emission strengths alone does not define the observed concentration levels of benzene.

These findings are very important because they are the basis for an effective control of benzene concentration. In fact, in the hypothesis of similar emission factors, sites or conurbation characterised by shallow mixed layers will experience benzene levels much higher than sites characterised by strong or moderate atmospheric turbulence.

The details of *Figure 1-6* show that the episode in the late morning (Feb. 14th) was due to a combination between traffic intensity and atmospheric stability. The same period of the day before, the stability was relatively weak and only a smaller benzene peak

appears. Night-time peaks are associated to strong stability. This association is evident if the parameter $(1/Heq)$ is introduced when calculated from data related to atmospheric radioactivity. Since it is an indirect evaluation of the height of the mixing layer, it is very much consistent with data related to ambient concentrations.

Most monitoring networks are coupled to standard meteorological observation stations which provide data related to atmospheric turbulence and dispersion. For example, standard deviation of wind speed and direction may provide an independent way to estimate the turbulent mixing properties. Also changes in temperature and relative humidity may be useful for the evaluation of the atmospheric mixing properties. However, the temporal trend of Radon concentration follows the same general physical relationship typical of any pollutants, either primary or secondary, thereby it provides a more direct way to describe the atmospheric dispersion.

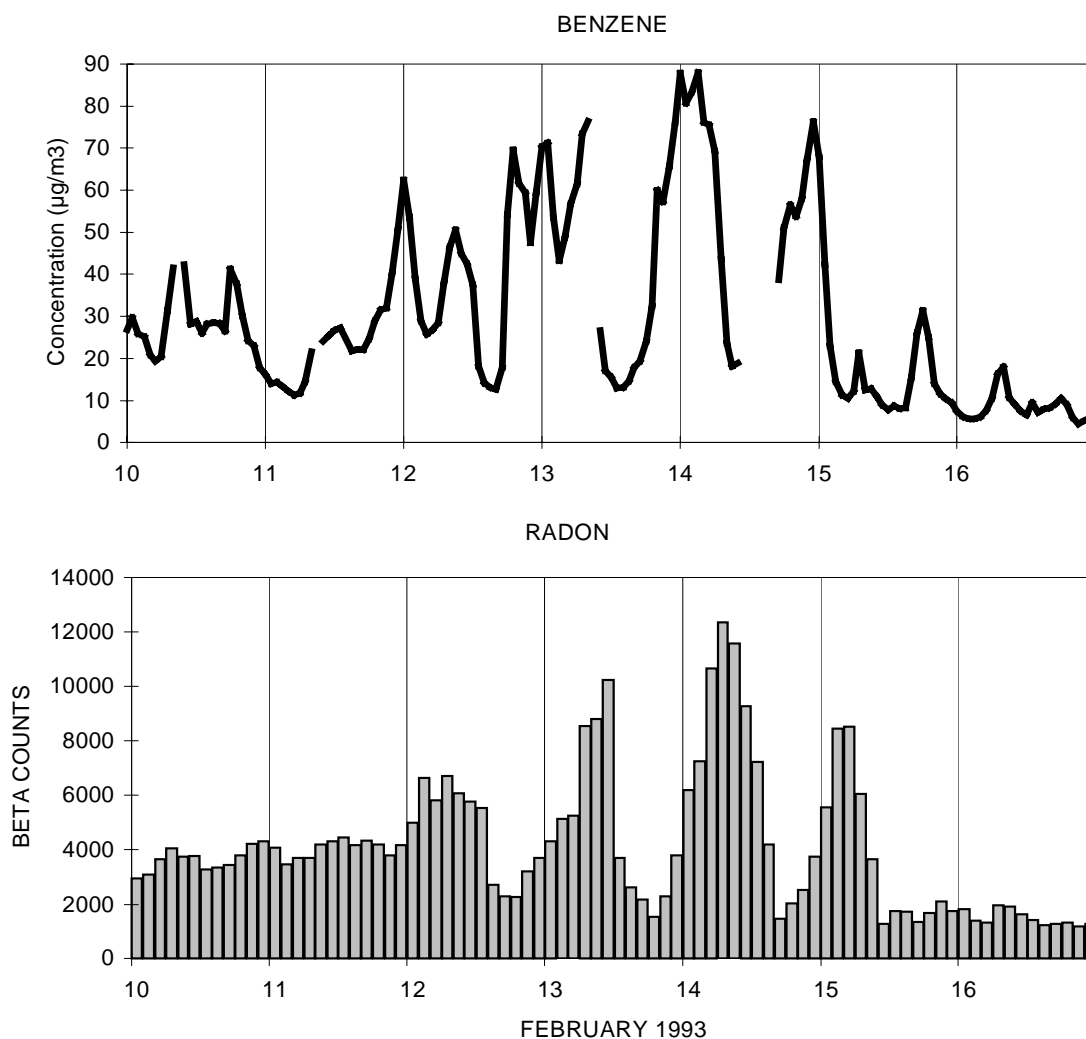


Figure 1.7 - Monitoring Benzene in a urban background station in Milan and natural radioactivity

1.4.2.2 Concentrations on the Street Scale

The level of benzene in streets depends on the local emission strength, the local dispersion and the local city background level. In streets with traffic, the levels are of course higher than the urban background levels and so is the probability of limit value exceedance. In busy streets the emission via the engine exhaust is considerably larger than the emission due to evaporation. The dispersion of pollutants in exhaust plumes and around buildings along streets is extremely difficult to describe in detail. One should, however, realise that in

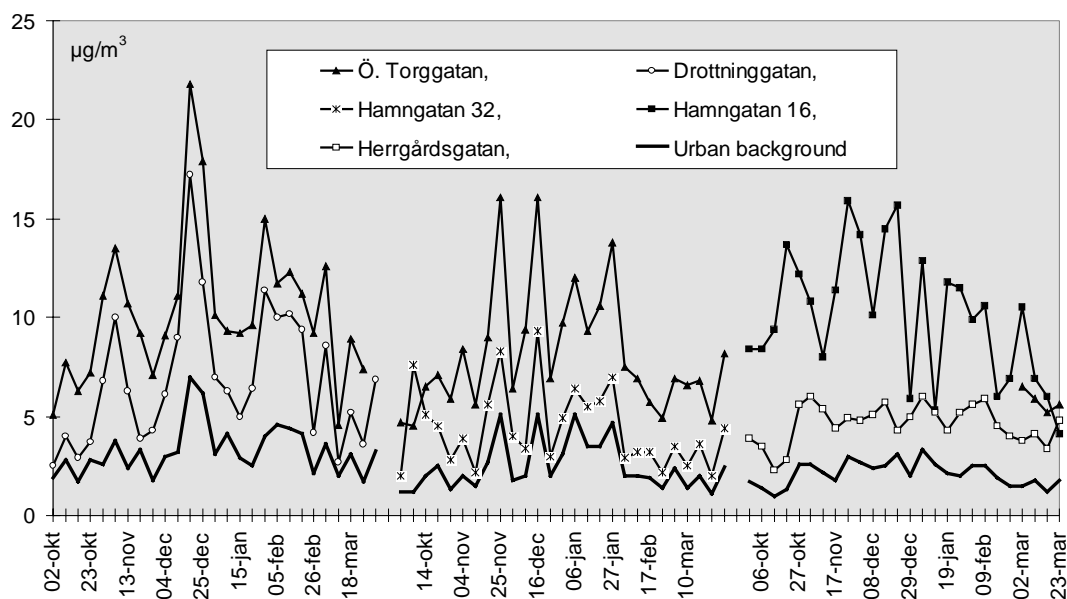
the case of benzene the long-term concentrations are more relevant than hourly peaks, and fortunately the average dispersion near streets depends less on the building configuration.

than the short-term dispersion. Also the traffic intensity, which strongly varies in the course of a day, can be regarded as a relatively constant source on a time scale of the order of a year. The influence of meteorology on pollutant dispersion in streets is generally smaller than on the dispersion of point source emissions. The moving traffic induces a considerable turbulence by itself, and also the mechanical turbulence generated by buildings lessens the effect of atmospheric stability variations. Due to the elongated shape of the traffic source the sensitivity of the concentration to wind direction is low compared to that of point sources.

The highest pollution levels are found in busy street canyons, relatively narrow streets between continuous buildings. Since the benzene emission per vehicle-kilometer decreases with speed, high levels can also occur in congested streets. Levels near highways are usually of less concern, because of the relatively low emission per vehicle-kilometer and the larger distance of the population from the traffic.

Within streets considerable concentration gradients in the annual average concentrations exist. At the traffic side of the kerb the concentrations are higher than at the other side. The differences depend on the street and building configuration. Also the dependence on (sampler) height is larger in streets than elsewhere, especially at the kerbside. Consequently, harmonisation of the micro-siting of measuring stations within a street is very important for compliance checking.

Figure 1-8 illustrates the effect of differences in traffic intensity as well as the influence from ventilation on benzene concentrations.



Station	Vehicles/day	Urban topography	Winter means, $\mu\text{g}/\text{m}^3$		
			95/96	96/97	97/98
Östra Torggatan	11 000	Street canyon	10.3	8.2	
Drottninggatan	7 200	Street canyon	6.9		
Hamngatan 32	12 700	Open street		4.4	
Hamngatan 16	17 500	Open street			10.0
Herrgårdsgatan	<2000	Narrow street canyon			4.6
Urban background		Open square, 4m	3.3	2.5	2.1

Figure 1-8 - Weekly means of benzene in different streets and urban background in Karlstad, Sweden during three winter half-years 1995/96 - 1997/98

1.4.2.3- Concentrations on the Industrial Scale

In the case of industrial emissions the resulting air concentrations of benzene are again dependent upon the emission strength and the meteorological situation. As explained above in the introduction, the contribution of industrial emissions to the total exposure of the population to benzene is generally low because the emission rates are relatively low and because the number of people exposed in the vicinity of the industrial environments is low. This is the case, for example, in Venice (Italy) where an extensive industrial area is located nearby a densely populated city sector (Mestre-Marghera).

High peaks in benzene concentrations can occur in depending on the meteorological situation and industrial activity. *Figure 1-9* shows an event which peaked

near $100 \mu\text{g}/\text{m}^3$ and was observed every 10-15 days. The duration of the event is limited to a few tens of minutes. Thus its contribution to total exposure is very low. It is suspected that the source of benzene, in this case, is breathing of industrial tanks. Fuel distribution can be excluded because no concurrent emission of toluene was observed.

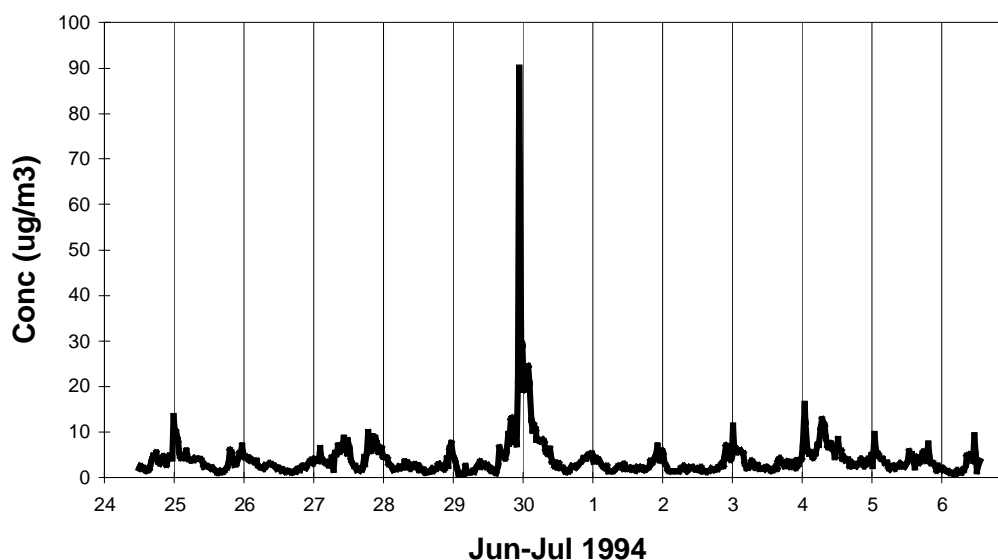


Figure 1-9 - An event of industrial pollution in Venice.

Source: CNR

Tables 1-XV and 1-XVI show benzene concentrations measured around two industrial sites in Germany; a cokery (Duisburg-Bruckhausen) and a distribution terminal in the harbour of big petrochemical plants.

Table 1-XV: Results of resampling of random samples of benzene from continuous measured time series.

Daily and 1/2-hourly means

Data: Cologne-Gordof; 1996; benzene; industrial site

Sample size	24-hourly values			1/2-hourly values		
	Mean value	Standard deviation	Standard deviation	Mean value	Standard deviation	Standard deviation
N	[$\mu\text{g}/\text{m}^3$]	[$\mu\text{g}/\text{m}^3$]	(%)	[$\mu\text{g}/\text{m}^3$]	[$\mu\text{g}/\text{m}^3$]	(%)
13	4.50	2.54	56.34	4.24	2.12	50.11
26	4.57	2.13	46.46	4.42	2.28	51.59
52	5.38	1.99	37.01	4.15	1.24	29.90
104	4.79	1.00	20.80	4.46	1.33	29.76
156	4.75	0.74	15.55	4.41	0.88	19.93
208	4.81	0.54	11.16	4.36	0.73	16.76
318	4.82	0.00	0.00	-	-	-
365	-	-	-	4.47	0.57	12.72

(Resampling from 318 valid daily mean values) (Resampling from 3135 valid 1/2 hourly values)

Table 1-XVI: Results of resampling of random samples of benzene from continuous measured time series. Weekly means

Cologne-Eifelwall, 1996, industrial site

Sample size	Mean values		
	Mean value	Standard deviation	Standard deviation
N	[$\mu\text{g}/\text{m}^3$]	[$\mu\text{g}/\text{m}^3$]	(%)
13	4.29	0.62	14.40
26	4.27	0.36	8.30
52	4.24	0.00	0.00

There is little systematic data on benzene concentrations around industrial sites, and although industrial sources in general do not play an important role in the exposure of the population, it is possible that in some locations such contributions could be significant and higher than those presented in these examples. More investigation is needed to ensure that the population is adequately protected.

1.4.3 – Trends in concentration

EC DGXI (1996) provides modelled estimates of benzene concentrations in seven cities, listed below in Table 1-XVII for 1990 and 2010 for urban background locations. The AEA Technology (1998, draft) report on the economic evaluation of limits for benzene provides data for 2010 for both urban background and kerb-side locations for three of these seven cities, integrating the effects of the legislation proposed following the completion of AOP1 and the proposed directive on air quality limits for SO₂, NO₂ and PM₁₀.

Based on different emission scenarios the benzene concentration in different cities has been calculated. Table 1-XVII represents the highest concentrations found in all 2 x 2 km cells of the 100 x 100 km domain modelled for each city. Results demonstrate that there should be a substantial reduction in benzene levels. It should of course be stressed that the results shown are modelled and subject to the compounded uncertainties of emission scenarios and other data inputs, model codes, etc. Particular uncertainty relates to the assessment of concentrations at kerb-side. Although the figures shown are prone to error, the trend and general magnitude of falling concentrations are likely to be robust.

Table 1-XVII - Modelled annual mean concentrations of benzene in seven cities in 1990 and 2010 based on different emission scenarios.

Source	EC DGXI (1996)	EC DGXI (1996)	AEAT (1998)	AEAT (1998)
Location	Urban	Urban	Urban	Kerb-side
Year	background	background	background	
	1990 (ug/m ³)	2010 (ug/m ³)	2010 (ug/m ³)	2010 (ug/m ³)
Athens	10.6	5.7	3.1	12.1
Cologne	7.8	2.8	1.6	6.3
Den Haag	6.2	2.3		
London	10.6	3.8	2.2	8.5
Lyon	10.3	4.4		
Madrid	11.4	4.8		
Milan	10.8	3.2		

1.5. - Current National Standards and Guidelines

Current National standards and guidelines in European Countries are summarised in the table below. Clearly, the legislation for benzene is largely insufficient since only a limited number of Countries have fixed values and a reference period of time. However, it is very important to observe that the recommended or the enforced standards are about 10 µg/m³ while the long-term guidelines are much lower.

Table 1-XVIII - Current National Standards and Guidelines

Country	Mean value for Time period	Concentration µg/m ³	Comments
Austria	annual	10	A long-term target value of 2.5 µg/m ³ has been proposed (no national legislation)
Belgium			
Denmark			

Finland				
France				
Germany	annual	15 a	10	(from 01/07/1998)
Great Britain	annual	16		recommended long-term goal of 1.3
Greece				
Italy	annual	15 a	10	(from 01/01/1999)
Liechtenstein				
Luxembourg				
Norway				
The Netherlands	annual	10	15 b	5 (guideline)
Portugal	annual	10	15	no nat.l legislation
Spain				
Sweden				1.3 (guideline)

Notes:

a: actual

b: for busy traffic situations

1.6 Summary

This chapter summarises knowledge about present day emissions and ambient concentrations of benzene in the European Union and expected trends.

It is pointed out that national emission data based on emission inventories may not be very accurate, and data from different Member States may not be directly comparable owing to different classification systems and methods of calculation. The results reported here are therefore subject to uncertainty. Clearly, better emission inventories are key elements for an effective benzene reduction program.

Combustion processes are the largest source of benzene in the atmosphere, with road traffic generally the biggest single source. Domestic combustion is an important source in some Member States.

Emissions of benzene have been declining in recent years, owing to legislation on vehicle emissions, industrial emissions and fuel distribution. The Air Quality Report of the first Auto-Oil Programme (AOP1) estimated a 56% reduction in urban emissions of benzene between 1990 and 2010. This did not include all the features of the final legislation adopted following AOP1 and work on other Air Quality Directives. These will lead to further reductions in emissions.

The air chemistry of benzene is discussed. Concentrations of benzene in the atmosphere depend not only on emissions, but also on local topographical and meteorological conditions. Generally speaking, concentrations tend to be highest in Mediterranean cities where windspeeds are normally low. Mountainous terrain can also lead to concentrations building up in a relatively stable airmass.

This chapter also presents data on concentrations within the European Union. There are relatively few data available and, as with emission inventories, results from different Member States are difficult to compare. In the absence of legislation on benzene there is no common agreement on methods used or on the siting of measurement stations. Generally speaking, concentrations are lowest in northern Europe and highest in southern Europe. Concentrations in heavily trafficked streets can be 3-5 times higher than in the urban background.

Concentrations are expected to fall by 2010. A study carried out by AEA Technology in parallel to the preparation of this paper suggests that annual average concentrations in the urban background should be less than $4 \mu\text{g}/\text{m}^3$ throughout the EU by 2010.

Finally, this chapter summarises current national ambient air quality standards for benzene.

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Umweltbundesamt

Berlin,

1997

Chapter 2

Benzene:

Risk Assessment

Preface

In this chapter the various health effects of benzene are described both in qualitative as well as in quantitative terms. The 1996 WHO Air Quality Guidelines for Europe are taken as the starting point for developing EC limit values. However, because the WHO document essentially considered published literature up to and including 1995, the present evaluation also addresses literature published since then, i.e. up to August 1997. In order to be able to distinguish between the WHO evaluation and the one presented here with respect to the considered literature and the conclusions arrived at, the WHO position will be referred to here as 'WHO (1996)' or '(WHO, 1996)'.

Internationally, different approaches are taken in performing risk assessment for chemical substances (Molenaar, 1994). These different approaches have lead to different limit values for the same substance, a situation that also holds for benzene. Therefore, to have a proper perspective on the recommended limit value presented here, some of these different approaches and limit values arrived at will also be presented here.

2.1. Human exposure to benzene

With respect to human exposure the main sources of benzene in air include cigarette smoke, combustion and evaporation of gasoline (which may contain up to 5% benzene), petrochemical industries, and combustion processes.

Daily mean ambient air concentrations of benzene in remote, rural, and urban areas are about 0.5, 1 and 5-80 $\mu\text{g}/\text{m}^3$, respectively (i.e. 0.16, 0.3 ppb and 1.6-6.3 ppb, respectively). Indoor and outdoor air levels may be higher near such sources of benzene emissions, such as major roadways and filling stations.

Inhalation is the dominant pathway for benzene exposure in humans. Intake of benzene by food and water is only a minor source. Smoking is a large source of personal exposure. High exposures can also occur during refuelling of automobiles; this activity, however, is of short duration, only infrequent, and, therefore, not substantially contributing to the integrated exposure dose. Extended travel in automobiles with elevated air benzene levels (from combustion and evaporative emissions) result in cumulative exposures that are second only to smoking. The contribution of this source to cumulative ambient benzene exposure may comprise about 30% when the travel time is one hour, an interval not untypical for urban and suburban commuting by the general population.

The average daily intake for an adult in Canada was estimated to be about 200 $\mu\text{g}/\text{day}$ in total: 14 μg from ambient air, 140 μg from indoor air, 1.4 μg each from food and drinking water and 50 μg from automobile-related activities. The corresponding calculated average daily intake in the USA is 320 μg , with a daily intake from ambient and indoor air ranging between 180 - 1300 μg . Cigarette smoking may add to that as much as 1800 $\mu\text{g}/\text{day}$ and passive smoking 50 $\mu\text{g}/\text{day}$. Driving a car during rush hours may give an additional significant intake of benzene, with mean values between 40 and 60 $\mu\text{g}/\text{m}^3$ (Wallace, 1989; Dor, 1995). Benzene concentrations in the interior of vehicles while driving have shown values of 10-120 $\mu\text{g}/\text{m}^3$, while refuelling exposures of 760 $\mu\text{g}/\text{m}^3$ (ranging from 0.01-2.7 mg/m^3), and 130 $\mu\text{g}/\text{m}^3$ (at a station with a vapour recovery system) have been reported. Based on assumptions of spending 2 hours per day in urban ambient air at 7 $\mu\text{g}/\text{m}^3$, 21 hours per day in indoor air at 4 $\mu\text{g}/\text{m}^3$, and 1 hour per day inside a vehicle at 50 $\mu\text{g}/\text{m}^3$ (typical for large roads and heavy traffic), calculated relative uptakes from urban ambient air, indoor air, air inside cars, and intake from food were 9; 53; 30 and 8%, respectively (WHO, 1996).

From the above it is clear that the diversity of general population residence, commuting, lifestyle and other activities leads to very different opportunities for benzene exposure, and herewith huge quantitative differences in actually experienced benzene exposures.

Personal inhalatory exposure to benzene was measured in a study carried out in Germany in 1990/1991 with 113 persons selected at random over the country. The geometric mean of personal exposure to benzene was found to be 11 $\mu\text{g}/\text{m}^3$, while the 95-percentile was 32 $\mu\text{g}/\text{m}^3$. About forty percent of the exposure could be explained by source, with 20% and 12% being related to passive smoking indoors and automobile-related activities (gas-filling and time in transit), respectively (WHO, 1996).

No clear statistical relationship was found between home front-door concentrations of benzene and personal exposure in rural areas whereas in urban areas front-door concentrations and personal exposure of benzene are highly correlated. However, there was only a small difference between the benzene exposure in rural and urban areas and thus the use of front-door concentrations of benzene as exposure surrogate will lead to misleading conclusions about the actual exposure (Raaschou-Nielsen et al, 1997).

2.2 Health Effects

2.2.1. The WHO 1996 Air Quality Guideline for benzene

In October 1996 the World Health Organisation adopted new Air Quality Guidelines for Europe. In developing the guideline for benzene, WHO considered published literature up to early 1995. Both health risk evaluation and Guideline paragraphs of this WHO document are described below.

2.2.1.1. Health risk evaluation

The most significant adverse effects from prolonged exposure to benzene are haematotoxicity, genotoxicity and carcinogenicity.

Chronic benzene exposure can result in bone marrow depression expressed as leucopenia, anaemia and/or thrombocytopenia, leading to pancytopenia and aplastic anaemia. Decreases in haematological cell counts and in bone marrow cellularity have been demonstrated in mice after inhalation of concentrations as low as 32 mg/m^3 for 25 weeks.

Rats are less sensitive than mice. In humans, haematological effects of varying severity have occurred in workers occupationally exposed to high levels of benzene. Decreased red and white blood cell counts have been reported above median levels of approximately 120 mg/m³, but not at 0.03-4.5 mg/m³. Below 32 mg/m³, there is only weak evidence for effects.

The genotoxicity of benzene has been extensively studied. Benzene does not induce gene mutations in in-vitro systems, but several studies have demonstrated induction of both numerical and structural chromosomal aberrations, sister chromatid exchanges, and micronuclei in experimental animals and humans after in-vivo benzene exposure. Some studies in humans have demonstrated chromosomal effects at mean workplace exposures as low as 4 to 7 mg/m³. The in-vivo data indicate that benzene is mutagenic.

The carcinogenicity of benzene has been established in both humans and in laboratory animals. An increased mortality from leukaemia has been demonstrated in workers occupationally exposed. Several types of tumours, primarily of epithelial origin, have been induced in mice and rats after oral exposure and inhalation exposure at 320-960 mg/m³; these include tumours in the Zymbal gland, liver, mammary gland and nasal cavity. Lymphomas /leukaemias have also been observed, but with lesser frequency. The results indicate that benzene is a multi-site carcinogen.

Because benzene is characterised as a genotoxic carcinogen and recent data gathered in humans and mice suggest mutagenic potential in vivo, establishment of exposure duration and concentration in the human exposure studies is of major importance for the calculation of cancer risk estimates. The Pliofilm cohort is the most thoroughly studied. It was noted that significant exposures to other substances at the studied facilities were probably not a complicating factor, but that exposure estimates for this cohort vary considerably. Three different exposure matrices have been used to describe the Pliofilm cohort, i.e., those reported by Crump and Allen (1984), by Rinsky et al. (1987), and a newer and more extensive one by Paustenbach et al. (1992).

The main difference between the first two is that the exposure estimates by Crump and Allen are greater for the early years during the 1940s. Paustenbach et al. (1992) have, among other things, considered short-term, high-level exposure, background concentrations and absorption through the skin, which leads to 3-5 times higher exposure levels than the ones by Rinsky et al (1987). Compared to the Crump and Allen (1984)

estimates, Paustenbach et al. (1992) arrives at higher exposure estimates for some job classifications, and lower for some others.

Within the most recently updated Pliofilm cohort, Paxton et al. (1994 a,b) conducted an extended regression analysis with exposure description for the 15 leukaemia cases and 650 controls. They used all three exposure matrices. The estimated numbers of cancer cases range from 0.26 - 1.3 excess cancer cases among 1000 workers at a benzene exposure of 1 ppm (3.2 mg/m³) for 40 years.

Crump (1994) calculated unit risk estimates for benzene using the most recently updated data for the Pliofilm cohort and a variety of models (Table 1). Multiplicative risk models were found to describe the cohort data better than additive risk models and cumulative exposure better than weighted exposures. Dose-responses were essentially linear when the Crump and Allen exposure matrix was used, but according to the author, there was evidence of concentration-dependent nonlinearity in dose-responses derived using the Paustenbach et al. exposure matrix. In that case, the best-fitting model was quadratic.

As can be seen in Table 1, the concentration-dependent model gives a much lower risk estimate than the other models when the Paustenbach exposure matrix is used. In such a model, the concentration of benzene is raised to the second power and thus given greater weight than the duration of exposure. Although there are biological arguments to support the use of a concentration-dependent model, much of the essential data are preliminary and need to be further developed and peer reviewed.

Models giving equal weight to concentration and duration of exposure have been preferred here for the derivation of a risk estimate. Using multiplicative risk estimates and a cumulative exposure model, Crump (1994) calculated a unit risk for lifetime exposure of $1.4 - 1.5 \times 10^{-5}$ with the Paustenbach exposure matrix and of 2.4×10^{-5} per ppb with the Crump and Allen exposure matrix. If expressed per $\mu\text{g}/\text{m}^3$, the unit risk would thus be $4.4 \times 10^{-6} - 7.5 \times 10^{-6}$. With an additive model instead of a multiplicative model, the risk estimate would have been somewhat smaller. If similar linear extrapolations were done on the occupational cancer risk estimates by Paxton et al. (Table 1), lower unit risks, by up to about an order of magnitude, would result.

2.2.1.2. WHO Guideline

Benzene is carcinogenic to humans and no safe level of exposure can be recommended.

For purposes of guideline derivation, the working group chose to use the 1994 risk calculation of Crump rather than to derive new estimates. It was recognised that the decision to use existing analyses of the most recently updated cohort ruled out inclusion of certain of the analyses noted earlier.

The geometric mean of the range of estimates of the excess lifetime risk of leukaemia at an air concentration of $1 \mu\text{g}/\text{m}^3$ is 6×10^{-6} . The concentrations of airborne benzene associated with an excess lifetime risk of 1/10,000, 1/100,000 and 1/1,000,000 are, respectively: 17, 1.7 and $0.17 \mu\text{g}/\text{m}^3$.

TABLE 1. Model-dependent worker risk and lifetime unit risk estimates for exposure to benzene for the Pliofilm cohort by Crump, 1994 ^a				
Risk Estimate	Linear	Nonlinear	Intensity Dependent	Exposure reference
Cases/1000 workers exposed to 3.2 mg/m ³ (1 ppm)	5.1	5.0	5.1	Crump and Allen, 1984
	3.8	2.9	0.036	Paustenbach et al., 1992
Unit risk ppb ⁻¹	2.4 x 10 ⁻⁵	2.4 x 10 ⁻⁵	2.4 x 10 ⁻⁵	Crump and Allen, 1984
	1.5 x 10 ⁻⁵	1.4 x 10 ⁻⁵	1.7 x 10 ⁻¹⁰	Paustenbach et al., 1992
Unit risk ^b (µg/m ³) ⁻¹	7.5 x 10 ⁻⁶	7.5 x 10 ⁻⁶	7.5 x 10 ⁻⁶	Crump and Allen, 1984
	4.7 x 10 ⁻⁶	4.4 x 10 ⁻⁶	5.3 x 10 ⁻¹¹	Paustenbach et al., 1992

a. Multiplicative risk model, cumulative exposure.

b. Calculated by converting ppb to µg/m³

2.2.2. New scientific information since WHO 1996

Since the work leading to the adoption of the WHO Guideline further work has been published. The paragraphs below describe this recent work, thereby focussing on issues identified as critical for this evaluation, i.e. haematotoxicity, genotoxicity and carcinogenicity. If considered necessary, the findings of the WHO document are shortly summarised.

2.2.2.1. Metabolism

The metabolism of benzene in animals and humans appears to be qualitatively similar (WHO, 1996; Snyder and Hedli, 1996). The oxidative metabolism occurs primarily in the liver through the cytochrome P-450 2E1 system (CYP 2E1). The assumed primary

reactive metabolite, benzene-oxide, was recently demonstrated in in vitro studies with mouse, rat, and human liver microsomes and appeared relatively stable (Lovern et al, 1997).

The major portion of benzene-oxide is non-enzymatically rearranged into phenol, which subsequently may be converted by enzymatic and/or non-enzymatic rearrangements into catechol, 1,2,4,-trihydroxybenzene, hydroquinone, and the ring-opened muconaldehyde (that may also be formed directly from benzene-oxide). Benzene-oxide may, on the other hand, also conjugate to glutathione, a detoxification pathway resulting in the excretion of mercapturic acids. Other detoxification pathways involve sulfation and glucuronidation of phenol, catechol, hydroquinone, and trihydroxybenzene.

Phenol is the predominant metabolite in humans and is excreted in urine as sulfate and glucuronide conjugates. Hydroquinone can be further oxidised to benzoquinone (Smith et al, 1989); this unstable and reactive benzene metabolite can be detoxified by conjugation to glutathione and reduction by NAD(P)H:quinone oxidoreductase (DT-diaphorase; NQO1).

Though the liver is a central organ in benzene metabolism, bone marrow, the target-organ for benzene-induced toxicity in both animals and humans (see paragraphs 2.2.2.1. and 2.2.3.1.), can also metabolise benzene into the above-mentioned metabolites. Myeloperoxidase (MPO) is the enzyme within the bone marrow that oxidises hydroquinone into the short-lived semiquinone radical intermediate and the reactive benzoquinone; bone marrow cells also have NQO1 (Schattenberg et al, 1994; Ross et al, 1996). The haematotoxicity of benzene probably relates to the relatively high concentrations of benzene metabolites that have been found in this haematopoietic compartment in experimental animals (Irons et al, 1980; Ganousis et al, 1992).

Mice have a greater overall capacity to metabolise benzene than rats and humans. Mice, also metabolise more benzene into hydroquinone than rats, which may partly explain the higher sensitivity of mice to benzene toxicity. In all species studied, a greater proportion of benzene is converted to hydroquinone and ring-opened metabolites at low doses than at high doses due to saturation of metabolism-routes, especially in the mouse (Henderson, 1996; Weisel et al, 1996; Rothman et al, 1996). The average half-time of benzene in humans is 28 hours (WHO, 1987). In rats and mice, metabolites are fully excreted in the urine within 40 h of dosing by any route of administration (WHO, 1993).

For two critical enzymes in benzene metabolism, i.e. CYP2E1 and NQO1, polymorphisms have been observed (Hayashi et al, 1991; Uematsu et al, 1991; Ross et al,

1996). The consequences of this on benzene-induced toxicities will be discussed in paragraph 2.2.3.1..

Toxico-kinetic and -dynamic models, some physiologically based, have been developed for rats and mice and some are used for risk assessments based on animal cancer data (WHO, 1996; Cox, 1996). However, very different time patterns of benzene dose administration that, unexpectedly, result in the same blood AUC (area under the curve) for benzene, still produce different profiles of benzene metabolites (Crump and Allen, 1984; Watanabe et al, 1994), and unpredictable haematotoxic effects (Green, 1981), partly due to some yet unclear metabolite interactions (Medinsky et al, 1996; Snyder and Hedli, 1996). Additionally, kinetic data in humans are sparse (only some data on blood and urinary levels of benzene and its metabolites are available), the type of leukaemia found in animals differs from that found in man, and the underlying dynamic processes haven't been sufficiently resolved yet. Therefore, to date there are insufficient grounds for the use of these models in cancer risk assessments for humans.

With respect to human biomonitoring, a correlation is found between phenol excretion in urine and a high exposure level of benzene (above 10 ppm, or 32 mg/m³). At lower concentrations the integrated benzene exposure is reflected in the amount of benzene excreted in breath (WHO, 1987). Also, urinary levels of unmetabolized benzene have been found a reliable indicator at these lower exposures (Kok et al, 1996). Of the urinary metabolites of benzene, levels of the benzene-specific metabolite trans, trans-muconic acid, and of S-phenylmercapturic acid appeared more reliable exposure indicators than the levels of phenolic metabolites, i.e. at exposure levels down to 0.1 ppm (Popp et al, 1994; Melikian et al, 1994; Boogaard and van Sittert, 1996; Hotz et al, 1997).

The excretion of 8-hydroxydeoxy-guanosine, a form of oxidative DNA-damage induced by benzene (see paragraph 2.2.2.2.), correlated with benzene exposure in petrol filling station attendants (Lagorio et al, 1994), and may even be detected at exposure levels as low as 0.13 ppm (i.e. 8 hours time weighted average ; 8h TWA; Nilsson et al, 1996).

2.2.2.2. Effects on experimental animals and *in vitro* test systems

2.2.2.2.1. Haematotoxicity

The myelotoxicity of benzene in animal species seems to be the result of relatively high concentrations of metabolites in the bone marrow on the one hand, and their (in)direct toxicological properties on the other. The ability of bone marrow cells to metabolise benzene and the resultant local high concentrations of metabolites has been demonstrated for mice and rats by Irons et al (1980) and Ganousis et al (1992), respectively. One reason for this is the presence in this tissue in both animals and humans of relatively high peroxidase levels (i.e. MPO), an enzyme that catalyses the conversion of hydroquinone to benzoquinone (Schattenberger et al, 1994), but also the observation that phenol apparently acts as an activator of this peroxidase-catalysed reaction (Medinsky et al, 1996).

The mechanism underlying this bone marrow toxicity is still not clearly elucidated. Several potential mechanisms can be provided. It may be due to the binding of reactive metabolites of benzene to macromolecules, i.e. proteins and DNA (see paragraph 2.2.2.2.). On the other hand, some of these metabolites are capable of generating reactive oxygen species (Kolachana et al, 1993; Zhang et al, 1993; Shen et al, 1996), that themselves may induce the toxic response (Parke and Sapota, 1996). Finally, benzene metabolites were shown to directly or indirectly modulate various cytokine- and growthfactor routes in animal and human bone marrow culture cells, though the underlying mechanisms are not resolved (Kalf et al, 1996; Hazel et al, 1996; Irons and Stillman, 1996; Farris et al, 1997). Thus, after inhalation of 320 mg/m³ or higher for one or several weeks a substantial increase in apoptosis was observed in bone marrow B- and thymic T-lymphocytes, together with a compensatory-like replication of primitive progenitor cells in the bone marrow of mice (Farris et al, 1997). Of course, benzene-induced haematotoxicity and myelodysplastic syndromes may be due to particularly one or a combination of these above mentioned mechanisms (Pryatt et al, 1996), and may also be dependent upon the exposure level.

2.2.2.2.2. Genotoxicity

Interaction with DNA.

Whereas metabolites of benzene were shown to be able to form covalent adducts in mammalian and human cells in vitro, such adduct formation in vivo could not be demonstrated for relevant human exposure routes (WHO,1996; Levay and Bodell, 1992; 1996). Since then, Pathak and co-workers were able to demonstrate DNA adduct formation in mouse bone marrow cells and lymphocytes after twice daily high i.p. doses of benzene

(440 mg/kg), but not after single applications of the same total daily dose (Pathak et al, 1995; Levay et al, 1996); these adducts were similar to those found after in vitro treatment of mouse bone marrow cells with hydroquinone (Bodell et al, 1996). Tuo et al (1996), using the alkaline Comet assay, also demonstrated genotoxic effects in bone marrow cells in mice after a single oral dose of 40 mg/kg.

Interaction with DNA-handling proteins.

Benzoquinone and p-biphenoloquinone covalently bind to cysteinyl-groups of mammalian microtubule proteins under cell free conditions (Pfeiffer and Metzler, 1996). Probably by alkylating this same cysteinyl-group hydroquinone, benzoquinone and trans,trans-muconaldehyde, among others, inhibit human topoisomerase II in vitro (Chen and Eastmond, 1995; Hutt and Kalf, 1996; Frantz et al, 1996).

Mutations in vitro.

Tsutsui found a very weak mutation induction by benzene at the TK and HPRT loci in SHE cells (Tsutsui et al, 1997).

The benzene metabolites hydroquinone and the ring-opened trans, trans-muconaldehyde were only very weakly mutagenic in Salmonella tester strain TA 104 (Hakura et al, 1996). The benzene metabolites catechol, and to a lesser extent hydroquinone and phenol gave a very weak induction of mutations in TK and HPRT loci in SHE cells (Tsutsui et al, 1997).

Chromosomal effects in vitro.

Next to its potential of inducing structural chromosomal aberrations in mammalian cell cultures (WHO,1996), benzene was also demonstrated to induce aneuploidy in SHE cells (Tsutsui et al, 1997).

Besides inducing micronuclei and SCE in mammalian cells (WHO,1996), several metabolites of benzene were since then shown to induce aneuploidy in mammalian cells: catechol in SHE cells (Tsutsui et al, 1997), 1,2,3-trihydroxybenzene in a HL-60 cell line (promyelocytic human leukaemic cells; Zhang et al, 1994), and hydroquinone both in cultured human lymphocytes (Eastmond et al, 1994), and in the human lymphoblast cell line GM09984 (Stillman et al, 1997).

Mutations in vivo.

Since the results reported by WHO in 1996, two additional studies have appeared. Using *Lac I* transgenic mice Provost et al (1996) found significant increases of

Lac I mutation frequencies in tissues of spleen and bone marrow, but not of lung in B6C3F1 mice exposed to 200-750 mg/kg by gavage.

Using their p^{un}/p^{un} C57BL/6 mice Schiestl et al (1997) observed deletion type mutations in a *pun* duplicated sequence in the offspring upon i.p. injection of 200 mg/kg benzene.

Chromosomal effects in vivo.

Benzene and some of its metabolites can induce structural and numerical chromosome aberrations, SCE and micronuclei by various routes of exposure (WHO, 1993). Most studies were performed with fairly high concentrations. More recently this finding was strengthened by Farris et al (1996) who observed an induction of micronuclei in mice after a 6 weeks exposure to 100 ppm, but not to 10 ppm of benzene.

Interestingly, Angelosanto et al (1996) found micronuclei in a target tissue for benzene-induced carcinogenesis, i.e. the rat Zymbal gland.

WHO (1996) reported that benzene was negative in dominant lethal tests with mice and rats. However, some other studies were demonstrating transplacental cytogenetic effects in mice. Of several metabolites tested, only hydroquinone gave rise to micronuclei in foetal cells of mice (WHO, 1996).

2.2.2.2.3. Carcinogenicity

Benzene has been shown to be carcinogenic in mice and rats in several studies. Various types of lymphomas/leukaemias have been found, but the majority of neoplasms are of epithelial origin (WHO, 1993 & 1996). This pattern of target organs may at least partly be explained by the fact that organs like bone marrow, Zymbal gland, and Harderian gland contain peroxidases, which activate phenols to toxic quinones and free radicals, and contain high levels of sulfatases, which can deconjugate sulfate-conjugated phenols (Low et al, 1995).

Since then benzene was tested for carcinogenicity only in a transgenic mouse model, i.e. Eμ-pim-1 mice, known to have increased sensitivity towards lymphomagens (Breuer et al, 1989). Unexpectedly, benzene appeared negative in this transgenic mouse model (Störer et al, 1995).

2.2.2.3. Effects on humans

2.2.2.3.1. Haematotoxicity

Several types of blood dyscrasias, including pancytopenia, aplastic anaemia, thrombocyto-penia, granulocytopenia and lymphocytopenia have been noted after exposure to benzene. As in experimental animals, the primary target organ of benzene that results in haematological changes is the bone marrow. It has been suggested that the cells at highest risk are the rapidly proliferating stem cells (WHO, 1993).

In an evaluation of the literature data, a WHO Task Group (WHO, 1993) drew the conclusion that bone marrow depression or anaemia would not be expected to occur in workers exposed for 10 years to 3.2 mg/m³ (1 ppm) or less. This is supported by recent observations by Collins et al (1997) showing no increase in the prevalence of lymphopenia (considered the earliest and most sensitive indicator of benzene haematotoxicity) among workers exposed to an 8h TWA of 0.55 ppm.

There are multiple clinical reports suggesting people vary greatly in their susceptibility to adverse health outcomes from benzene exposure (Aksoy, 1988). Individuals experiencing this so-called 'benzene poisoning' also appear to have a substantially increased risk for haematological disorders (myelodysplastic syndromes) and malignancies (Yin et al, 1987). One reason for this could be inter-individual variation in metabolic activation and/or detoxification. Indeed, recent studies have found an association between this benzene poisoning phenomenon and specific activities of critical metabolic routes: i.e. people carrying a specific mutation in the NQO1 gene. CYP2E1 polymorphism did not appear to influence occupational benzene poisoning risk (Ross et al, 1996; Rothman et al, 1997).

2.2.2.3.2. Genotoxicity

Interaction with DNA

So far, there have been no published reports of specific DNA adduct formation in tissues of benzene exposed individuals.

Nilsson et al (1996) also found a small, though not significant increase in DNA strand breaks in leukocytes in the same subjects. At similar exposure levels Andreoli et al (1997) found increased DNA damage, assayed by the alkaline single cell electrophoresis assay, in gasoline station workers as compared to controls.

Mutations

WHO (1996) described one somatic mutation assay as an endpoint in benzene exposed humans, i.e. the glycophorin A (GPA) mutation assay reported by Rothman et al (1995). These authors studied heavily benzene-exposed workers (8h TWA of 31 ppm) and their results suggests that benzene induces gene-duplicating mutations, presumably through recombination events, but not gene-inactivating mutations due to point mutations or deletions.

Since then no new reports have appeared within this field.

Chromosomal effects

Both structural and numerical chromosome aberrations have been observed in workers exposed to benzene levels down to around 10 ppm; the exposure levels were in most cases high enough to produce haematological effects as well (WHO, 1996; Zhang et al (1996). In a recent study involving people exposed to relatively low benzene exposure levels, i.e. 8h TWA around 1 ppm, no increases in chromosome aberrations (measured as micronuclei) were observed in lymphocytes and buccal cells (Surrallés et al, 1997).

2.2.2.3.3. Carcinogenicity

Several clinical and epidemiological studies have shown that long-term exposure to benzene can lead to leukaemia. Consequently, benzene has been classified as a human carcinogen (Group 1) by IARC (1982).

An evaluation of the epidemiological evidence made by WHO (1996) is described in paragraph 2.1. of this chapter. Literature published since that described by WHO (1996) will be outlined below.

Schnatter et al (1996a) used a different approach than that used by a.o. Crump (1994), who calculated unit risks for lifetime exposure to 1 $\mu\text{g}/\text{m}^3$ in analysing the Pliofilm cohort (see WHO, 1996). Schnatter et al (1996a) allocated workers into specific exposure-concentration categories, i.e. 0-260 ppm, based on their maximally exposed job/department combination over time and the associated long-term average concentration. Their analysis suggests that critical concentrations of benzene exposure must be reached, i.e. 50-60 ppm (for median exposure estimates) or 20-25 ppm (for lowest exposure estimate), in order for the risk of leukaemia or, more specifically acute myeloid leukaemia, to be expressed.

In a cohort of 4172 workers of a chemical plant having exposures up to 632 ppm-years positive SMR's for leukaemias (general, chronic lymphatic, and acute nonlymphatic) as well as elevated rates of central nervous system cancers (Ireland et al, 1997) were found, though there was no trend with increasing cumulative exposure.

A large study from China encompasses 28460 workers, employed in a variety of occupations including coating applications, rubber plants, chemical industries, and shoe production in 12 cities between 1972-1981 (Yin et al, 1987; 1989). There were 25 cases of leukaemia (mainly acute forms) compared to 4 cases in a control population consisting of 23257 unexposed workers in other factories in the same cities (SMR=574). There was also a significant increase in lung cancer (SMR=231) (Yin et al, 1989). In a follow-up, the cohort has been expanded to include 74828 benzene-exposed and 35805 unexposed workers employed for any length of time during 1972-1987 in 712 factories in 12 cities (Travis et al, 1994; Dosimeci et al, 1994, 1996; Li et al, 1994; Yin et al, 1994, 1996a,1996b; Hayes et al, 1996, 1997). This cohort somewhat differs from the other cohorts discussed here in that the studied worker-years were relatively young, i.e. 60% of the person-years were from below the age of 30, and about 50% of the them represented females. The observed numbers of leukaemia cases were 49 in the exposed population (mainly acute forms) and 9 cases in unexposed workers. Statistically significant increases were observed for acute myelogenous leukaemia (RR=3.1), malignant lymphoma (RR=4.5), and lung cancer among males (i.e. in lung, trachea, and bronchus combined; RR=1.4). Haematopoietic malignancies as a group were also found to be significantly increased at estimated cumulative exposures below 10 ppm-years (RR=2.5; Hayes et al, 1996). Non-significant excesses were also noted for chronic myelogenous leukaemia and acute lymphocytic leukaemia. Eighteen cases of non-malignant haematolymphoproliferative disorders were observed in exposed workers only, among which a significant number of 9 cases of aplastic anaemia.

In a recent paper, Hayes et al (1997) found increased risks for the combination of acute myeloid leukaemia and related myelodysplastic syndromes (RR=3.2) at average benzene levels of less than 10 ppm, though 95%-confidence intervals were still fairly broad. For this combination of pathological lesions they also found a link with especially recent exposure, i.e. during the last ten years. Despite the statistical potential the size of this cohort offers, large uncertainties exist with respect to the experienced exposures. Only very few historical benzene measurements were available, especially for the first 25 years, i.e. from 1949 to 1975 (Dosimeci et al, 1996). Exposure estimates for certain job/calendar periods ranged from < 1 ppm to > 50 ppm, and cumulative exposure estimates ranged from <10 to

> 400 ppm-years. Estimates of the exposure to benzene were highest for the rubber and plastics industry (100 mg/m³), and for rubber glue applicators (170 mg/m³; Dosemeci et al, 1994).

In order to get more confidence to these exposure estimates, Dosemeci et al (1996) have tried to validate their exposure assessment method indirectly by verifying its relationship with cases of clinically diagnosed benzene poisoning. Although the authors claim their results to suggest that the estimated exposure values are valid enough, exposures of individual cases remain uncertain. Risk assessments, e.g. estimates of additional lifetime risk from 45 years of exposure to 1 ppm benzene using best-fitting models, haven't been provided yet. Because of the relatively young mean age of workers that entered the cohort and the still existing relatively high benzene concentrations, future follow-ups of this cohort may provide valuable information on quantitative risks associated with these benzene exposure.

In case-control studies on petroleum refinery workers by Schnatter et al (1996b), Clavel et al (1996), and Rushton and Romaniuk (1997) no increased risk with cumulative benzene exposures was found for the 31, 226, and 91 cases, respectively. Rushton and Romaniuk (1997) found indications for a relation between acute myeloid leukaemia risk and peak exposures. However, exposure levels in these studies were generally low. In the studies by Schnatter et al cumulative exposures varied from 0 to 220 ppm-years (with daily average exposures from 0.01 to 6.2 ppm). A similar range of cumulative exposures were found in the Rushton and Romaniuk study, though for 81% of the cases this was below 5 ppm-years. Cumulative exposures did not exceed 45 ppm-years in the study by Clavel et al (with mean exposures of 0.2 ppm).

In order to have sufficient numbers of leukaemia and to be able to analyse tumours specifically by cell-type, Wong and Raabe (1995; Raabe and Wong, 1996) combined all cohort studies of petroleum workers in the US and United Kingdom. This combined cohort consisted of more than 208000 workers, which represented over 4.6 million person-years of observation. Based on a meta-analysis of the combined data, using national populations as controls, the SMR for acute myeloid leukaemia was 0.96. Also, no increased risk of other types of leukaemia were observed. Stratified analyses of refinery studies only or to studies with at least 15 years of follow-up yielded similar results. Mean measured exposure levels for general plant operations at petroleum refineries were generally low, i.e. < 1 ppm for 60% of the subjects. Mean measured levels in the US were 0.22 ppm (0.7 mg/m³; Runion, 1988).

Jakobsson et al (1993) reported an excess risk of acute myeloid leukaemia among male petrol station attendants, using occupational information obtained from the Swedish 1970 census and follow-up in the Swedish Cancer Register from 1971-1984 (WHO, 1996). This cohort was updated up to 1987 by Lynge et al (1997), and expanded with cohorts of service station workers from Norway, Finland, and Denmark, resulting in a total of 19,000 workers. Estimates of mean exposures experienced were 0.5-1.0 ppm (as an 8h TWA) for all workers. For male Swedish workers (i.e. those involved in fuel retailing) that represented about 50% of the total number of male person-years in this Nordic cohort, no increased risk for leukaemia, but again an increased risk of acute myeloid leukaemia was observed (compared to national incidence rates), i.e. 8 observed versus 3.86 expected (SIR=2.1). For this cohort as a whole, however, no increased risk for leukaemia, nor for acute myeloid leukaemia was observed. Other specific findings were slightly increased risks for kidney, pharyngeal, laryngeal, and lung cancer (SIR's of 1.3, 1.6, 1.4, and 1.2 respectively), and a clear previously unnoticed risk of nasal cancer (SIR=3.5).

It should be noticed here, that there are multiple clinical reports suggesting that people vary greatly in their susceptibility to adverse health outcomes from benzene exposure (Aksoy, 1988). Individuals experiencing this so-called 'benzene poisoning' also appear to have a substantially increased risk of developing haematological disorders (myelodysplastic syndromes) and malignancies (Yin et al, 1987). Reasons for variations in susceptibility to benzene-induced adverse effects probably rely in inter-individual variations (polymorphisms) in benzene metabolising enzymes (Rothman, 1997).

2.3. National and other Health-based Air Quality Guidelines

A number of Member States and other countries have developed guidelines and standards for benzene in ambient air. Various methodologies have been adopted.

2.3.1. On National basis

Austria

The Austrian Academy of Science has developed air quality criteria for selected VOCs including benzene. It concluded that:

- there is sufficient evidence to classify benzene as carcinogenic to humans
- no safe threshold can currently be derived

- linear regression analysis indicates a risk between 4 and 8×10^{-6} (per annum [*is this correct?*] and $\mu\text{g}/\text{m}^3$)

From this risk assessment a target value of $2.5 \mu\text{g}/\text{m}^3$ (annual mean) was derived as a long-term goal

France

The French National Health Council assessed the risks of benzene in 1997. They recommended two limit values, to protect against different effects.

- **Effects on the lymphohaematopoietic system:** In order to protect against a number of effects including depression in numbers of lymphocytes and red cells, and a reduction in immune function the Council applied safety factors to a Lowest Observed Adverse Effects Level of 10 ppm. Applying the classic security factors of 10 for interspecies variation, 10 for intraspecies variation and 10 for use of a LOAEL gives a guideline of $50 \mu\text{g}/\text{m}^3$ as a 24 hour value. A further factor of 2 was applied for infants and pregnant women who constitute a susceptible population for these risks. The final recommended limit value is therefore $25 \mu\text{g}/\text{m}^3$.
- **Carcinogenic effects:** The Council based its conclusions on the recent analysis of the WHO with respect to leukaemia and on consideration of a large study in China (Yin, 1996). Taking the risk factors from these analyses led to the conclusion that exposure to benzene (including exposure from tobacco smoke) is at present responsible for 62 - 152 cases of leukaemia per year and 38 - 90 cases of lymphoma. This represents 2% of total deaths due to these diseases. They recommended an annual limit value of $10 \mu\text{g}/\text{m}^3$ to take effect immediately, and a target of $1.7 \mu\text{g}/\text{m}^3$, corresponding to an additional risk of contracting leukaemia of 1×10^{-5} . This latter value could be rounded to $2 \mu\text{g}/\text{m}^3$.

Germany

The ministers for the environment of the German States have proposed guide values (annual means) for benzene of 6.3 and $2.5 \mu\text{g}/\text{m}^3$, respect. An exceedance of the first value stipulates further examinations in the licence procedure for new benzene emitting plants under the rule of the Federal Ambient Air Protection Law. The second (lower) annual mean should be striven at in air quality management plans.

These guide values are not legally binding and were until now not transferred into national legislation. There is, however, a binding limit value of 10 µg/m³ (from July 1998 onwards), which stipulates, if exceeded, the examination of reduction measures at traffic hot spots with adjacent living quarters or other long term exposition (compare chapter 1.5).

The model underlying the proposed guide values of 6.3 and 2.5 µg/m³ takes into consideration the existence of seven carcinogens with major importance for ambient air and strives at the limitation of the total (summed up) risk caused by these carcinogenic compounds (Länderausschuß für Immissionsschutz, 1992). Together with certain reserves for other carcinogens, which may have possibly to be regulated at a later stage, the additive risk of the first set of guide values corresponds to a total risk of 1:1,000 and of the second set to 1:2,500, respect. For benzene a unit risk of $9 \cdot 10^{-6}$ was assumed, which is well within the range discussed in this paper.

Corresponding to the dual strategy of ambient air quality standard setting and emission control, strict emission standards have been set for the licence procedure of industrial facilities (5 mg/m³ benzene for installations emitting more than 25 g/h). This strict emission standard follows the principle of minimisation, which states that the emissions of carcinogenic substances in waste gases shall be limited to the largest possible extent by giving consideration to the principle of proportion (Art. 2.3 of the Technical Instructions on Air Quality Control).

The Netherlands

In 1987, a Health Council Committee (Health Council of The Netherlands, 1997) ruled that benzene is carcinogenic. Benzene has a very special place among those substances, which the Council has ruled to be carcinogenic. On the one hand, the underlying mechanism of carcinogenicity is very poorly understood, while on the other hand, an exceptionally large amount of high-quality epidemiological data is available.

In accordance with the classification system used in 1987 (which still applies today) to evaluate substances for carcinogenic properties (Health Council of The Netherlands, 1994), including the derivation of a toxicology-based recommended exposure limit, it is essential that the mechanism of carcinogenicity be identified. This classification system distinguishes two distinct types: carcinogens with a stochastic mechanism of action,

which do not have a fixed exposure level at, or below, which the cancer risk is zero, and carcinogens with a non-stochastic mechanism of action, which do have such concentrations (thresholds).

In 1987 there was no doubt about whether benzene was carcinogenic in humans or whether its carcinogenicity was based on a genotoxic effect (the capacity to irreversibly modify the information stored in DNA). What was unclear, however, was whether this mechanism of action was stochastic or non-stochastic in nature. At the time, caution dictated that a stochastic mechanism of action be presumed. The "linear extrapolation" required in such cases to estimate the concentration corresponding to a particular probability of cancer, could be carried out using the results of epidemiological studies. These findings consisted of data on the cancer risk of employees who had experienced long-term exposure to an average of 128 mg of benzene per m³ of air. In 1987, the Committee ruled that such an approach could be assumed (on the basis of specific aspects of the available data) to produce overly safe results, i.e. results that were "excessively low". They accordingly arrived at a recommended exposure limit of 12 µg of benzene per m³ of outdoor air, one hundred times greater than the figure derived using linear extrapolation.

A decade later, benzene is once again being evaluated by the Committee, at the request of the Minister of Health, Welfare and Sport and the Minister of Housing, Spatial Planning and the Environment. There appears to be a great deal of new data, particularly concerning the mechanism of action and the probability of cancer occurring among individuals exposed to benzene.

While this new data has provided much greater insight into the mechanism of the carcinogenic and genotoxic effect, there are still significant gaps in knowledge. However, the available data does highlight the fact that benzene is a genotoxic carcinogen with an "unusual" genotoxicity profile. This is because genotoxicity tests and research into its interaction with DNA have demonstrated that benzene reacts differently to other genotoxic carcinogens. The reason for this, however, is unclear. On the basis of the available data, the Committee is unable to determine whether or not benzene has a stochastic mechanism of action. Accordingly, they feel that the approach adopted in 1987 is still the soundest option available. Nevertheless, there are now grounds for a rigorous re-appraisal of the logic, which assesses the results of linear extrapolation as being too low. One such development is the availability of new epidemiological data derived from a large scale study involving a group of employees in the petrochemical industry. This study is particularly significant because of the size of the group (208,000 individuals) and the

benzene concentration (an average of 0.7 mg of benzene per m³ of air) involved. The results showed that there was no increase in the probability of acquiring the type of cancer attributed to benzene, namely acute non-lymphatic leukaemia.

The concentration value was adapted to allow the figures to be applied to the general population, who experience continual, lifelong exposure. The resultant value was 35 µg per m³. This figure, in the Committee's view, lends support to its assumption that the exposure-response curve in the relevant range for extrapolation is sub-linear rather than linear. It is not possible, however, to derive the exact configuration of the exposure-response curve using currently available data. The above-mentioned concentration is approximately three times greater than that contained in the toxicology-based recommended exposure limit proposed a decade ago. The latter corresponds to an "accepted" (extra) risk of one case of acute non-lymphatic leukaemia per million mortalities, namely 12 µg of benzene per m³ of outdoor air. Accordingly, the Committee feels that the above-mentioned toxicology-based recommended exposure limit is still sound.

Sweden

At the request of the Swedish Environmental Protection Agency a health risk evaluation of benzene was performed by the Institute of Environmental Medicine in 1994, and a guideline value for ambient air was recommended (Swedish Institute of Environmental Medicine, 1994).

It was stated that epidemiological studies have shown that exposure to benzene may lead to leukaemia, especially acute myeloid leukaemia, but it was also noted that an increased incidence of all lymphatic and haematopoietic cancer and of multiple myeloma, as well as lung cancer, was reported in some studies. Animal experiments have shown that benzene may give rise to many different tumour forms in rats and mice.

Although at that time a mutagenic activity of benzene had not been demonstrated, benzene was regarded as a genotoxic compound because of its DNA damaging activity. As a consequence, the Swedish risk assessment was based on quantitative extrapolation of cancer risks. Calculations of unit risks for the general population were done based on published occupational risk estimates from the Pliofilm cohort (Rinsky et al, 1987, Paxton et al, 1994 a,b, Crump, 1994) and ranged between 3.4×10^{-6} - 2.7×10^{-5} per ppb. The more conservative of the unit risk estimates for leukaemia by Crump (1994) was used in the final evaluation (2.4×10^{-5} per ppb equal to 7.5×10^{-6} per µg/m³ with a multiplicative risk model, cumulative exposure and exposure matrix according

to Crump and Allen 1984). As benzene was regarded as genotoxic the so-called intensity-dependent model, which would give a unit risk estimate several orders of magnitude lower, was considered as biologically less relevant. The recommended guideline value was set at the concentration that would correspond to an increased lifetime risk of leukaemia of 1×10^{-5} , that is 0.4 ppb or $1.3 \mu\text{g}/\text{m}^3$ as a long-term average.

Based on the increased risk of leukaemia, leukaemia/lymphoma, lymphoma, zymbal gland / carcinomas, squamous cell carcinomas or alveolar/bronchial carcinomas in animal / experiments, different models would yield a theoretical human cancer risk of 1×10^{-5} at 0.2-50 ppb. As the lower part of this interval was considered to be the most relevant one, a conservative risk assessment based on animal data was said to be in concordance with the one based on human data.

The recommended guideline value of $1.3 \mu\text{g}/\text{m}^3$ has not been transformed into formal standards, but it has been used for comparison with actual pollution levels in urban areas, and it was also put forward as a target (rounded to $1 \mu\text{g}/\text{m}^3$) by a recent Governmental Commission on Environmental Health. In this case it was also regarded as an indicator of carcinogenic volatile hydrocarbons in ambient air.

UK Guideline

An Expert Panel on Air Quality Standards (UK, 1994) has concluded that benzene increased the risk of certain types of leukaemia in workers in certain industries with heavy exposure to benzene. Studies in laboratory animals have shown similar effects, and have suggested moreover that benzene exerts its effects by damaging the genetic make-up of cells - in other words it is a genotoxic carcinogen. This means that it is impossible to determine a concentration to which people might be exposed at which there is no risk detectable by existing methods. Still, the Panel believed that it is feasible to recommend an air quality standard which presents a risk to the UK population which is exceedingly small and unlikely to be detectable by any practical method.

For purpose of guideline derivation, the Pliofilm cohort (Rinsky et al, 1987) and a cohort considering workers in chemical industries by Wong (1987) were evaluated (see paragraph 2.2.2.3.3.). From these studies it was concluded that the risk of leukaemia in workers was not detectable when average exposures over a working life were around 500 ppb (i.e. $1.6 \text{ mg}/\text{m}^3$). Taking a factor of 10 to correct for working life versus lifetime, and a factor 10 for intraspecies differences (in the absence of any suitable data), the Panel arrived at a recommended Air Quality Standard of 5 ppb (i.e. $16 \mu\text{g}/\text{m}^3$), measured as a running

annual average. The Panel noted that past exposures were only approximated and likely underestimated, thus probably overestimating the likely risk. Nonetheless it was stated that the Panel recognised that current average concentrations of benzene in the UK's air (which rarely exceed this concentration) present an exceedingly small risk to health. Also, the Panel further recommended a target Standard of 1 ppb (3.2 µg/m³), bearing in mind that benzene is a genotoxic carcinogen and, in principle, exposure to such substances should be kept as low as practical.

USEPA (Update of 1985 interim risk assessment)

The US.EPA has recently reviewed the evidence relating to the risks of benzene. Their conclusion is that there is insufficient evidence to reject a linear dose-response curve for benzene at low-dose exposures and that the approach of using a linear dose-response curve is still to be recommended. They give a range of risk estimates for leukaemia at 1 µg/m³ from 2.5×10^{-6} to 7.1×10^{-6} . The WHO risk estimate is within this range.

2.3.2. Methodology proposed by Industry

Of the various leukaemias encountered in occupational settings with benzene exposure, only acute myeloid leukaemia is clearly linked to this agent. Recent data on acute myeloid leukaemia induced by therapeutic treatment indicate that benzene leukaemogenesis is a complex multi-step process (Irons and Stillman, 1996), involving both cytotoxic and cytogenetic mechanisms. Recent research on the mechanism of benzene induced leukaemogenesis further supports this concept. The myeloid progenitor stem cells are uniquely susceptible to certain benzene metabolites resulting in premature cell proliferation and initiation of the leukaemogenic process leading to acute myeloid leukaemia.

Other cell lines, which give rise to other leukaemias, lack the *in situ* cell chemistry to form and retain the toxic benzene metabolites (Kalf et al, 1996; Hazel and Kalf, 1996; Farris et al, 1997). It is assumed that an early event in acute myeloid leukaemia is the induction of proliferation of early multipotent myeloid cells and premature proliferation of progenitor cells by quinone metabolites. Subsequently, during this cell division phase (i.e. in a more susceptible condition) these quinone metabolites and other benzene metabolites cause both genetic and epigenetic effects: including mitotic spindle interaction and topoisomerase II inhibition, which are consistent with clastogenicity and leukaemogenesis (Concawe, 1996).

This concept is not consistent with the one-hit hypothesis, and a safety factor approach is recommended. By using epidemiology on acute myeloid leukaemia, and by categorising exposure in terms of the long-term average maximally exposed job a NOAEL could be detected at 1 ppm (3.2 mg/m³), and a LOAEL of 20 -50 ppm: i.e. no increased risk for leukaemia was observed at dose-levels lower or equalling 1 ppm (Schnatter, 1996a). Using a collective safety factor of 24.6 (incorporating occupational to environmental exposure, sensitive subgroups (children and obese individuals), intraspecies differences (CYP2E1 polymorphisms and differences in ‘dynamics’), one arrives at “a science based” Air Quality Standard of 128 µg/m³, which is considered “to protect against benzene related adverse health effects in any segment of the general population” (Concawe, 1996). It is suggested that a second phase of analysis is required beyond this first risk assessment phase, during which risk/benefit, cost effectiveness and precautionary principles should be applied to arrive at a final legal standard.

2.4. Evaluation of human health risks

2.4.1. New scientific information since WHO 1996

From the work published since WHO (1996) it emerges that there is a substantial amount of new data on benzene and its metabolites with respect to metabolism and kinetics, interaction with specific cell types within the bone marrow and with specific biomolecules and associated toxicity, and with respect to human cancer risks associated with its exposure. These new findings will all be discussed in the next two paragraphs.

2.4.2. Discussion

The association between benzene exposure and the risk to humans of leukaemia, especially acute myeloid leukaemia, is widely recognised. Benzene is classified as a human carcinogen both by IARC and within the EU. Besides, it is regarded a genotoxic chemical.

Several well documented studies published over the last two years have confirmed that workers exposed to high occupational levels of benzene are at higher risk for leukaemia. Reported associations with other types of lymphohaematopoietic cancers as well as elevated lung and nasal cancer are inconsistent.

Also, widely accepted is the precautionary convention that for genotoxic carcinogens safe exposure levels cannot be established. Because of this most risk assessments employ non-threshold, linear extrapolation models to estimate risks associated

with low exposures levels. However, with benzene the discussion on exposure guidelines is currently focused on the issue whether carcinogenic mechanisms and processes which occur at high occupational exposure levels, e.g. in the Pliofilm cohort, are also occurring at the much lower environmental exposures. There are some observations that feed this discussion and do suggest that non-threshold linear extrapolations based on the Pliofilm data may overestimate risks at the substantially lower environmental levels.

First of all, some of the risk assessments based on the Pliofilm data also suggested sublinear dose-response shapes for benzene-induced cancers when assuming specific exposure matrices (Rinsky et al, 1987; Brett et al, 1989; Crump, 1994). It should be recognised, however, that lack of data at the lower environmental exposures (typically below 10 ppb) cannot be replaced by modelled data retrieved from exposures orders of magnitude higher (around 30 ppm), regardless of the level of sophistication. Also, because still some uncertainties remain with respect to the experienced exposures within this cohort (Crump, 1996). More recent occupational studies, on the other hand, have tried to identify risks of benzene exposure in nowadays industries, with levels of benzene exposure much lower than those estimated for the Pliofilm cohort: 0.1-1 ppm. Most studies conclude that no increased risk of leukaemia could be demonstrated at these levels (Raabe and Wong 1996, Rushton and Romaniuk 1997, Schnatter et al 1996). In some instances this could be due to limited power of the studies to detect a possible small increase in risk, but it could also indicate that risk does not show a linear increase with increasing exposure, or even support the hypothesis that some sort of threshold exists for carcinogenic effects to occur. Notably, the meta-analysis of Wong and Raabe (1995; Raabe and Wong, 1996) on a cohort of over 208000 workers supports the view that benzene is either not carcinogenic at the experienced exposure levels, or at least less potent as anticipated from the Pliofilm data using linear extrapolation.

Secondly, the carcinogenic effects observed at occupational levels of benzene may not be solely driven by genotoxic mechanisms: blood and bone marrow toxicity may be involved or may even be conditional. The high exposure conditions in the Pliofilm cohort were found to be associated with haematotoxicity, i.e. decreased blood cell counts (Kipen et al, 1988; Cody et al, 1993), and an increased incidence of non-malignant myelodysplastic syndromes (Paxton et al, 1994). This condition of benzene-induced haematotoxicity may substantially increase the risk (orders of magnitude) of developing haematological disorders (myelodysplastic syndromes) and malignancies, as has been demonstrated for susceptible individuals experiencing the so-called 'benzene poisoning' syndrome (Yin et al, 1987, 1996b; Rothman et al, 1997). In an evaluation of the literature data, a WHO Task Group

(WHO, 1993) drew the conclusion that bone marrow depression or anaemia would not be expected to occur in workers exposed for 10 years to 3.2 mg/m³ (1 ppm) or less. At these exposure levels so far no increased cancer risk has been observed (as indicated above). This also implies that these haematotoxic effects will not occur at the much lower environmental exposure levels of several ppb. Also, in experimental animals carcinogenic exposures clearly exceed those reported to be haematotoxic (WHO, 1993).

Thirdly, it is recognised that benzene does have a peculiar genotoxic profile. i.e. it is hardly, if at all, able to induce gene-mutations, despite its potent clastogenic potency. One reason for this may be the lack of evidence for direct DNA interaction under normal in vivo conditions: despite the demonstrated ability of several benzene metabolites to form DNA adducts under in vitro conditions, DNA adduct formation in bone marrow cells in experimental animals in vivo could only be demonstrated under quite specific and very high exposure regimes (Pathak et al, 1995; Levay et al, 1996). These genotoxic effects have already been observed at clearly lower exposure levels and may well be explained by indirect mechanisms. Covalent binding to S-cysteinyl residues of proteins in bone marrow in experimental animals, as well as in haemoglobin and albumin in blood of both animals and humans, have been observed at these lower exposure levels (Bechtold and Henderson, 1993; Yeowell-O'Connell et al, 1996 Rappaport et al, 1996). Though yet not demonstrated in vivo, similar interactions have been demonstrated in vitro with proteins critical to DNA stability, i.e. microtubulines and Topoisomerases. The genotoxic effects may (also) be induced indirectly via reactive oxygen species and oxidative DNA damage (i.e. 8-hydroxy-deoxyguanosine), that are demonstrated in mouse bone marrow after benzene treatment at comparably low exposure levels.

One further complicating observation is the fact that at environmental exposure levels of benzene, other exogenous or endogenous sources appear to be major contributors of endogenous levels of phenol, catechol, hydroquinone, and trans,trans-muconic acid (Maga, 1978; Carmella et al, 1982; McDonald et al, 1993a; 1993b; Deisinger et al, 1996; Ruppert, 1997).

Taken together, the above data indicate that it is reasonable to assume that benzene-induced effects at low exposure levels differ quantitatively as well as qualitatively from those induced at high occupational exposures. One has to acknowledge, however, that neither epidemiology, nor any other discipline, is likely to provide conclusive information on the exact shape of the dose response curve for cancer at the benzene exposures of concern,

i.e. environmental levels. Nonetheless, from the above some inferences concerning the shape of the dose-response curve can be made.

First of all, one may consider whether the available data justify a non-threshold linear extrapolation methodology or allow a threshold approach. Relevant to decide on this is knowledge about the exact mechanism of carcinogenesis. Basic to applying the non-threshold linear extrapolation method is the assumption that the underlying mechanism of tumour formation is a direct interaction of the carcinogen with DNA. Whether this situation holds for benzene, however, is as yet unclear. Direct DNA interaction, i.e. DNA adduct formation, is observed only at exceptional and high exposure regimes, well above dose levels known to induce genotoxic effects. Moreover, the genotoxic profile of benzene lends support for the absence of direct DNA interactions, and evidence is available for some indirect mechanisms. Still, some minor, yet unidentified adducts may have escaped detection by the applied ³²P-postlabeling assays (Blaesdale et al, 1996). Therefore, in the absence of sufficient evidence, on precautionary grounds a non-threshold linear extrapolation method seems most appropriate.

A second important question here is whether the available data provide enough credence for assuming a sublinear shape of the dose-response curve for carcinogenic effects. Both epidemiology and animal experiments clearly show that carcinogenic effects occur at benzene dose levels also known to be haematotoxic. Together with the observation that susceptibility to haematotoxicity by benzene evidently predisposes to myelodysplastic syndromes as well as haematopoietic malignancies, this target organ toxicity is considered a promotional condition to tumour development. The absence of carcinogenic effects at non-toxic exposure levels in a recently reported large cohort lends support to this view (see section 2.4.3)

2.4.3. Evaluation

For purpose of guideline derivation for benzene essentially two epidemiological studies seem to be of major importance, i.e. analysis of the Pliofilm cohort by Crump (1994), and the meta-analysis by Wong and Raabe (1995).

WHO (1996) decided to use the 1994 risk calculation of Crump. Crump used the updated Pliofilm cohort data, various dose-response models, and two exposure matrices, i.e. that of Crump and Allen (1984), and that of Paustenbach et al. (1992) (see paragraph 2.2.3.3). Multiplicative risk models were found to describe the cohort data better

than additive risk models and cumulative exposures better than weighted exposures. Dose-responses were essentially linear when the Crump and Allen exposure matrix was used, whereas the model that best fitted the Paustenbach et al. exposure matrix was quadratic.

For derivation of a risk estimate, WHO preferred models giving equal weight to concentration and duration of exposure. Using multiplicative risk estimates and a cumulative exposure model, Crump (1994) calculated unit risks (for leukaemia) for lifetime exposure to 1 µg/m³ of 4.4×10^{-6} with the Paustenbach exposure matrix, and 7.5×10^{-6} with the Crump and Allen exposure matrix (see Table 1). The geometric mean value of the above unit risks of 6×10^{-6} was chosen by WHO as the recommended guideline. The concentrations of airborne benzene associated with an excess lifetime risk of 1/10 000, 1/100 000 and 1/1000 000 are, respectively: 17, 1.7, and 0.17 µg/m³. It was noted by WHO that if linear extrapolations were done on the occupational cancer risk estimates by Paxton et al (1994), about a ten-fold lower risk estimate would have been obtained.

WHO identified a number of uncertainties in their analysis. Amongst other things they noted difficulties in choosing models for deriving risk estimates for the general population from data on occupational exposures. Workers are exposed to much higher concentrations than the general population and for relatively short periods. It is not clear how best to extrapolate such worker exposures to the much longer population exposure to lower environmental concentrations. On the other hand, there are few data on exposure of children. In addition, the actual exposures the workers have experienced still haven't been clearly established (Crump, 1996). WHO concluded that models giving equal weight to concentration and length of exposure were to be preferred. They noted that there are arguments for using models, which give more weight to concentration, and that these result in substantially lower risk estimates, i.e. several orders of magnitude lower (Table 1). However, arguments in favour of this latter approach were considered preliminary and needing further development.

It may be mentioned here, that Crump (1994) in this analysis of the Pliofilm cohort (see also Table 1) preferred the intensity dependent model fits together with the exposure estimates of Paustenbach et al (1992), which resulted in a unit risk (per µg/m³) of 5.3×10^{-11} , i.e. 1.10^{-6} lifetime risk associated with exposures of 18870 µg/m³ (\approx ppm).

The risk estimates by WHO (1996), based on linear extrapolation of the Pliofilm cohort data, do not seem to match the results of recent occupational studies, among which the meta-analysis of Wong and Raabe (1995) seems to be of major importance. In their

comprehensive analyses of data from the petrochemical industry, including 208.000 petroleum workers with an estimated average exposure of 0.7 mg/m³, Wong and Raabe identified 148 cases of acute myeloid leukaemia, where 155 were to be expected, given standardised mortality rates (Wong and Raabe, 1995). However, based on the WHO assumed excess lifetime risk of leukaemia of 6.10^{-6} at ambient concentrations of 1 µg/m³ (WHO, 1996), of which over 80% were acute myeloid leukaemia (Crump, 1994), a clear additional number of acute myeloid leukaemia cases in this Wong and Raabe cohort should have been observed (above the 155 expected cases). This number can be estimated using the average working period of employees in this meta-analysis and the exposure experienced. Mean follow up by Raabe and Wong was 22,4 years, but the mean duration of exposure was 18.4 years (personal communication). Rushton and Romaniuk (1997), in their cohort study in the petroleum industry in the United Kingdom, report a mean duration of employment of 21,4 years, Schnatter (1996,a,c) reports average exposures of about 28 years. It is not exactly stated, however, how many of these years reflect jobs associated with (substantial) benzene exposure. A conservative approach for this type of industry here may be 10 years, as suggested by the Dutch Health Council (1997). Therefore, average exposure periods of 10 to 20 years seems to span the range of reported values. Given this, the expected additional number of cases of acute myeloid leukaemia would amount to 36 and 72, respectively, by calculated average lifetime exposures of 34 and 68 µg/m³ (see footnote for conversion of occupational to environmental exposure; Crump, 1994). Both these expected elevated risks are outside the confidence interval of this large cohort (124-186, $\alpha=0,05$, $\beta=0,20$). Thus, these recent epidemiological data clearly indicate a sublinear association between exposure and response, and demonstrate that linear extrapolation of occupational risk estimates based on high exposure conditions, such as the Pliofilm cohort, is likely to produce a substantial overestimation of the leukaemia risk at lower exposures.

There are also some uncertainties associated with this meta-analysis study of Wong and Raabe (1995). First, there are some uncertainties associated with the exposure workers have actually experienced in the various cohorts. Although the authors have carefully considered study design and data quality (e.g. death certificates, employment history and exposures; thereby excluding some studies) uncertainties remain concerning the actual exposures of the workers. Also, it cannot be excluded that some workers may have had hardly any exposure to benzene, which might mask a possible effect. Secondly, a meta-analysis may incorporate studies of different quality, with the danger of diluting relevant dose-response data. These factors are all of concern when performing a meta-analysis, though not exclusively associated with this type of epidemiological study. On the other hand, the very reason to perform a meta-analysis is to utilise information hidden in various

sets of exposure response estimates to gain resolution power. Additionally, not all studies have been weighed equally in this analysis: studies with smaller confidence intervals were given more weight in the overall result.

2.5. – Recommendations for developing limit values

From section 2.4. it is evident that assessment of the risks of benzene is not without uncertainty. In view of these uncertainties the Working Group asked for further advice on the risks of benzene in the light of evidence published since the WHO Guideline was developed. Accordingly DGXI, in co-operation with WHO, convened an ad hoc group of experts in the field in Brussels on 13 January 1998.

2.5.1 Advice from the ad hoc Expert Group

The Expert Group was of the view that the evidence that has accumulated since the WHO Guideline was developed does not allow the uncertainties that WHO identified in their analysis to be removed. That is, it is still not possible to say what the best model is for extrapolating from worker exposure to environmental exposure of the whole population. Nor, despite evidence that benzene is an unusual carcinogen, do animal and other data allow a threshold to be identified below which effects are not expected.

The group concluded that though it was not possible on present evidence to give a precise estimate of the risk associated with benzene it was possible to define a range within which that risk was likely to lie. The procedure followed by the WHO working group was considered to result in the highest plausible estimate of risk – an excess lifetime risk of leukaemia at an air concentration of $1 \mu\text{g}/\text{m}^3$ of 6×10^{-6} . Unit risks in the order of 10^{-10} and 10^{-11} derived by some authors (see section 2.4 above) were felt to be too far outside the general range of estimates to be relied upon with good supporting evidence for the models used. The lowest unit risk which the group felt was likely to be plausible was in the order of 5×10^{-8} – an estimate which is consistent with the Netherlands Health Council analysis of the Wong and Raabe meta-analysis described above.

This wide range cannot be narrowed on scientific grounds without further evidence about the mechanism by which benzene causes leukaemia. The Group considered that there was not sufficient evidence at present to justify setting a limit value for shorter time periods. It concluded that an alert threshold for benzene was not appropriate.

2.5.2 Recommendations of the Working Group on Benzene

The Working Groups on individual pollutants have been asked by the Commission to base their initial recommendations for goals for air quality based on their assessment of risk. This is particularly difficult in the case of carcinogens. Converting unit risks to goals means deciding on a level of risk which will be tolerated.

The European Parliament and the European Council, when considering the proposal for a Directive on Drinking Water, agreed that an excess lifetime risk of 1 in a million should be taken as the starting point for developing limit values.

Taking this as a precedent, the range of unit risks given above (6×10^{-6} to 5×10^{-8}) has been converted into annual average concentrations which would, over a lifetime, equate to an excess risk of contracting leukaemia of 1 in a million. The resultant range of concentrations is 0.21 to 20 $\mu\text{g}/\text{m}^3$. The Working Group recommends that this range should be taken as a starting point for developing proposals for a limit value, defined as an annual average concentration

The Working Group accepted the advice of the ad hoc Expert Group that there is not sufficient evidence at present to justify setting a limit value for shorter time periods and that an alert threshold for benzene was not appropriate. It noted that provided annual average concentrations were kept low, short-term maximum concentrations should also be low.

footnote (Crump, 1994):

general population: life expectancy 70 years; $20 \text{ m}^3/\text{day}$;

working population: 250 days/year; $10 \text{ m}^3/8\text{-hour working day}$.

2.5.3. Ongoing research

In order to narrow down the range of unit risks given above it is necessary to have more information about whether benzene acts via a conventional genotoxic mechanism, a non-genotoxic mechanism, or a mixed mechanism. Given the substantial amount of ongoing research on this topic the Working Group feels that it is reasonable to expect that considerably more information will become available within the next 5 years or

¹ 0.17 has been rounded to 0.2 for clarity.

so. This will allow greater certainty as to whether benzene is or is not a conventional genotoxic carcinogen at low doses.

Concerning the question of whether benzene can induce carcinogenic effects other than AML, and whether short-term exposures can cause effects, the Working Group considers that the available epidemiological studies do not constitute a substantial and coherent body of evidence. They are also not backed up by a plausible toxicological mechanism. However, a number of further epidemiological studies are now underway into these questions.

The Working Group therefore recommends that the scientific evidence relating to benzene should be reviewed again after a period of approximately 5 years.

footnote (Crump, 1994):

general population: life expectancy 70 years; 20 m³/day;

working population: 250 days/year; 10 m³/8-hour working day.

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Chapter 3

Benzene:

Assessment Methods

Scope

Within chapter 3, the methods and tools for the assessment of benzene concentrations in ambient air are presented, including network design and quality assurance.

3.1 - Introduction

When limit values are set, the Framework Directive (FWD) on ambient air quality states that ambient air quality shall be assessed in the Member States. Monitoring is mandatory in agglomerations and zones where the concentrations are near to or exceeding the limit value in accordance with FWD. Modelling and other methods may be used to supplement monitoring since for a complete assessment of the air quality situation monitoring on a combination of spatial and temporal scales as well as modelling is necessary. If the concentrations are lower, measurement remains mandatory but a lower intensity of measurement combined with models may be used. Where concentrations are very low sole use may be made of modelling or objective estimation techniques. Daughter legislation must fill in details of requirements for the assessment of air quality, including the requirements of the methods to be used, details of location of monitoring stations and so forth.

There are several aims of assessing benzene in the air. The most important is to identify concentration levels in areas where people are staying, living and working, and to identify areas where air quality standards are exceeded. For abatement of pollution, the identification of major sources is also an important aim and monitoring of the consequences of an abatement strategy. The need for measurements is obvious in urban air. However, to evaluate the regional concentrations of benzene, it is recommended to perform measurement campaigns and to apply the dispersion models from the main sources.

For air quality monitoring in urban areas, it may be necessary to distinguish between the air pollution situation in urban background and situations near significant sources such as at roadside directly exposed to benzene from traffic. "Urban background" defines the sites at some distance from the streets, mainly influenced by the total pollution load in the urban air rather than a few specific sources. The separation between the two types of sites is of importance for estimation of population dose. Most people are living and working in the urban background air. During road transport many people are exposed for

shorter time to high concentrations of benzene. However, minor groups of the population may spend considerable time in the street environment and may in this way be heavily exposed to traffic exhausts. The difference between roadside and urban background is also of great importance for the selection of control measures. Decreasing the general exposure of benzene in urban background will require emission reductions, whereas improvement of air quality at a specific kerbside could also be obtained merely by changing the traffic situation.

3.2 - Description of monitoring methods

The monitoring of benzene for regulatory purposes require methods suitable to measure concentrations in the range relevant for Europe, i.e. 0-500 $\mu\text{g}/\text{m}^3$, with a sufficiently high accuracy. There are several methods for benzene in this range. Most methods measure simultaneously several other pollutants. Several methods are described in the second part of this section. This list includes reference to the methods as well as a brief description of advantages and disadvantages. Furthermore, detection limits and time resolution of the methods are indicated. The choice of methods is dependent on the specific physical and meteorological conditions and the purpose of the monitoring. Where more methods can be used, it is necessary to consider the advantages and disadvantages of them in order to take the right choice. Although many methods exist for measuring benzene, however only well documented techniques should be used. Currently a CEN working group (TC 264/WG 13) works on a standard covering measurement of benzene in ambient air "Selection of reference method for determination of benzene in ambient air". The methods considered in the WG are identical with those listed in this section. Many of the techniques have gas chromatography as the analytical technique.

The most commonly used methods are performed in two stages: sampling (pre-concentration) and gas chromatographic analysis. The sampling stage may be performed with automatic or manual systems by pumping air through an adsorbing device and the sample may be recovered for the analysis using solvent or thermal extraction. A third important aspect in the analysis of benzene is related to the calibration method, since the analytical method is not absolute.

Many kind of sampling devices are actually employed. Devices employing strong adsorbents like active charcoals are mainly related to manual methods because strong adsorbents need long-time sampling procedure and solvent extraction. Devices employing weak adsorbents, like Tenax, Chromosorb and graphitized carbon blacks, may be used both in manual and automated systems. In fact weak adsorbents are usually thermally desorbed and the adsorbing material is reusable. Their high sensitivities in the analysis allow also a short time sampling (half an hour or less), and many commercial instruments allowing a semi-continuous sampling-analysis cycle are actually available. Automatic systems are available which allow to perform both sampling and analysis stages and to store the analytical data. These systems are suitable for semi-continuous air monitoring and may be positioned at fixed or mobile monitoring stations. An alternative to the active (pumped)

sampling system is to employ passive devices, which allow a passive (diffusive) enrichment of the species of interest.

The only available quasi-continuous measurement method for benzene is an optical measuring technique (DOAS). The technique is based on differential adsorption, i.e. the difference between local maxima and minima in the adsorption spectrum of the probed gas. DOAS is a remote sensing technique and measures the average concentration over the monitoring path in the atmosphere. A detailed description and main characteristics of the analytical methods intended for benzene measurement is given below

On-line gas chromatographs are available either as BTX-monitors (Benzene, Toluene, Xylene), measuring benzene, toluene, ethyl benzene and xylenes or more capable of measuring C2-C10 hydrocarbons. These instruments are based on the same principle. Sample air is sucked through a trap kept at relative low temperature (about -190° C to 40° C) where benzene is retained. Afterwards, benzene and the other relevant species are injected into the gas chromatograph by thermal desorption, either directly or via a secondary, cryo-focusing trap. The detection limit using Flame Ionisation Detection (FID) is 0.1-0.03 $\mu\text{g}/\text{m}^3$. On-line BTX monitors work with a time resolution of 15-20 minutes. However, the method is semi-continuous by sampling about 20 minutes of e.g. each half-hour or hour. Continuous monitoring is possible using sequential sampling on several tubes. Results obtained with on-line GC's can be transmitted directly to the central laboratory and thus on-line data are available with these methods. The method is relatively expensive because a monitoring system is needed and each analytical instrument covers only one location. A German standard (DIN 33961 part 1 and 2) with minimum requirements and a test for single cycle analysers (=BTX analysers) is available. A simplification of the method includes a gas chromatograph equipped with a UV photo ionisation detector (PID).

Canister sampling is performed in two ways either as grab sampling or as pumped sampling. The grab sampling is carried out by opening an evacuated canister, which instantaneously fills the canister with ambient air up to ambient pressure. Alternatively, air can be pumped into the canister over time in order to obtain an integrative sample. The canisters are then brought to the laboratory where they are analysed by gas chromatography (GC). The detection limit is 0.3 $\mu\text{g}/\text{m}^3$. Sampling is discontinuous and statistical manipulation is needed to give representative time picture of the benzene concentration. The pumped canister method is not applicable to benzene because of wall effects in the canister. The grab sampling is very sensitive to the relative humidity; therefore it is necessary to control the relative humidity in the canister. A German standard is available

(VDI 3482-2,3). In addition, the canister must be carefully cleaned and checked before it can be used again.

Pumped sorbent tube sampling is performed by pumping ambient air through a tube filled with a sorbing material. The trapped benzene is removed by solvent extraction or thermal desorption followed by GC analysis. Time resolution from a half an hour to 24 hours is possible. The method is a reliable and of low cost. The method has been widely used in workplace air and a general CEN standard is available on the requirements and tests methods of sorbent tubes (prEN 1076) which covers ambient air as well. Also, German standards for pumped tube sampling both with solvent extraction (VDI 3482-5) and with thermal desorption (VDI 3482-4) are available.

Diffusive sampling of benzene is performed by placing benzene adsorbent in a glass or metal tube. The sampler collects benzene by diffusion (following Fick's first law) due to the gradient established between ambient air and the adsorbing material. Benzene is removed from the sampler by solvent extraction or thermal desorption and in both cases benzene is analysed by GC. Detection limit is about $0.5\mu\text{g}/\text{m}^3$ and $0.03\mu\text{g}/\text{m}^3$ respectively. Automatic thermal desorption units are commercially available, which contributes to the cost efficiency. The method is accredited in Sweden. Diffusive samplers do not require any electrical power and it is therefore, possible to measure benzene with a high space resolution. However, a sampling time of at least 1 week is needed and thus the method is unfitted for process studies e.g. to investigate the relation between emission and concentration. The method is a cheap and reliable tool for measuring benzene in ambient air and it is commonly used for work place measurements where a CEN standard is available (EN 838 and WG 11 has made general requirements for applying diffusive samplers for ambient air measurements (CEN TC264/WG 11/N 15-17)).

DOAS (Differential Optical Absorption Spectroscopy) is an open path optical measuring technique applicable for a number of gases which includes benzene (Platt and Oernerm 1983). DOAS is based on the differential absorption of UV-visible light (difference between maximum and minimum absorption of fine structure in an absorption feature). The detection limit is about $1.5\mu\text{g}/\text{m}^3$ with a time resolution of 1 min under optimum conditions. The method measures along an optical path of typically 250 m to 800 m. There is no chemical interference in this method as no sample is taken and many components are measured simultaneously. The instrument can deliver on line data. However, there are problems with measurements at low visibility (e.g. foggy conditions), and problems with calibration (e.g. calibration gases) have still to be solved. There is no

national or international standard available for DOAS measurements of benzene but recently Brocco et al. (1997) have published an inter-comparison of an on-line GC instrument and a DOAS instrument. Furthermore, work is in progress in Germany on a VDI standard concerning DOAS. Although early measurements by Gunnar and Barrefors (1996) do not show sufficient reliability for this technique, recent data gathered in Villa Ada, Rome, shown in *Figure 3-1*, demonstrated that a slightly modified commercially available DOAS may be considered an interesting tool for the measurement of ambient levels of benzene. It is worth stressing that the deviations observed against a conventional GC analyser (Chrompack) are also including differences in location. In fact, this DOAS is sensing the atmosphere at 30 m in elevation and at 150 m optical path, while the GC is point-sampling at 2 m above the ground. A great advantage of DOAS is its capability of measuring many other important pollutants such as ozone, nitrogen dioxide, sulphur dioxide, formaldehyde and others.

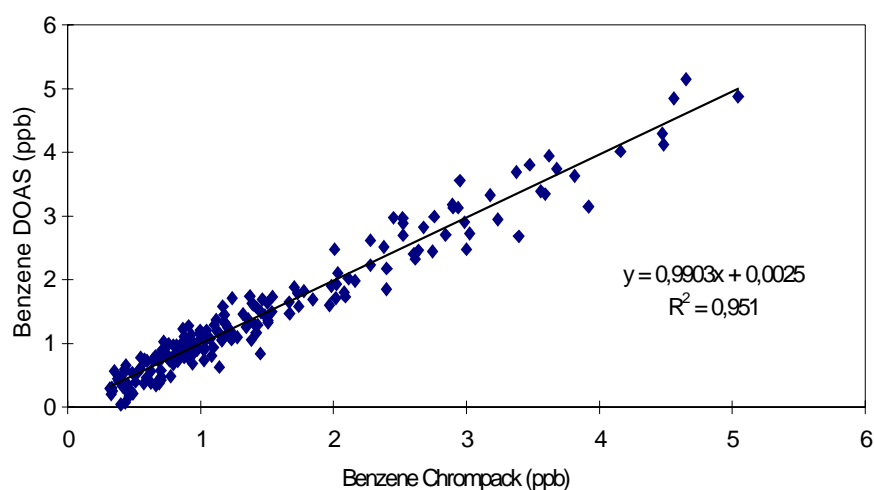


Figure 3-1 - Comparison between Automated Gas-Chromatograph and DOAS for the evaluation of ambient concentrations of benzene. Villa Ada station, Rome, Spring 1997.

The automatic and manual methods mentioned allow point measurements which are representative for the monitoring site and for an area around the site. Its dimension is determined by emissions and other characteristics of the surroundings.

Discontinuous point measurements

Discontinuous methods are normally used for daily to monthly sampling. Active as well as passive sampling methods are included. The manual discontinuous methods require relatively cheap and simple equipment; they are relatively uncomplicated to use. However there are disadvantages such as the need for manpower for sampling and analysis, the limited time resolution and the time delay until measurement results are available.

Recommendations for the reference method to be used

There are a number of requirements for the reference method to be used for the mandatory air quality monitoring. It should:

- be accurate and precise;
- have few and small interferences;
- fully comply with the Directive requirements;
- give data in the correct time scale;
- be cost-effective;
- be easily applied and operated.

A choice of a suitable reference method for benzene in the atmosphere to meet these requirements is pumped sampling on tubes followed by GC analysis including the calibration technique. The standard for the reference method will be prepared by CEN.

3.3 - Network design and siting criteria

The aims and objectives of the network required by EU are clearly stated in the Framework Directive. The legal requirements of the Directive for assessment of ambient air quality are given in Article 5. In addition, the aims of the Directive, as given in Article 1, also need to be considered:

- establish objectives for ambient air quality in the EC designed to limit or prevent harmful effects to the environment as a whole and to human health;
- assess the ambient air quality in Member States in a uniform manner;
- make available to the public information on ambient air quality;
- maintain good ambient air quality and improve poor ambient air quality.

The starting point of each network design must be a clear picture of the aims of the measurements and the questions to be answered by them. The Articles 1, 5 and 6 in conjunction with Articles 8 and 9 of the Framework Directive on ambient air quality assessment and management (FD) applied to the monitoring of benzene state that :

- The current air quality should be maintained and, possibly, improved.
- The air quality in Member States shall be assessed throughout their territories on the basis of common methods and criteria, the information obtained being adequate and made available to the public.
- Monitoring campaigns and strategies should be addressed also to understand the physical processes (emission rates, diffusion and turbulent mixing) which are responsible for the current levels of benzene.
- Zones (dependent on the pollution burden) shall be drawn up by the Member States.
- Member States shall undertake a preliminary assessment of benzene levels in ambient air before limit values of the daughter directives will come into force.
- Measurements are only mandatory in zones where benzene levels exceed the upper assessment threshold (UAT, see Section 3.8), agglomerations not constituting a special zone in the case of benzene, because no alert thresholds can reasonably be set for this compound.
- For zones in which benzene levels are lying between the upper and lower assessment threshold (LAT, see Section 3.8), a combination of measurements and modelling techniques may be used.
- For zones with benzene levels below the lower assessment threshold, the sole use of modelling or objective estimation techniques (e.g. interpolation, indicative measurements) shall be possible.

From these requirements it can be concluded that an important aim of the measurements is compliance checking throughout the Member States. Also, the exposure of the population to benzene has to be assessed. The assessment must include sites which are representative for the exposure of the majority of the population as well as sites where the maximum exposure of smaller parts of the population may occur and places where the highest benzene concentrations have to be expected in conjunction with an exposure over the time scale of the limit value (hot spots).

Ideally, such an exposure assessment should result in maps showing the spatial distribution of benzene concentrations and, in combination with the population density and activity patterns, would allow to calculate the number of persons exposed to certain

benzene doses. On the basis of measurements alone, this complete spatial distribution cannot be evaluated, at least not with reasonable costs. Therefore, a combination of measurements, model calculations, indicative measurements and interpolation techniques is necessary to arrive at such an ambitious aim. In the case of benzene, there are two other important boundary conditions for measurement planning:

- Since long term exposure is relevant (compare Chapter 2), the monitoring of long averaging times (annual means) is sufficient to assess benzene levels. No peak values in or near real time values have to be measured. However, short term measurements may be important to understand the processes (emission or dispersion) leading to current levels of benzene.
- Human health is the protected interest.

In combination with the low benzene concentrations in rural areas (compare chapter 1) monitoring at background sites is in general not of relevance for compliance checking. Articles 8 and Article 11 of the FD add another requirement for benzene monitoring. As the Member States have to report reasons for exceeding benzene limit values and have to prepare and implement plans to reach the limit values in due time, the identification of relevant benzene sources, the cause-effect analyses and the control of the efficiency of abatement actions are further important goals for benzene measurements. Additional information relevant for measurement planning is also given by the ERLAP and the EEA in the "Guidance Report on Supplementary Assessment under EC Air Quality Directives".

Bearing in mind that the design of measurement networks for the enforcement of the Framework directive should follow a harmonised approach for all pollutants as far as possible for the sake of minimising monitoring costs, also the already existing basic documents for other pollutants (SO₂, NO₂, PM₁₀, Pb) should be taken into account as starting points for a network design.

In order to "assess the ambient air quality in Member States in a uniform manner" the network should be designed in similar way in all Members States. These sites will constitute the European Ambient Air Quality Directive Network (EAAQDN) analogous to the EMEP monitoring network for rural areas in Europe. The information on air quality shall be made available for the public and for the decision makers. The data will be reported by the Commission in accordance with Article 11. In addition the information shall be

available, i.e. by actual issue of exceedances of limit values. The maintenance of good air quality and improvement of poor air quality require good air quality planning tools. The tools will normally be available in the Member States, but the network shall as far as possible be designed in a way that the necessary data will be available for planning.

The essential aim of network design is to establish the number of monitoring sites required and their location in relation to emission sources and to the population at risk. Moreover, it is essential to identify the necessary additional tools for assessment of the air quality in relation to limit and alert values. The overall number of monitoring stations established will depend on:

- ambient concentrations, in relation to limit values;
- the population likely to be exposed to such concentrations;
- the scale and extent of environmental effects;
- the spatial variability of the pollutant under consideration (benzene)

3.3.1 - Site selection and number of measurement sites

Taking into account the requirements outlined above, there are four typical broad categories or important micro-environments where benzene levels should be monitored:

Table 3-I

Site	Characterisation
Urban background	Residential areas in conurbation and towns. The sites should be representative for larger parts of the cities and should not be directly impacted by traffic or other benzene sources
Road side	Block of flats, dwelling houses, hospitals or kindergartens adjacent to street canyons or other traffic hotspots with high traffic density such as parking garage outlets, petrol stations and tunnels, if significant and relevant in terms of exposure of the population
Industrial	Residential quarters adjacent to industrial sources like cokeries, petrochemical plants or distribution terminals for benzene or benzene containing liquids
Rural background sites	

The number of stations necessary for compliance checking depends inter alia on the size of the zones to be assessed, on the spatial arrangement of the important sources

(busy streets, industries) within these zones, and the spatial variability of the pollutant. As benzene is predominantly caused by low emitting sources (e.g. traffic, industrial diffusive sources), the spatial variability near sources will generally be high, so that great care must be taken to choose the appropriate measurement sites. There is no perfect recipe for this task, which will work under all circumstances.

Urban Background

Contrary to the high spatial variability of benzene concentrations near sources, the urban background levels within one country are rather similar (compare the tables in Chapter 1). This is quite plausible if one takes into account that under similar meteorological conditions, the urban background of benzene will be caused for more than 90% by the traffic density, factors like the gasoline quality, the percentage of cars equipped with catalytic converters or the age of the car fleet roughly being similar. Consequently, the urban background within an agglomeration or zone can be assessed by one or few measurement sites, provided that the sites are representative for a larger residential area (exposure!) and the direct influence of near emitting sources (e.g. busy streets, gasoline stations, industries) is avoided. Because of the (smaller) gradient of benzene concentrations from downtown areas to suburbs within an agglomeration, measurements should predominantly be performed in residential quarters in downtown or near downtown areas.

In addition to the above mentioned factors, the necessary number of measurement sites depends on the availability and the application of other assessment tools, as emission inventories model calculations or indicative measurements. That is the reason why two different sets of numbers (N_o with full assessment, N_i based on measurements alone) are foreseen by the guidance document from ERLAP and EEA. On the basis of the arguments presented so far, the working group on benzene has come to the conclusion that the formula for the determination of N_i proposed by the Position Paper on Particulate Matter is a reasonable approach also for benzene:

The number of urban background sites $N_i = 4\sqrt{I}$ (I = the number of inhabitants of the agglomeration zone or agglomeration or zone - millions)

With full assessment, this number of urban background measurement sites per zone can be reduced, with a minimum of $N_o = 1$.

It has been already mentioned that measurement of annual means is sufficient for compliance checking. Therefore the urban background can be monitored by spot check measurements in a cost effective way, which saves, inter alia, costs for monitoring stations.

It can be expected that urban background levels in somewhat smaller cities in the range of 50,000 to 250,000 inhabitants do not differ much from the levels measured in conurbation without important industrial sources. Therefore the working group recommends carrying through indicative measurements (e.g. passive sampling, active sampling with reduced sample size) also within some of these medium sized cities per member state. Benzene levels in comparable medium sized cities can then be objectively estimated.

Road Side

Roads can be regarded as extended line sources with a "tube" of more or less elevated benzene levels attached to them. Because of this fact and because of the number of busy streets within an agglomeration or zone, it is impossible to assess this concentration field by measurements alone. A combination with model calculations and indicative measurements and an extrapolation to similar streets is indispensable. There is the additional problem of micro-siting of road side measurements. Estimates based on benzene measurements within street canyons will overestimate the exposure, because no one is standing outdoors within street canyons for years. For the same reason, measurements near motorways without adjacent residential quarters or other targets to be protected (e.g. hospitals, schools) can be left apart. On the other hand, measurement sites away from busy streets will measure nearly city background air and underestimate exposure.

The measurement sites should therefore be chosen in or in front of residential quarters directly adjacent to street canyons with a high traffic density. Indicative measurements with passive samplers and/or diffusion modelling should be used for the proper placing of the roadside measurements. It should be taken into account that a non negligible fraction of benzene emissions is due to evaporation, thus parked cars should be taken into account as sources, irrespective of traffic density.

There is a general consensus that Ni should consist of fixed road side measurement point per zone or agglomeration. In zones above one million inhabitants, this fixed site should be complemented by one additional site per million inhabitants or more if the assessment is very incomplete. The additional site(s) can be changed over the years to cover several streets, the minimum measurement period being one year. When full assessment is available (No), the working group is of the opinion that it is justified to tie the minimum number of roadside measurements not to each zone, but to Member State as such,

because air pollution in other streets may be estimated by street pollution modelling. Consequently the number in the case of full assessment is proposed to be

$$N_o = 1 + \sqrt{P} \quad (P = \text{population of the country - millions})$$

Industrial

Monitoring of industrial hotspots should be tailor made. Notwithstanding this principle, some general rules can be given, as relevant benzene emitters will in most cases consist of low emitting diffusive sources.

The first problem to be solved is to decide which industrial benzene emitters are relevant and how to locate them. A straightforward way to do so would be to define a certain threshold of annual emissions as relevant. This possibility seems to be simple at a first glance. In reality, however, the additional air quality concentration load by low emitting diffusive sources depends so heavily on local circumstances as the height of the outlet(s), topography, the distance from sensitive targets, the temperature of the effluents etc. that no general threshold can be defined.

The other possibility is to look at the estimated, calculated (by diffusion modelling) or measured (e.g. by indicative measurements) additional pollution burden of an industrial source. Such a source clearly can be regarded as relevant for continuous monitoring if

- the benzene levels are 50 % or more above the measured urban background and in addition
- the benzene concentrations are above the upper assessment threshold.
- the proposed percentage of 50 % stems from the accuracy of indicative measurements (± 30 %) and modelling (± 50 %).

A further indicator of a relevant industrial share of benzene levels can be the benzene to toluene ratio. Near roadsides and in urban background, typical toluene to benzene ratios are between 3 and 2.5 (see Figure 1.1). A significant deviation (e.g. < 2) of this ratio points to other relevant benzene sources. This indicator is valid only for urban areas because in rural areas, the toluene to benzene ratio can be < 2 simply because of the faster photochemical decay of toluene during transport.

The following guidelines can be given to the location of measurement sites:

- For compliance checking, measurement site(s) should be chosen where the exposure to benzene levels will be highest, that is high benzene concentrations combined with long residence times of people. This will generally be the case at the edge of residential quarters in the main wind direction nearest to the source.
- Other wind directions have to be taken into account, if there are residential quarters closer to the emitter other than in the main wind direction.
- Because of the high spatial variability near low emitting sources, indicative measurements and/or model calculations should be used to find the correct measurement sites and supplement the measurements.

Figure 3-2 in Section 3.6 (*#Still correct?*) presents an example from an old cokery in Rhine-Ruhr-region, Germany. The diffusive samplers arranged in a grid of 250 x 250 m within the residential quarter show a clear pattern of the spatial benzene concentration, which corresponds to the results from the model calculation based on an emission inventory. According to the diffusive sampling, the site with the highest exposure is directly neighboured to the east/northwest of the batteries of the cokery. Consequently, the site of the continuous monitoring (MILIS), installed before the first results of the diffusive sampling became available, would ideally have been installed some 250 m more to the North East. It can be also concluded from *Figure 3-2* that urban background levels (about 3 $\mu\text{g}/\text{m}^3$) are reached about 1 km away from the source.

In this particular case, no other adjacent residential quarters are impacted by the source. Generally, this can be the case and should then be examined at least by indicative measurements and/or modelling. Following the example given, the strong temporal variability of benzene levels near low emitting industrial sources has been outlined. This prevents the use of spot check measurements within an expanded uncertainty range of $\pm 10\%$. Hence continuous monitoring should be used in these cases. Continuous monitors have the additional advantage that their results can be used for the clear identification of sources, for example by plotting the results as functions of the wind direction.

In line with the arguments presented above, the working group recommends the following numbers for Ni and No in the case of industrial hot spots:

Ni = >1 (depending on the size and position of residential quarters)

No = 1 (supplemented by indicative measurements and/or modelling)

Rural Background

Rural sites are of no priority for compliance checking as such. However, to obtain reference data from relatively unpolluted air masses and to assess regional transport phenomena, it is recommended that levels should be monitored at some background sites per member state.

Again, the approach chosen by the working group on particulate seems to be applicable also for benzene. Consequently, the following number N_i is recommended for rural areas:

N_i (rural) = $A/50,000$ (A = the area of the country in square kilometres)

With full assessment, this figure may be reduced to N_o (rural) = 1 per Member State.

Table 3.II summarises the minimum numbers of measurement points proposed by the working group for the different micro-environments:

Table 3-II

Site	N_i	N_o
Urban background, per agglomeration or zone	$4\sqrt{I}$, I= number of inhabitants in millions	1
Rural background, recommended per Member States	$A \times 50,000^{-1}$, A = area of Member State in km^2	1
Roadside, per agglomeration or zone	1 additional site per 1 million inhabitants or more (1-10)	$1+\sqrt{P}$, P = population of Member State (million)
Industrial	> 1 (continuous)	1 (continuous)

Micro scale considerations for site locations

Most criteria for the microscale siting of measurements, which were given by the working groups for other pollutants, apply for benzene as well.

- Benzene should be sampled within an unrestricted air flow without any obstructions in the vicinity of the sampler (e.g. a minimum of 1 metre away from buildings, trees, etc.)
- Great care should be taken not to sample the exhausts or evaporative losses of measurement vans or from the outlet of stations, pumps, etc.
- The inlet sampling point should be between 1.5 m and 4 m above the ground. In the case of background measurements (urban, rural) higher positions up to ten metres may be considered, if long path measurements (e.g. DOAS) are applied.
- Roadside sites should be positioned at the building line of residential buildings adjacent to busy streets.
- In order to save costs, benzene sampling (also grab sampling) can be co-located with measurement stations for other pollutants, especially for background measurements.
- The sampling sites should be fully documented according to the Guidance document of EEA and ERLAP.

In addition, interfering sources, security, access, electrical power and telephone, "visibility" of the site - public profile, safety of public and operators, planning requirements, and others, should also taken into account.

3.4 - Other assessment techniques: air quality modelling

Assessment of air quality is an important issue in many areas, especially in the urban environment. The most credible, complete and useful assessment is always obtained by combining measurements and modelling results. The monitoring at chosen sites provides data for the pollution situation and its temporal variability. Dispersion model extends the knowledge by computing concentration fields as a function of time at various spatial scales. Under the Directive, if the air quality is close to the limit value, modelling alone can not and may not be used to assess the air quality situation and exceedances of air quality standards. Models are also useful for the

- exploratory assessments in absence of measurements and for planning of measurements and location of monitoring sites;
- understanding the pollution situation in relation to factors such as special dispersion conditions and to temporal and spatial emission variability;
- relating air pollution to sources and sectors as input information for abatement;
- calculating future pollution levels as a consequence of future emission scenarios.

A variety of air pollution models have been developed for various spatial and temporal scales of urban air pollution situations, and for the various applications mentioned above. The models can be separated into four classes:

- models for pollution near streets and roads;
- models for pollution near point sources;
- integrated urban scale models, taking account of all source categories, giving concentrations in a grid net and in selected receptor points;
- population exposure models.

For the evaluation of possible air quality standards exceedances, the integrated urban models are the most useful. Single point source models will only provide information on the contribution from a point source, which is of limited use for the total assessment. Since traffic emissions to a great extent will determine the air quality of benzene, street environment models are useful to assess the zones with risk for exceedances, and for the evaluation and extrapolation of measurement results to larger zones. This type of model is also relatively simple and easy to use for an unskilled user. The results are however, only indications of the real situations and must be evaluated further using monitoring data and more advanced models.

There are a number of well-established models in use in urban areas in different parts of Europe. No general recommendation of models can be made here. However, the model must fulfil the requirements and be thoroughly validated against monitoring data.

The necessary initial requirements relevant to the successful application of a model focus on :

- input data accuracy and its dependency to the model output;
- proper model parameterisation and initialisation;
- methodologies for judging to what extent model results represent reality.

As a consequence of the above, model validation (typically by the aid of available analytical solutions) should be considered as an indispensable part of the model development process, whereas an already validated model should be subject to a genuine evaluation procedure in order to ensure that potential users can assess the degree of reliability and accuracy inherent in the given model (Coseman *et al.*, 1992).

An increasing demand of air quality assessment is foreseen and will be the driving force towards further development and improvement of dispersion models. Various models are needed. Operational models are an important tool for city planning. On-line models are used for air pollution forecasting at pollution episodes to show present and near-future risks. Models for regulatory purposes are used to demonstrate zones of compliance/non-compliance with air pollution directives.

To be powerful tools, the models must fulfil certain quality criteria. Work on quality assurance of models is important and has recently started within different organisations. Accuracy can be documented in terms of uncertainties in input quantities and in model formulation, and could be demonstrated in the validation process. Input, in the form of emissions and dispersion conditions, is necessary at a similar spatial and temporal scale as the output concentrations to be calculated by the model. Data on emissions is required with sufficient spatial and temporal resolution to describe the important gradients occurring in a zone.

Local Scale Models

The following table 3-III gives a rough overview of a number of existing local scale models and their characteristics.

Table 3-III

Model name	Model category
AUSTAL 86	Gaussian
CAR	Semi-empirical
CAR-Parking	Semi-empirical
PHOENICS	Eulerian
CAR-FMI	Gaussian
CONTILINK	Gaussian
CTDMPLUS	Gaussian
HPDM	Gaussian
IFDM	Gaussian

INPUFF	Gaussian
ISCST 2	Gaussian
OSPM	Street pollution model
PLUIMPLUS	Gaussian
ROADAIR	Gaussian
SCALTURB	Gaussian
UK-ADMS	Gaussian

The state of the art for these models is described in details elsewhere. Among these, is important to cite the CAR-Parking model. It is developed to calculate benzene concentrations in the vicinity of the parking garages. Used data are about usage, number of cars, speed, duration of stay, building dimensions, ventilation and type of surroundings. The model includes a module for calculating the emission from the garage. The model can be used for 70-80% of the configurations of the garages. The model is validated by a measurement campaign around 3 parking garages in the city of Utrecht, Netherlands (Boeft *et al.*; 1996; Zannetti *et al.*; 1993). Furthermore, the OSPM is developed to describe the pollution in street canyon. Input data to this model is meteorological data, emission factors from cars and concentrations above roof tops. The model describes the flow and dispersion in a street canyon (Berkowicz *et al.* 1997).

3.5 - Data quality objectives

Data quality objectives must be established in order to comply with the monitoring objectives. They will be defined in terms of required precision and accuracy, minimum time coverage and minimum data capture. The precision and accuracy are expressed as maximum uncertainty on the basis of the results of the benzene. The major constituents of a quality assurance programme concern:

- network design number of stations, siting criteria;
- measurement technique, sampling, analytical and calibration procedure;
- equipment evaluation and selection: validation of methods, test of instrument performances;

- routine site operation: calibration under field condition, maintenance, management and training.

An acceptable error for mandatory measurements is expected to be about 20% (*#this is very low see comments by Ballesta*). This figure takes into account various deviations, including:

- the losses due to sampling (5%);
- the calibration errors (primary calibration, transfer standard, routine calibration under field conditions): $\pm 10\%$;
- the analytical errors (noise, non-linearity of the instruments, atmospheric pressure, temperature): $\pm 5\%$.

Non mandatory or indicative measurements may be carried out with lower accuracy and precision. For example, in the case of passive samplers, typical errors of 20% and even more are easily experienced. However they are still acceptable, providing that the expected concentration levels are sufficiently far below the recommended standard.

Another important requirement for benzene analysis resides in the general structure of quality assurance within individual Member States. This requires, at least, that measurements should be carried out by accredited laboratories in accordance with approved methods.

The network management structure must be able to fulfil the following requirements:

- national focal point;
- national co-ordination of data;
- harmonised methodology for statistical evaluation;
- minimum data capture;
- standardised reporting directive;
- exchange of information decision.

The calibration and quality assurance should be based on common requirements in the Member States. Generic capability transfer and harmonisation must include clear and detailed operational manuals and guide books on:

- site operation;
- Quality Assurance/Quality Control on samplers and analytical equipment;
- data handling
- training, workshops, information exchange/technology transfer.

As far as the accuracy and precision of the applied method are concerned, the Working Group has agreed that the overall figures should be:

Mandatory measurements : 20% of the limit value

Indicative measurements : 30% of the limit value

Modelling estimation : 50% of the limit value

Objective estimation : 100% of limit value

3.6 - Random or continuous measurements

A complete resolution in time of a series of measurements can only be obtained by continuously operating instruments. This is mandatory, when it comes to the monitoring of short time peak levels of the pollution in real time as, for example, for smog alert purposes. Continuous measurements are, however, quite costly. Because of high investment and running costs, networks with only continuously operating instruments with on site analyses tend to have few stations and consequently a rather poor resolution in space. On the other hand, random sampling with subsequent analysis in the laboratory is cheap enough to allow for more sampling points in a certain zone, thus giving a better resolution in space at the expense of an additional uncertainty in time resolution. Especially for compounds like benzene with effects from chronic exposure and hence an assessment on the basis of annual averages, at random sampling and analysis offers a cost effective alternative to continuous measurements, provided that the sample size is big enough to yield an acceptable overall accuracy.

The working group thinks that an expanded uncertainty of $\pm 10\%$ (on the 95 % confidence level, that is 2 times the standard deviation) compared with continuous measurements is acceptable for compliance checking. It should be borne in mind that this

additional uncertainty refers to the poorer time resolution, but may be out-balanced by a better representativeness in space, if several sampling points are chosen. Consequently, at random measurements for benzene are equivalent to continuous measurements, provided that

- the sample size is big enough to yield an expanded uncertainty compared with continuous measurements $\leq \pm 10 \%$ (95 % confidence level)
- the sampling dates be evenly spread during the measurement period (normally one year), which can be easily realised if they are chosen at random.

The necessary sample size to keep the expanded uncertainty below $\pm 10 \%$ can be calculated by resampling of stochastic samples from a continuous time series of monitoring data, in this case for benzene. Three time series from urban background sites (Eschweiler, Brühl and Köln-Eifelwall) and two series from industrial hot spots (Duisburg-Bruckhausen and Köln-Godorf) were chosen for this exercise. In the cases of Köln-Eifelwall and Köln-Godorf, time series from three years (1994 - 1996) were considered.

Resampling was performed by means of a computer program with replacement and without stratification. From each time series, a total of 100 stochastic "bootstrap" samples of the considered size N were taken on the basis of daily means (24-values) and 1h-values. For each bootstrap sample, the statistic of interest (arithmetic mean) was calculated. From the resulting bootstrap distribution of the mean value, the overall uncertainty including the uncertainty due to stochastic sampling (standard deviation) can be calculated (compare Table 3-IV). It can be concluded from the table that samples of 104 daily means or more from urban background sites have standard deviations $< 5 \%$ and thus expanded uncertainties $\leq 10 \%$, whereas a sample size of 360 1/2h-values is necessary to reach this accuracy. In addition, Table 3 - V shows that in the case of the time series from industrial hot spot with strong concentration fluctuations in time, more than 200 daily means are necessary, so that random measurements do not offer an advantage any more. The industrial hot spots represent a cokery (Duisburg-Bruckhausen) as well as a distribution terminal in the harbour of big petrochemical plants.

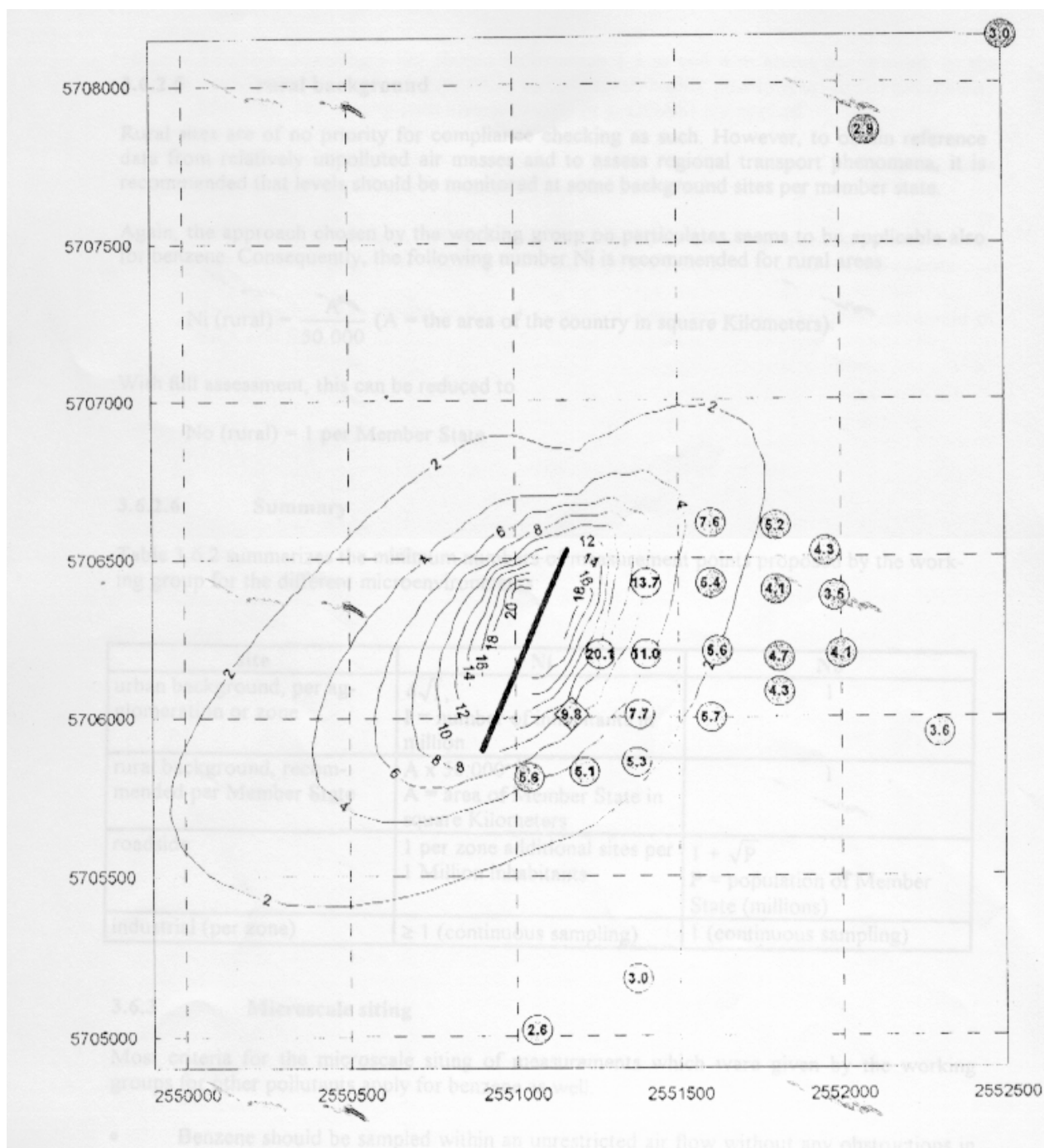


Figure 3.2 - Results from passive sampling of benzene (Sept. 96 - June 97; numbers in circles) and from diffusion and modelling (isolines) of cokery emissions for the same period ($\mu\text{g}/\text{m}^3$). Sampling was performed in a 250 x 250 m grid in a residential quarter east of the cokery. In addition, some more distant sites representing the urban background were measured. Continuous active monitoring was performed at the site represented by a rhomb.

Table 3-IV: Results of resampling of random samples of benzene from continuous measured time series.

Daily and ½-hourly means

Data: Cologne - Eifelwall; 1996; benzene; urban background

Sample size N	24-hourly values			½-hourly values		
	Mean value [µg/m³]	Standard deviation [µg/m³]	Standard deviation (%)	Mean value [µg/m³]	Standard deviation [µg/m³]	Standard deviation (%)
13	2.65	0.40	15.11	2.62	0.54	20.50
26	2.70	0.32	11.80	2.76	0.43	15.62
52	2.71	0.21	7.67	2.75	0.33	12.04
104	2.70	0.13	4.81	2.74	0.21	7.60
156	2.69	0.09	3.20	2.69	0.21	7.61
208	2.69	0.06	2.23	2.69	0.15	5.68
322	2.69	0.00	0.00	-	-	-
365	-	-	-	2.73	0.12	4.50
(Resampling from 322 valid daily mean values)				(Resampling from 3134 valid 0.5 hourly values)		

Data: Hannover-Linden; 1996; benzene; road side

Sample size N	24-hourly values			½-hourly values		
	Mean value [µg/m³]	Standard deviation [µg/m³]	Standard deviation (%)	Mean value [µg/m³]	Standard deviation [µg/m³]	Standard deviation (%)
13	9.53	0.872	9.20	9.45	1.676	17.70
26	9.28	0.611	6.60	9.18	1.087	11.80
52	9.24	0.440	4.80	9.23	0.832	9.00
104	9.27	0.276	3.00	9.20	0.565	6.10
156	-	-	-	-	-	-
208	9.26	0.150	1.60	9.26	0.412	4.40
365	9.27	0.000	0.00	9.26	0.296	3.20
(Resampling from 365 valid daily mean values)				(Resampling from 17569 valid 1/2 hourly values)		

Data: Cologne-Gordof; 1996; benzene; industrial site

Sample size	24-hourly values			½-hourly values		
	Mean value	Standard deviation	Standard deviation	Mean value	Standard deviation	Standard deviation
N	[µg/m³]	[µg/m³]	(%)	[µg/m³]	[µg/m³]	(%)
13	4.50	2.54	56.34	4.24	2.12	50.11
26	4.57	2.13	46.46	4.42	2.28	51.59
52	5.38	1.99	37.01	4.15	1.24	29.90
104	4.79	1.00	20.80	4.46	1.33	29.76
156	4.75	0.74	15.55	4.41	0.88	19.93
208	4.81	0.54	11.16	4.36	0.73	16.76
318	4.82	0.00	0.00	-	-	-
365	-	-	-	4.47	0.57	12.72

(Resampling from 318 valid daily mean values)
hourly values)

(Resampling from 3135 valid 1/2

Table 3-V: Results of resampling of random samples of benzene from continuous measured time series. Weekly means

Hannover, 1990, road side

Sample size	Mean values		
	Mean value	Standard deviation	Standard deviation
N	[µg/m³]	[µg/m³]	(%)
13	17.67	1.10	6.20
26	17.65	0.57	3.30
52	17.65	0.00	0.00

Hannover, 1993, road side

Sample size	Mean values		
	Mean value	Standard deviation	Standard deviation
N	[µg/m³]	[µg/m³]	(%)
13	12.43	0.98	7.90
26	12.37	0.49	3.90
52	12.40	0.00	0.00

Hannover, 1994, road side

Sample size	Mean values		
	Mean value	Standard deviation	Standard deviation
N	[µg/m³]	[µg/m³]	(%)
13	11.81	0.55	4.60
26	11.82	0.32	2.70
52	11.83	0.00	0.00

Hannover, 1996, road side

Sample size N	Mean value [$\mu\text{g}/\text{m}^3$]	Mean values	
		Standard deviation [$\mu\text{g}/\text{m}^3$]	Standard deviation (%)
13	9.90	0.55	5.50
26	9.96	0.27	2.70
52	9.92	0.00	0.00

Cologne-Eifelwall, 1996, urban background

Sample size N	Mean value [$\mu\text{g}/\text{m}^3$]	Mean values	
		Standard deviation [$\mu\text{g}/\text{m}^3$]	Standard deviation (%)
13	2.68	0.24	8.80
26	2.64	0.15	5.60
52	2.67	0.00	0.00

Cologne-Eifelwall, 1996, industrial site

Sample size N	Mean value [$\mu\text{g}/\text{m}^3$]	Mean values	
		Standard deviation [$\mu\text{g}/\text{m}^3$]	Standard deviation (%)
13	4.29	0.62	14.40
26	4.27	0.36	8.30
52	4.24	0.00	0.00

The results shown in the Table above allow the following statements:

1. If the number of 24-hourly benzene measurements taken in a measurement period (1 year) is reduced from 365 to $N = 104$ randomly distributed daily samples, the resulting standard deviation of the yearly mean value due to random sampling would be less than 5 % at sites in urban background. Close to heavy traffic carrying roads, the number of random 24-hourly measurement may even be reduced to $N = 52$ with the same effect.
2. If the number of ½-hourly benzene measurement taken in a measurement period (1 year) is reduced from 17520 to $N = 208$ randomly distributed samples, the resulting standard deviation of the yearly mean value due to random sampling would be less than 5 % at sites close to heavy traffic carrying roads. In the urban background, the resulting standard deviation of the yearly mean value due to random sampling would be 5.7 % at the monitoring site considered.

3. If the number of weekly means of benzene measurement in a measurement period (1 year) is reduced from 52 to $N = 26$ randomly distributed samples, the resulting standard deviation of the yearly mean value due to random sampling would be less than 5 % at road sides or slightly above 5 % (5.6 %) at urban background sites.
4. Close to industrial hot spots with strong fluctuation of benzene concentration in time random measurements should not be recommended for compliance checking. The industrial hot spot considered represents a distribution terminal in the harbour of big petrochemical plants. Similar results were obtained by an analysis of a short time series measured in the vicinity of an old cokery.
5. For indicative measurements in urban background and close to traffic hot spots, a minimum of $N = 52$ randomly distributed measurements of $\frac{1}{2}$ or 1 hour sampling period is recommended in the measurement period (1 year). This would lead to a standard deviation of resulting yearly mean values due to random sampling of less than 12.5 %.
6. Considering 24-hourly measurements, minimum of $N = 26$ randomly distributed samples is recommended for indicative measurements in urban background and close to heavy traffic hot spots. This would lead to a standard deviation of resulting yearly mean values due to random sampling of less than 12.5 %.

For this exercise, the following recommendations of the working group can be extracted:

	Urban sites, road side	Industrial hot spots
For compliance checking	104 (24 h); 208 ($\frac{1}{2}$ h or 1 h), 26 (weekly samples)	continuous or quasi-continuous monitoring
Indicative measurements	26 (24 h); 52 ($\frac{1}{2}$ h or 1 h), 13 (weekly samples)	208 (24 h); 365 ($\frac{1}{2}$ h or 1 h), 13 (weekly samples)

Reliable results for indicative measurements (expanded uncertainty ≤ 25 %) can already be obtained with a small sample size of ≥ 26 daily means or ≥ 52 1h-averages for urban sites. From this exercise, it can be concluded that the following sample sizes N are necessary:

	urban sites	industrial hot spots
for compliance checking	104 (24 h); 360 (1 h)	continuous or quasi-continuous monitoring
indicative measurements	26 (24 h); 52 (1 h)	104 (24 h); 250 (1 h)

In conclusion, the working group also agrees that the minimum time coverage of the measurements should be:

- almost continuous measurements: 100%;
- indicative measurements: 50% (every second day, or at random, or 6 months per year by example). A lower coverage can be discussed according to the concentration levels and possible time trends of atmospheric pollution and other factors.

3.7 - Information on air quality to the public

All information on air quality shall be available to the public and mass media. As means to involve the public in the efforts to fulfil the aims of the Framework Directive, responsible authorities shall actively and regularly disseminate information on the air quality. Appropriate ways can include e.g. summarising papers but also day-by-day reports in newspapers, local radio and television or permanent presentations screens at public locations etc. To improve the understanding and concern for the air quality the development of simple methods for school children, citizen groups etc. to study and monitor the situation shall be encouraged (Nilsson, 1995).

However, it should be taken into account that for benzene, unlike other atmospheric pollutants, no short-term limit values are recommended. Thus information to the public will need to be related to long term limit values. Clear information about the significance of short-term concentrations (for instance daily or hourly means) in relation to longer term exposure should be given to the public.

It is suggested that benzene is an important topic to present to public in coincidence or before the Directive implementation. Review articles on popular press and TV spots are the ideal tools to inform the public about the risks related to benzene exposure and for suggesting practical behaviour in urban areas (Public environmental hygiene). A great deal of information should be addressed to benzene health effects in order to show the relative risks at different concentration levels. It is also suggested to elaborate sufficiently accurate emission inventories at national, regional and local levels in order to clear the sources of benzene and how these sources are supposed to be controlled in the development of directive.

3.8 - Upper and lower assessment thresholds

Art. 6 of the Framework directive sets out the requirements for measurements and other assessment techniques depending on the pollution burden as follows:

Zone and/or pollution level	Assessment technique
<ul style="list-style-type: none"> • above the limit value • above x % of limit value (upper assessment threshold – UAT) • agglomerations in the case of pollutants with alert thresholds(not relevant for benzene) 	Measurement mandatory but other techniques may also be used
Below x % but above y % of the limit (lower assessment threshold – LAT)	Combination of modelling and lower intensity of measurement
Below lower assessment threshold	Sole use of modelling or objective estimation techniques possible

The interannual variability S_V of the annual averages and/or percentiles was used as a basis by the previous working groups for SO₂, NO₂, Lead and Particulate to arrive at numbers for the UAT and LAT. The rationale behind this approach is that assessment regimes with higher levels of uncertainties should be allowed only for zones where the limit values are definitely met, irrespective of variations of the pollution levels from year to year.

An analysis of the time series (annual averages from 1989 to 1995) from 7 urban background stations and 2 traffic exposed stations in Germany was performed and the interannual variations, corrected for the long term trends and the additional variations introduced by grab sampling (15 % in these cases), were calculated. The interannual variability S_V (over the time period considered (7 years) was 20 % or less (for details refer to Table 3-VI). If a 95 % confidence interval for the definition of the UAT is chosen (that is twice the standard deviation), a value of 60 % for the UAT related to the limit value can be inferred. A similar approach using 3 times the standard deviation yields 40 % for the LAT.

Consequently, the proposed values for the upper and lower assessment thresholds are as follows:

Assessment threshold	% of limit value	Comment
Upper Assessment Threshold	60 %	2 x standard deviation
Lower Assessment Threshold	40 %	3 x standard deviation

Table 3-VI: Analysis of benzene trends at selected sites in Germany and calculation of the interannual variability S_y (in $\mu\text{g}/\text{m}^3$)

Year	Stations (urban background)					
	Essen		Bonn		Bottrop	
1989	3,02	1	4,25	1	9,74	1
1990	3,93	2	3,25	2	5,60	2
1991	5,14	3	4,10	3	4,74	3
1992	3,71	4	2,56	4	3,61	4
1993	3,25	5	2,26	5	3,75	5
1994	3,81	6	1,97	6	2,38	6
1995	2,20	7	2,85	7	3,83	7
S_y	0,92		0,63		1,53	

Year	Stations (urban background)			
	Datteln		Düsseldorf	
1989	3,62	1	4,64	1
1990	3,32	2	3,70	2
1991	3,90	3	5,78	3
1992	2,54	4	3,74	4
1993	2,74	5	3,09	5
1994	2,00	6	4,21	6
1995	3,68	7	3,81	7
S_y	0,70		0,88	

Year	Stations (urban background) Schwerte		traffic exposed				urban background Wesseling	
			VDDF		VESN			
1989	5,74	1	1		19,73 1		8,35 1	
1990	2,83	2	22,75 2		12,66 2		9,88 2	
1991	6,66	3	21,34 3		11,84 3		6,87 3	
1992	3,18	4	17,67 4		11,19 4		4,93 4	
1993	2,94	5	15,49 5		8,85 5		5,06 5	
1994	2,51	6	16,30 6		9,99 6		4,15 6	
1995	3,60	7	11,10 7		7,15 7		4,28 7	
Sy	1,51		1,34		2,08		1,12	

The relative standard deviation S % was calculated from the absolute variance S_y by relating S_y to the average of the annual means of each station. As the benzene trends were measured by grab sampling, S % was corrected for the additional uncertainty S_g introduced by grab sampling (15 %) as follows:

$$S_v (\%) = \sqrt{S_{\%}^2 - S_g^2}$$

Benzene Calibration Method

Method	Description	Reference	Advantage	Disadvantage
Static volumetric method	A known liquid volume of benzene to a known volume of air.	ISO 6144, VDI 3490	Primary calibration method. Cost effective method. Also suited for other pollutants. Precise and accurate (uncertainty < %).	Control of the purity of benzene.
Permeation method	Benzene permeation through a membrane into a flow of carrier gas at a constant temperature. The loss of benzene is determined by weighing.	ISO 6349	Primary calibration method. Diffusion rate determined by weighing. Continuous production of calibration gas. Cost effective method. Precise and accurate.	Control of the purity of benzene.
Dynamic volumetric method	Introduction of a given rate of a gas into a constant flow rate of a complementary gas. The gas mixture is in general a high concentration gas mixture.	ISO 6145	Gas cylinders are commercially available. Easy to handle. Certified standards are available from NIST (USA).	Unknown accuracy. No primary standard. The certified standard is expensive.

Benzene Sampling Methods

Method	Description	Reference	Advantage
1	Laminar flow manifold	Flow 150 l min ⁻¹ , tube diameter 15 cm Inlet material: glass, stainless steel, teflon	EPA Isokinetic sampling, sample unaffected
2	Turbulent flow manifold	Modular sugar cane design. Inlet material: glass, stainless steel, Teflon	Low cost, modular construction
3	Direct connection of analyser inlet to station sampling head		Low cost, efficient sampling without losses

Review of existing measurement methods

Method	Average time	Detection limit	Reference	Advantage	Disadvantage
Pumped sampling on tubes with thermal desorption-GC	0.5-24 hour	0.14 0.4	prEN 1076, VDI 3482-4, ISO/TC 146/Sc 6 N 19-20	<ul style="list-style-type: none"> - Low cost - Many sampling sites with one GC analytical instrument - Work with toxic species is minimised - Calibration with spiked tubes 	
Pumped sampling on tubes with solvent extraction-GC	3-12 hour 24 hour	0.14 0.4	prEN 1076, VDI 3482-4, ISO/TC 146/Sc 6 N 19-20	<ul style="list-style-type: none"> - Low cost - Many sampling sites with one analytical instrument - Analysis is made on a cheap GC 	<ul style="list-style-type: none"> - Toxic solvents are needed
Diffusive sampling with solvent extraction-GC	1-4 weeks	0.5	CEN/TC 264/WG 11/N 15-17	<ul style="list-style-type: none"> - No electrical power is needed for sampling - Same comments as in No. 2 	<ul style="list-style-type: none"> - Long sampling time needed - Same comments as in No. 2
Diffusive sampling with thermal desorption-GC	1-4 weeks	0.5	CEN/TC 264/WG 11/N 15-17	<ul style="list-style-type: none"> - No electrical power is needed - Same comments as in No. 1 	<ul style="list-style-type: none"> - Differences to active sampling of about 20% - Long sampling time needed
Canisters Thermal Desorption	seconds to minutes	0.3	VDI 3482-2,3	<ul style="list-style-type: none"> - No electrical power is needed - Same comments as in No. 1 and 2 depending on the analysis technique 	<ul style="list-style-type: none"> - Differences to active sampling of about 20% may occur - Only grab samples (with short average times) can be taken (discontinuous measurements)
BTX monitors	1/2 to 1 hour	0.16	DIN 33961-1,2	<ul style="list-style-type: none"> - High time resolution - Real time data - Analysis of BTX simultaneously 	<ul style="list-style-type: none"> - High cost - Need of a monitoring hut with air condition - Need of carrier gas supply and burner gas (for FID)

On line GC instruments	1/2 to 1 hour	0.1	ISO	<ul style="list-style-type: none"> - High time resolution - Real time data - Analysis of C2-C12 simultaneously 	<ul style="list-style-type: none"> - High cost - Need of a monitoring hut with air condition - Need of carrier gas supply - Instruments from some companies need
DOAS	30 seconds	1.5	Validation report under preparation by UBA, Germany	<ul style="list-style-type: none"> - High time resolution - Real time data - Measurements over a long path - No chemical interference - Multicomponent measurements 	<ul style="list-style-type: none"> - High cost - Measurements over a long path - Zero point offset problems -Not sufficient documentation available - Difficulties with measurements at low visibility - Problems with calibration

3.9 Summary

Monitoring methods are generally based on gas chromatography, with either active (pumped) or passive (diffusive) sampling and thermal or solvent desorption prior to analysis. Automated instruments with active (pumped) sampling and thermal desorption are available, which allow for quasi continuous monitoring. Advantages and disadvantages as well as typical uncertainties of the different methods are given. Pumped sampling on tubes followed by GC analysis including calibration is recommended as basis for a reference method. A detailed reference method will be worked out by CEN.

Any network design for compliance checking must take the requirements of the Framework directive as starting points. In addition, it has to be borne in mind that for benzene long term exposure with possible adverse effects on human health in areas representative for the majority of the population as well as at hot spots has to be assessed. Consequently, monitoring should cover the following microenvironments: urban background, road side, residential quarters near industrial sites and rural background (for reference data only).

The following minimum numbers of monitoring stations N per zone or agglomeration are proposed:

Site	N_i (without full assessment)	N_0 (with full assessment)
urban background	$4 \sqrt{I}$ I = number of inhabitants in million	1
road side	1 per zone; 1 additional station per 1 million inhabitants	$1 + \sqrt{P}$ P = Population of Member State (million)
industrial	≥ 1 (tailor made)	1
rural background	1 per 50.000 km ²	1

A full assessment is only possible by combining modelling with monitoring. This holds especially true for road side locations. For this purpose, a variety of air pollution models for various spatial and temporal scales exist. An overview of existing local scale models and their characteristics is presented, but no general recommendations are given by the working group.

The considerations for microscale siting are very similar to those laid down in the first daughter directive.

Principles of Quality assurance are described, and the working group recommends the following acceptable overall accuracies (trueness and precision) for assessments: mandatory 20 %, indicative 30 %, modelling 50 %, objective estimation 100 % of limit values.

The working group feels that random and continuous measurements can be regarded as equivalent, provided that the sample size of the random measurements is big enough to yield expanded uncertainties ≤ 10 %, and that the sampling dates be evenly spread during the measurement period. Necessary sample sizes can be calculated by resampling of stochastic samples from continuous time series. Examples for urban background, road side and industrial locations are presented.

Upper (UAT) and lower assessment thresholds (LAT) were derived from the interannual variability of annual averages from 9 stations. The working group recommends 60 % as UAT and 40 % as LAT.

Finally, the working group stresses the importance of informing the public on long term benzene levels and explaining the significance of short term concentrations in relation to longer term exposure.

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Chapter 4

Benzene:

Economic Analysis

4.1 Introduction

All Working Groups preparing technical position papers on ambient air quality are asked by the Commission to develop their recommendations for air quality objectives on the basis of their assessment of the risks of the pollutant with which they are dealing. Legislation setting ambient air quality limit values does not however merely list objectives. It sets binding targets and binding dates by which they must be met. Working Groups are therefore asked also to take into account practical considerations in framing their final detailed recommendations. In particular they are asked to identify cost-effective means by which recommended objectives can be met, to recommend timetables and to identify the benefits of meeting the targets and the consequences of not doing so. If it is not possible to identify reasonable means of reaching a desired target within a reasonable timescale, then economic analysis can play an extra role in helping identify interim targets.

Economic analysis is a specialist task. DGXI therefore engaged a team of consultants, led by AEA Technology, to help the Working Group with this part of their assignment. They were asked: to assess likely concentrations of benzene across the Union in the year 2010, taking into account the effects of existing and planned legislation; to determine whether further action would be needed to reach targets of 10 $\mu\text{g}/\text{m}^3$, 5 $\mu\text{g}/\text{m}^3$ and 2 $\mu\text{g}/\text{m}^3$ by that date; and if further action would be needed, to identify the least cost means; to assess the benefits of meeting these targets.

4.2 Results of economic analysis

A full report of the study is available in a separate document².

A number of difficulties were encountered during the course of the work, which the consultants considered were priorities for further data collection and research activities. Firstly, they found that, as found also in Chapter 1 of this document, emission inventories between different countries are inconsistent. Secondly, the cost-benefit assessment was made extremely difficult by the lack of good exposure-response data for benzene. A third difficulty concerned the overall framework for the analysis. The consultants suggest that it would be preferable in future analyses to take a broader approach, considering a larger number of pollutants (e.g. SO₂, NO₂, benzene, and ozone) simultaneously. This would allow better integration of the secondary effects of abatement measures for individual pollutants, for example through reductions in emissions of other pollutants under consideration. Overall this should lead to a more optimal selection of abatement technologies.

Analysis concentrated on three were extrapolated to the rest of the European Union. The Steering Group for this work requested that the following values be investigated as possible limits in this study:

- 2, 5 and 10 ug/m³ as annual average to be attained by 2010.

These limits were to be investigated as they applied in both urban background and hot-spot locations.

The sole benefit considered is reduction in the risk of contracting leukaemia. There are suggestions that benzene could have other effects, such as lung cancer. However, as noted by the Ad Hoc Group of Experts on the risks of benzene there are only isolated studies showing such effects and there is no agreement amongst experts as to potential mechanisms nor potential unit risks. Benzene has no recorded direct effects on the environment. It is an ozone precursor, though its ozone creation potential is relatively low.

The methodology for this study follows to a large extent extrapolation of the results of the Auto-Oil programme. Auto-Oil provided detailed modelled assessments of urban background air quality across 7 cities, these cities being broadly representative with respect to air quality of all cities in the European Union. Auto-Oil also provides a set of data and

² AEA Technology: Economic Evaluation of Air Quality Targets for CO and Benzene – available from DGXI

assumptions that have been widely reviewed, discussed and agreed by European decision makers and other interested parties already.

The baseline scenario used here incorporated the Auto-Oil Directives on fuel quality (including the reduction in maximum benzene content of petrol to 1%) and vehicle emissions and the first daughter Directive on SO₂, PM, NO₂ and lead, using results from an earlier study conducted for the Commission. There is emerging evidence that the measures considered in that earlier study would not be sufficient to meet the limits contained in the first daughter Directive. Given the commonality of sources for the pollutants considered, and the particular effect of transport in areas where exceedences are most likely it is possible that this will mean that the present analysis overestimates future benzene levels and therefore costs.

Emissions of benzene are expected to fall greatly by 2010 as a result of the legislation included in the baseline scenario. The study predicts that background concentrations will fall to some 3.2 µg/m³ even in Athens, the most polluted of the cities studied in Auto-Oil. Benzene in the future will therefore be a problem only in hotspots – primarily heavily trafficked urban streets.

Aggregated results for urban background and hot-spot locations are shown in Table 4.1. A number of uncertainties have been explored in these tables:

- Emission scenarios. Three scenarios were examined, requiring high (H), medium (M) or low (L) further reductions to meet targets.
- Relationship between urban background and hot-spot concentrations
- The risk factor determining the number of cancers likely to be linked to a given level of benzene
- Whether measures are strongly targeted (optimised abatement case - opt) or weakly targeted (generalised abatement case - gen) at the locations where exceedences occur.

Table 4.1 . Aggregated results of the analysis for benzene, estimating costs and benefits throughout the EU. Cells with ‘0’ entered represent cases where no exceedence is predicted.

Limit µg/m ³	Location	Emissions	Impacts (cases)		Benefits (kEuro)		Costs (kEuro)	
			Low	High	Low	High		
2	urban back	L - opt	0.0003	0.034	0.67	119		890
		M - opt	0.0059	0.59	12	2,107		71,800
		H - opt	0.010	1.0	20	3,583		207,850
2	hot spot	L - gen	0.081	8.1	162	14,344		9,774,150
		M - gen	0.13	13	265	23,151		23,059,710
		H - gen	0.16	16	330	28,691		34,491,730

2	hot spot	L - opt	0.037	3.7	74	6,879	976,220
		M - opt	0.077	7.7	153	12,463	3,539,690
		H - opt	0.13	13	263	20,713	8,389,050
5	urban back	L - opt	0	0	0	0	0
		M - opt	0	0	0	0	0
		H - opt	0	0	0	0	0
5	hot spot	L - opt	0.0030	0.30	5.9	1,058	24,330
		M - opt	0.010	1.0	20	3,511	226,360
		H - opt	0.019	1.9	37	5,619	465,280
10	urban back	L - opt	0	0	0	0	0
		M - opt	0	0	0	0	0
		H - opt	0	0	0	0	0
10	hot spot	L - opt	0	0	0	0	0
		M - opt	0	0	0	0	0
		H - opt	0.0040	0.40	7.9	1,404	45,590

There is a tendency for costs to significantly exceed benefits where exceedences are likely to occur, except in the case of a target of $10 \mu\text{g}/\text{m}^3$ with abatement closely targeted on areas of exceedance. There are several points that should be noted here however:

1. In many cases it is likely that concentrations estimated here are overestimated. Further abatement to that considered here in the baseline scenario may well follow without further action to control benzene. This may arise through measures needed to control other air pollutants, congestion, and emissions of greenhouse gases following the agreement of the Kyoto protocol and the need to reduce other impacts of transport. A further factor is the potential introduction of new technologies, which could make an impact on benzene levels by 2010.
2. The consultants did not consider direct secondary effects of abating benzene, for example on ozone levels, or indirect secondary effects via reductions in concentrations of other VOCs, NO_2 and particulate matter. They considered the logic for including such effects (see table) within the context of the Framework Directive unclear. In this case it is likely that the so-called secondary effects would be much larger than the primary effects. If this were so it would probably be more efficient to develop abatement strategies primarily to address these larger benefits and to ensure that the potential for reducing benzene concentrations was considered simultaneously.

Abatement measure	Burden affected	Impacts affected
Traffic calming, public transport subsidies, etc.	Emission of all transport pollutants (SO_2 , NO_x , PM_{10} , VOCs, CO_2 etc.. generation of related secondary pollutants such as ozone)	Effects on health, materials, ecology
	Risk of accidents	Death and injury, material damage
	Congestion	Travel time

	Noise	Amenity
Emission constraints	Emission of all transport pollutants (SO ₂ , NO _x , PM ₁₀ , VOCs, CO ₂ etc.)	Effects on health, materials, ecology

3. In many cases the extent of exceedence was tightly constrained, geographically and with respect to the amount of exceedence. This makes it more likely that the measures taken for reasons raised at [1] could lead to certain limits being met without controls being directed specifically at benzene. The clear exception to this was the limit of 2 µg/m³ applied in hot-spots.
4. There are significant problems in the quantification of benzene risks. The unit risks found in the scientific literature vary a great deal. Following the advice of the Ad Hoc Group of Experts on health risks and the recommendation of the Working Group a range of unit risks differing by a factor of 100 was explored in this study. Further research on the mechanism of benzene effects may reduce this uncertainty in the near future. As already explained above there are also at present few data on personal exposure to benzene. This too seems likely to improve in future years.

4.3 Discussion

Cost benefit analysis is a relatively new tool in analysis of carcinogenic compounds. There are few published studies in the literature. Genotoxic carcinogens are also a very sensitive political and public issue. It is important therefore to be clear about the role of such analysis in helping legislators to arrive at decisions.

Firstly, it should be understood that the above results are not an estimate of the costs and benefits of reducing benzene concentrations from today's levels to the target concentrations included in the analysis. Concentrations will fall by 2010 as a result of legislative decisions already taken – most notably the Auto-Oil Directives, the IPPC Directive, the proposed Directive setting limit values for sulphur dioxide, nitrogen dioxide, particulate matter and lead and the proposed Solvents Directive. The figures above include neither the costs nor the benefits relating to these results. They are the estimated costs and benefits for further action beyond these existing plans.

Secondly it is extremely important also to understand the uncertainties identified by the consultants and the extent to which they were able to deal with these in their analysis. The most important of these uncertainties were the quantification of both current and future emissions, model error, the relationship between background concentrations (for which

most data are available and which can be modelled most accurately) and hotspot concentrations, the size of the risk associated with benzene, the extent to which the population is actually exposed to different concentrations in different types of location, the valuation of benefits, the integration of secondary costs and benefits of abatement options, and the extent to which results for the three cities studied can be extrapolated to the EU as a whole.

As far as possible, the consultants integrated these factors into their study during the main part of their work or during sensitivity analysis. This is reflected in the ranges of their estimates. The largest uncertainty factor incorporated into the analysis is the risk associated with benzene. With a factor of 100 between the highest and lowest unit risk estimates this dominates the benefits results. Some uncertainties could not be incorporated. Among these the two most important are the extent of secondary benefits due to the implementation of measures that would reduce benzene concentrations and the extent to which measures which would reduce concentrations of benzene will be implemented anyway for other reasons.

The consultants estimated that the potential reduction in the number of cancers per year (beyond the reduction due to existing plans) would be relatively low for all limit values tested (see table 4.1 above). Estimated costs exceed estimated monetary benefits for both the 2 and 5 $\mu\text{g}/\text{m}^3$ targets at the kerbside. For the 10 $\mu\text{g}/\text{m}^3$ target, benefits were found to be larger than costs, but only when abatement measures are closely targeted to the areas where exceedance occurs.

This picture would be likely to change if either secondary benefits or measures to meet other targets were included. Potential secondary benefits include abatement of other pollutants and in the case of non-technical measures, alleviation of congestion and noise. These benefits could be substantial. However, other important pollutants are being dealt with by separate legislation. For some, including particulate matter, Council has just adopted a Directive setting limit values. As far as possible the effects of this are already built into this analysis. The remaining secondary benefits would be those of going further than the Common Position. There are not sufficient data available to take into account reducing congestion or noise. In any case, an economic analysis of reducing benzene concentrations which showed that the great majority of the benefits would be obtained for example, from reductions in other pollutants which are regulated separately, would seem to be of limited use in analysing what action should be taken on benzene itself.

On the other hand, it can be argued that some of the measures which would reduce concentrations of benzene beyond current plans will in fact be taken in coming years for other reasons. If so, the costs should not be assigned wholly to benzene. The proposals recently adopted by the Commission on ambient air quality standards for ozone and national emission ceilings will, for example, require reductions in emissions of VOCs generally. Measures taken to reduce traffic congestion would also reduce benzene concentrations. Implementation of the Kyoto protocol will affect global energy consumption and hence further decrease benzene emissions. It is not possible to make any precise estimate of the extent to which such actions would reduce the costs of achieving benzene targets on the basis of presently available data. But in the view of the Working Group it is likely that estimated costs would begin to exceed estimated benefits at a concentration below 10 $\mu\text{g}/\text{m}^3$.

Chapter 5

Benzene:

Discussion and final recommendations

5.1 Summary of Chapters 1-4

5.1.1 Chapter 1

Chapter 1 of this document discusses available data on present day benzene emissions and concentrations in the European Union and expected trends in coming years. The major source of benzene across the EU is combustion, of which traffic is the largest component. Emissions are expected to fall substantially in the period to 2010 compared with 1990 levels. There are no systematic data on present day concentrations, but cities studied in the Auto-Oil programme showed concentrations in the urban background of 6 – 12 $\mu\text{g}/\text{m}^3$ for 1990. Measurements show that concentrations have already decreased in some cities. It is expected that these concentrations will be reduced to below 4 $\mu\text{g}/\text{m}^3$ in all cities by 2010, primarily as a result of new emission limit values for vehicles and a reduction in the maximum benzene content of petrol to 1% from 2000. Other data shown in Chapter 1 show that concentrations can vary a great deal across the Union, particularly when hotspot situations are taken into account. There are a number of potential reasons for this. Some, such as the age of industrial plant or of the vehicle fleet, can in principle be managed. Some, such as climate or local topography cannot.

5.1.2 Chapter 2

Chapter 2 deals with the risks associated with benzene. Most authorities agree that benzene should be classified as a known human genotoxic carcinogen. There are open questions about its mechanism of action, particularly at low doses, but at present no threshold for effects has been identified. It is impossible to estimate precisely the risks associated with exposure to environmental benzene. The largest body of evidence is concerned with exposure of industrial workers to relatively high concentrations for relatively short periods of time. There are many uncertainties when extrapolating from these data to exposure of the whole population to lower concentrations over a lifetime. WHO in developing its 1996 guidelines used a linear model to extrapolate. They noted some uncertainties but did not feel it possible to recommend any other way of modelling the data. An ad hoc group of experts which reviewed evidence published since WHO carried out their work was of the view that this evidence does not allow the uncertainties identified by WHO to be removed. That is, it is still not possible to say what is the best model for extrapolating from worker exposure to environmental exposure of the whole population.

Nor, despite evidence that benzene is an unusual carcinogen, do animal and other data allow a threshold to be identified below which effects are not expected.

The ad hoc group concluded that though it was not possible on present evidence to give a precise estimate of the risk associated with benzene it was possible to define a range within which that risk was likely to lie. The procedure followed by the WHO working group was considered to result in the highest plausible estimate of risk – an excess lifetime risk of leukaemia at an air concentration of $1 \mu\text{g}/\text{m}^3$ of 6×10^{-6} . Unit risks in the order of 10^{-10} and 10^{-11} derived by some authors, were felt to be too far outside the general range of estimates to be relied upon with good supporting evidence for the models used. The lowest unit risk which the group felt was likely to be plausible was in the order of 5×10^{-8} . They did not feel that present evidence supported the setting of a short-term limit value. Consideration could be given to this in future of more evidence accumulated. In the meantime however, reducing annual average concentrations should also reduce shorter-term peak concentrations.

Working Groups on individual pollutants are asked by the Commission to base their initial recommendations for goals for air quality on their assessment of risk. This is particularly difficult in the case of carcinogens. Converting unit risks to goals means deciding on a level of risk which will be tolerated. The European Parliament and the European Council, has agreed a proposal for a Directive on Drinking Water, in which an excess lifetime risk of 1 in a million is taken as the starting point for developing limit values. Taking this as a precedent, the range of unit risks given above (6×10^{-6} to 5×10^{-8}) has been converted into annual average concentrations which are estimated, over a lifetime, to equate to an excess risk of contracting leukaemia of 1 in a million. The resultant range of concentrations is 0.2 to $20 \mu\text{g}/\text{m}^3$.

The Working Group notes that there are epidemiological studies suggesting risks of other effects of benzene, from both long-term and short-term exposure. The number of such studies dealing with any particular effect is small and they are not at present supported by work suggesting plausible mechanisms. There is no consensus on the extent of any such risks. There is much research now underway on the mechanism by which benzene causes leukaemia and on whether benzene has other effects on human health. The Working Group recommends that the accumulating scientific evidence on benzene should be reviewed again in approximately 5 years' time.

5.1.3 Chapter 3

Chapter 3 deals with assessment of benzene concentrations and recommends methods of measuring it. It is important to be aware when setting standards of the accuracy with which concentrations can be measured or otherwise assessed. As Chapter 3 shows, there are uncertainties associated with all methods of assessment, including measurement, and these tend to increase as the concentrations to be assessed decrease.

5.1.4 Chapter 4

Chapter 4 summarises the results of the consultancy study on the economic evaluation of air quality limit values for benzene. The consultants point out a number of important uncertainties in the study. Benefits estimates are highly uncertain owing to lack of agreement on risks and lack of data on human exposure and costs are probably overestimated. Caution is therefore needed in interpreting the results.

The consultants found that the estimated potential reduction in the number of cancers per year beyond the substantial reduction which will occur due to existing legislation would be relatively low for all limit values tested. This is the case even if the most conservative attitude is adopted to risk and exposure. Estimated costs exceed estimated monetary benefits for both the 2 and 5 $\mu\text{g}/\text{m}^3$ targets at the kerbside. For the 10 $\mu\text{g}/\text{m}^3$ target benefits were found to be larger than costs, but only when the most conservative attitude is taken to risks and when abatement measures are closely targeted to the areas where exceedance occurs. It should be noted that costs do not fall evenly across Member States. The highest costs would be borne by Mediterranean cities such as Athens.

Secondary benefits of measures to reduce concentrations of benzene, such as reductions in concentrations of other pollutants, or in emissions of greenhouse gases were not included. They are potentially much larger than the benefits associated with further reductions in benzene concentrations, but tend to be the subject of separate legislative action. On the other hand if further action were taken with one or more of these benefits as a primary goal, then this would reduce the cost of achieving limit values for benzene. Such further action will be needed in order for example to implement the Kyoto protocol, and to reduce acid rain and ozone formation. Meeting limit values should therefore be easier to attain than the results suggest for all Member States.

5.2 Considerations to be taken into account in setting limit values for benzene

Benzene is the first carcinogen to be considered under the new framework for ambient air quality limit values set up by the Directive on Ambient Air Quality Assessment and Management. There are no existing ambient air quality limit values for carcinogens, although such limit values have been developed for drinking water.

There are a number of factors to be taken into account in framing legislation on benzene. These include:

- the risks to human health;
- the obligation under the Treaty to implement the precautionary principle;
- the extent to which risk is acceptable;
- the measures that can be taken to reduce benzene concentrations;
- the speed with which they can be implemented across the whole of the EU;
- the extent to which society is prepared to bear the costs.

The primary consideration is the risk to human health. The Working Group has not found it possible to estimate this risk precisely and has given a range within which the unit risk of contracting leukaemia from exposure to benzene (the additional risk of contracting leukaemia if exposed to $1 \mu\text{g}/\text{m}^3$ for a lifetime) is most likely to lie. This range is 6×10^{-6} to 5×10^{-8} . Even if the risk could be quantified an extra step is however required in order to determine the basis for a limit value. Since on current evidence no threshold can be identified setting a target means deciding what level of risk is tolerable. This is not a decision that can be taken on technical grounds alone. The Working Group notes the decision by the European Council and the European Parliament in the context of drinking water that an additional lifetime risk of 1 in a million should be taken as the starting point for determining limit values. Translating the range given above into an annual average concentration which equates to an additional lifetime risk of contracting leukaemia of 1 in a million gives a range of concentrations of 0.2 to $20 \mu\text{g}/\text{m}^3$.

This wide range cannot be narrowed on scientific grounds without further evidence about the mechanism by which benzene causes leukaemia. The Working Group considers it reasonable to expect that further evidence will become available over the next five years or so which will throw more light on this question. It notes that further research is also underway on other possible effects of benzene. It considers that the results should be reviewed in approximately 5 years time. In the meantime it recommends that exposure to benzene in ambient air should be as low as reasonably achievable.

This leads inevitably to the question of what is reasonably achievable. The analysis of the costs and benefits of meeting limit values for benzene described in Chapter 4 is a useful input, but the answer depends also on the attitude adopted to risk in the light of uncertainty, and on willingness to undertake further actions to reduce risk given that uncertainty. Clearly the decisions to be made are socially and politically important and the Working Group considers them beyond its remit. However, in order further to assist both the Commission in developing its proposal for a Directive and those involved in the adoption of legislation the Working Group has decided to put forward three illustrative options, developed on the basis of its technical analysis.

5.3 Options for consideration

The Working Group has adopted the following principles in developing the options below:

- concentrations of benzene in the air shall not increase;
 - exposure to benzene in the ambient air should be as low as possible;
 - an annual average limit value should be set;
 - the limit value should apply everywhere including hot spots;
 - there is not sufficient evidence for setting a separate short-term limit value.
- An annual average limit value applying in hotspots will however reduce peak exposure.

5.3.1 Option 1

Decision makers may consider that a conservative attitude should be adopted towards the risk associated with benzene and the precautionary principle implemented to the maximum possible extent. A concentration of $0.2 \mu\text{g}/\text{m}^3$, which equated to a additional risk of 1 in a million on the most conservative view of risk (see 5.1.2 above) is close to that found in remote areas such as Antarctica and is not achievable in areas of economic activity. Given however that people do not spend entire lifetimes in areas of maximum benzene concentration the Working Group considers that a limit value in the lowest end of the range, i.e. $2 - 5 \mu\text{g}/\text{m}^3$, to apply in hotspots as well as the urban background, would provide a very high level of protection to the population.

The Group notes that achieving such a limit value in the relatively short timescale of 2010 could entail considerable costs in addition to those which will be incurred because of recently agreed legislation on benzene, such as new fuel quality standards. If decision makers consider that a limit value should be set for 2010 they may consider that a limit value of $5 \mu\text{g}/\text{m}^3$ would implement the precautionary approach whilst making allowance for the practicalities of the short timescale. The Working Group notes that costs are likely to be lower than those estimated in the study described in Chapter 4 because of action which will be taken to reduce concentrations of other pollutants such as ozone. It is not however possible to make an estimate of the extent to which costs might be lower.

5.3.2 Option 2

Decision makers may feel that in the light of the uncertainties associated with the risks of benzene and the expectation that further evidence on its mechanism of action will become available, and given the information also on costs, a more measured approach should be taken.

Concentrations of benzene will decline from present day levels as a result of legislation already agreed. They will not however decline at the same rate or to the same extent across the European Union. The conclusion may therefore be that an initial limit value should be set to ensure good progress everywhere whilst making explicit provision for a re-examination of the evidence when more data are available. In that case a two stage process could be set up, analogous to that agreed for particulate matter. A first stage limit value would be set to be met as soon as possible – for example $10 \mu\text{g}/\text{m}^3$ to be met in 2007. A second stage limit value would be set for 2015, at the lower end of the range examined ($2 - 5 \mu\text{g}/\text{m}^3$) but this would be reviewed at some suitable point.

A review should take place when more scientific data are available on which to judge the risks associated with benzene, and when more data are available from Member States on concentrations and practicalities as a result of implementation of the legislation. The Working Group notes that a possible disadvantage of a two-stage process is that action plans for benzene would for the first few years relate only to the Stage 1 limit value. Ideally information should be gathered during Stage 1 on measures which might be taken to reach the Stage 2 limit value. The Working Group recommends that if a two-stage approach is chosen, decision-makers should consider whether Stage 1 should include provision for gathering such information.

The Working Group recommends also that the Commission and legislators should consider integrating a future review of benzene with work on other pollutants. This would avoid some of the difficulties in economic analysis of having to assign costs of measures that may be taken on other grounds wholly to benzene.

5.3.3 Option 3

Option 3 is similar to Option 2 in giving greater weight than Option 1 to the uncertainties associated with benzene and making explicit provision for review. Option 2 gives a relatively short time horizon to planners and less certainty over the longer term. It also means, as noted in 5.3.2, that information needed for Stage 2 may not be collected in time for a review. Decision-makers may feel that it would be better to determine a single relatively ambitious limit value, in the range 2 – 5 $\mu\text{g}/\text{m}^3$, to be met over a longer timescale, for example 2015. Provision should however be made to review this limit value in ample time before it is met. In that case action plans would relate to this limit value and would provide information on potential abatement options which is not presently available.

A potential disadvantage of this option is that actions that could be taken relatively quickly may be deferred, in the knowledge that a review will be carried out well before the limit value must be met. Although the Air Quality Framework Directive includes provision for setting a margin of tolerance, which then declines over time to meet the limit value, it does not require that concentrations should be reduced immediately to below the margin of tolerance. Member States' obligation is to meet the limit value by the target date. However, the Commission will publish each year a list of areas that are above the margin of tolerance. These areas must also prepare within two years an action plan that shows how they will meet the limit value by the target date and this action plan will be made public. It may be considered that these transparency provisions will be sufficient to ensure early action.

5.4 Reviewing limit values

The difficulties in estimating the costs of action to reduce concentrations of benzene arise primarily from considering benzene in isolation. As this paper makes clear, actions, which would reduce concentrations of benzene, would have substantial secondary benefits. This can be looked at from another point of view. If such actions will be required anyway in order to meet other targets such as reductions in greenhouse gas emissions and

emissions of other air pollutants it does not seem sensible to assign all their costs to benzene abatement.

Problems of this sort are to some extent inevitable - it is impossible to undertake an integrated analysis of all potential targets and measures to meet them. Nevertheless, it is recommended that any review of limit values for benzene should be carried out as part of an integrated review, considering other important pollutants simultaneously.