Report nr. 758476003

INTEGRATED CRITERIA DOCUMENT BENZENE

W. Slooff (ed.)

February 1988

NATIONAL INSTITUTE FOR PUBLIC HEALTH AND ENVIRONMENTAL PROTECTION
BILTHOVEN
THE NETHERLANDS

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This investigation has been carried out on behalf and for the account of the Directorate-General for Environmental Protection, Direction Toxic Substances and Risk-management.
This document is the English edition of Basisdocument Benzeen, Rep.nr. 758476001.

Title	Integrated criteria document benzene
Keywords	criteria document, benzene, air quality, water quality, soil quality, standards, monitoring methods, measurement strategies, sources, emissions, production, dispersion, transformation, environmental concentrations, human toxicity, ecotoxicity, control techniques, cost of control, risk analysis
Date of publication	February 1988
Summary	This report contains a systematic survey and a critical evaluation of the most important data on the priority substance benzene on behalf of the environmental effect oriented policy

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SUMMARY

The present document contains data on benzene with respect to the sources and dispersion pattern (soil, water, air, biota), the risks of environmental concentrations for man, (parts of) ecosystems and materials, as well as the technical possibilities and economic consequences in relation to a reduction of these risks. This information serves as the scientific basis for the formulation of the effect-oriented policy in The Netherlands.

In 1981 a total of 1026 ktons of benzene was available for use in The Netherlands, of which 96 ktons was present in petrol. Apart from being a component of petrol, benzene is also used in The Netherlands for the production of ethyl benzene/styrene (73%), cumene/phenol (16%) and cyclohexane (11%). The use as a solvent has been greatly reduced in the last few years, especially by replacement with toluene.
In 1981 the direct emissions to the soil amounted to more than 23 tons in The Netherlands (transport accidents: 14 tons; leakage of storage tanks: 9 tons; wash-out into ground water from polluted areas: unknown), emissions to surface water were 243 tons (industry: 240 tons; transport accidents: 3 tons) and emissions to air amounted to about 8360 tons (road traffic: 7295 tons; other traffic: 130 tons; industry: 906 tons; space heating: 23 tons; smoking: 8 tons). In the same year the indirect emissions to soil were 22 tons (deposition), to surface water 3 tons (deposition), whereas an important though unknown reemission into air took place. Emissions from abroad play no part for soil, a slight one for water (5 tons a year) and an important part for air (> 30000 tons a year).

The role of the compartment of air clearly emerges in estimates of the distribution of benzene in the envrionment as well. Since direct emissions mainly occur to air and the emissions to soil and water (as a result of the small degree of adsorption, the relatively high vapour pressure and the small solubility of benzene in water) partly lead to reemissions, practically the total amount (about > 99%) is encountered in the atmosphere. Partly as a result of this, the potential removal (export) in air is the largest (about > 99%). However, due to the before mentioned trans-frontier emission, the net removal (export: potentially about 95%) is negative. Elimination by decomposition takes place in all compartments of the environment: soil (only biodegradation in aerobic circumstances, half-life

unknown), surface water (biodegradation, half-life from a few days to weeks, while reaction with hydroxyl radicals leads to a half-life of several weeks to months), air (reaction with especially hydroxyl radicals, half-life about 5 days). Quantitatively the reaction in air is the most important way of decomposition. Biota absorb benzene rapidly and it is excreted partly unchanged and partly metabolized; benzene is not or hardly bioaccumulative. During biotic as well as abiotic transformations potentially harmful (intermediate) products as phenol and formaldehyde are formed. The quantities formed, however, can not be estimated by approximation.

Benzene can be measured well. Depending on the analysis techniques used the limits of detection amount to 10 μg.kg^{-1} in soil material, 0.005 μg.l^{-1} in (ground-, rain-, drinking- and surface) water, and 0.01 μg.m^{-3} in air. Techniques for sampling, storage, preparation and analysis are given. Concentrations in soil are low (ground water: < 0.005-0.03 μg.l^{-1} ; soil material appr.: < 0.01-0.06 μg.kg^{-1}), but they can be considerably higher locally (resp. > 5 μg.l^{-1} and > 5000 μg.kg^{-1}). Concentrations in fresh and salt surface water are resp. 0.01-0.1 μg.l^{-1} and 0.005-0.02 μg.l^{-1}. In regard to ambient air concentrations the national annual average is about 2 μg.m^{-3}; the concentrations in rural areas (1.1-8.1 μg.m^{-3}) are lower than those in urban areas (2-42 μg.m^{-3}), where especially during rush-hour high concentrations develop (up to about 100 μ.m^{-3}). The indoor air concentation is generally twice the ambient air concentration. An increase in this can occur if the house is situated on polluted soil (3-56 μg.m^{-3}), but especially if one smokes in the living accomodation (20-150 μg.m^{-3}). In cars averages of about 66 μg.m^{-3} are found. In drinking water the concentrations are < 0.005 μg.l^{-1} .The amounts in food are not known for the Dutch situation, but they are probably less than 100 μg.kg^{-1}. Also with regard to the working environment the data are limited: time weighted averages over an 8-hourly working day are generally less than 3000 μg.m^{-3}, but higher values do occur. Because of insufficient information the exposure level for man can only be approximated. It is a fact that the level is determined by the concentration in inhaled air and, possibly, in food. Via food a maximum of 185 μg per day (oral intake of 1850 g.day^{-1}, average content of 100 μg.kg^{-1}) is absorbed and a minimum of 15-85 μg per day via inhalation, assuming an absorption of resp. 100 and 50%. Therefore the basical level of absorbed benzene is 15-270 μg a day, depending on the

contribution of food. As a result of living in an urban area, driving a car or exposure to traffic rush hours (1 hour a day), smoking passively and actively, this level may be raised with resp. about 0-170, 15, 10-70 and 105-855 μg per day. In a working environment this level may be many times higher.
Exposure levels in aquatic ecosystems can be equated with the concentrations in water ($< 0.1\ \mu g.l^{-1}$). Those in terrestrial ecosystems are linked up with the habitat of the species and therefore they can not be indicated unequivocally.

Benzene is low acutely toxic for man: for mammals the LC50 (2-8h) is 15-60 $\mu g.m^{-3}$ and the LD50 is 1-10 $g.kg^{-1}$ body weight; for man 65 $\mu g.m^{-3}$ is considered to be lethal. During longer exposure times of laboratory animals and human beings, lower concentrations (about 150 $mg.m^{-3}$) cause damage to the haemopoietic system (anaemia, leucophenia, thrombocytophenia and aplastic anaemia). Benzene is carcinogenic in rats (orally and inhalatory) and mice (inhalatory) and at higher concentrations (about 325 $mg.m^{-3}$) it can induce leukaemia in human beings. Although negative in point/gen mutation tests, benzene may cause damage to chromosomes in plants and somatic mammal cell in vitro and in vivo; cytogenetric effects in peripheral lymphocytes have been found in persons with benzene haemopathy. Since there are no valid arguments to suppose the existence of a threshold value below which no damage would occur (see section 5.5.), a linear extrapolation model has been applied based on data of occupationally exposed subjects (inhalatory). It is concluded that a lifelong intake (inhaltory and/or orally) of about 1 (0.3-6) μg benzene a day would result in a risk of maximally 1 extra case of leukaemia per 10^6 individuals. Induction through occupational exposure excluded, the inhalatory exposure levels could cause 10 to 87 cases of leukaemia in The Netherlands every year. Via food this number might be increased with an additional 37 at a maximum. If exposure in the working environment as well as via food and smoking are left aside, the contribution in the risk by exposure to benzene in the environment (air) is maximally 4-40 extra cases of leukaemia in The Netherlands every year. This number (maximum value) can be compared to the risk which is considered to be just acceptable (IMP-Milieubeheer 1986-1990). Locally (urban areas) this acceptable risk is exceeded.
For aquatic ecosystems a no-effect-level of 100 $\mu g.l^{-1}$ has been derived from acute toxicity data, deduced via extrapolation models. For the benefit

of the protection of the aquatic environment one should also take into account the additive effect of other non-specifically acting substances. However, in view of the difference between exposure levels and the level for which ecotoxic effects can be expected (factor > 1000), benzene does not constitute a danger to the aquatic environment. Although for terrestrial ecosystems insufficient data are available to support a guideline, it is most likely that the exposure levels are not harmful here either in view of the large differences between observed toxic concentrations for invertebrates and plants (10^4-$10^6 \mu g.l^{-1}$) and nationally occurring concentrations in ground water (< $5x10^3$-$3x10^{-2} \mu g.l^{-1}$), between LC50-values for mammals ($1.5x10^7$-$6x10^7 \mu g.m^{-3}$) and nationally occurring concentrations in air (2 $\mu g.m^{-3}$), also in view of the limited bioaccumulation capacity of benzene and the observed LD50-values for mammals (10^6-$10^7 \mu g.kg^{-1}$).

As for measuring strategies only measurement plans at a local level are important for soil and groundwater. A distinction should be made between already existing cases of soil pollution and potential, more benzene specific, pollution situations. The measuring strategy to be followed in the first case depends partly on the seriousness of the pollution with other substances, the allocation of the area and the distribution risks. As for the more specific sources (e.g. storage tanks) measurements can be limited to a checking of the levels in the direct vicinity. For surface water only the determination of concentrations in effluents of the most important sources matters. For measurements in air plans are given for the source categories emissions from abroad, traffic and industry. In all cases dispersion models are needed for the measuring policy and interpretation of data.

Technical possibilities are indicated for controlling the emissions to soil, water and air, as well as, as far as possible, the cost of control. An international approach remains essential: a zero emission in The Netherlands would only decrease the national annual average in air from about 2 to about 1.5 $\mu g.m^{-3}$ if the contribution from abroad remains the same.

A comparison of the existing standards and guidelines with the environmental concentrations shows that in relation to the soil at a local level the testing values are exceeded (emissions in the past), whereas as far as the air is concerned, the proposed interim guideline (1 $\mu g.m^{-3}$) is exceeded

with a factor 2 nationally, and locally (urban area around sources) the interim limit value (10 $\mu g.m^{-3}$) is exceeded at some places with a factor 4.
As a consequence of autonomous developments (year 1990-2000) an emission reduction of 3445 tons on an annual basis is expected (soil 9 tons; water 56 tons; air 3380 tons) in The Netherlands. Assuming a proportionally similar reduction of the emission by road traffic and the stabilization of the remaining emissions in neighbouring countries, on a national scale an ambient air concentration of 1.3 $\mu g.m^{-3}$ and at a local scale in urban areas a reduction of concentration wit 40% are expected.
Emission control at relatively low cost can reduce the emission to water with 75 tons a year. If (year 2000) the international policy aimed at a maximum increase of the use of only LPG and threeway-or oxidation catalysts (for all cars) would be effectuated (total reduction of 1675 tons a year) as well, a further decrease in the ambient air concentration on a national scale to 0.9 $\mu g.m^{-3}$(below the interim guideline) is to be expected. In urban areas the emission reduction would decrease the maximum concentrations with more than 70%.
A further emission control (more than 600 tons a year) is possible though at higher cost (investment costs more than 1200 million guilders; annual costs a good 220 million guilders). As a result the national level could be reduced to approximately 0.8 $\mu g.m^{-3}$, but a further reduction in urban areas is not to be expected. It is concluded that a) the exposure levels are only hazardous to public health, b) occupationally exposed people and smokers constitute the main groups at risk and c) therefore the influence of indicated autonomous developments and measures on the incidence of leukaemia may perhaps be limited.

It is recommended to pay attention to the possible effectiveness of planological measures for traffic in regard to the emission reduction of road traffic in urban areas, as well as to food as a possible source of benzene and to other sources than smoking in indoor air and the pursueing of an international, integral source-oriented policy with regard to the reduction of the most important source (road traffic).

INTRODUCTION

The environmental policy in The Netherlands is in the first place aimed at achieving and maintaining an environmental quality, which guarantees the health and well-being of people and the preservation of animals, plants, goods and patterns of utilization in a general sense (IMP Milieubeheer 1986 - 1990). Adequate knowledge lacking it will, however, not be possible for some time to fully define the general environmental quality aimed at. Therefore, attention is concentrated first on factors which may present great risks, such as substances hazardous to the environment. A selection has been made of the many substances that are important because of emission or usage and a priority list has been drawn up. For most priority substances socalled Integrated Criteria Documents are written.

Arranged by substances or groups of substances, Integrated Criteria Documents contain data on sources and distribution patterns (soil, water, air, biota), the risks of present concentrations for man, (parts of) ecosystems and materials, and the technical and economical possibilities of reducing these risks. This information serves as a scientific basis for the formulation of the effect-oriented environmental policy. Environmental quality requirements and a general term of reference for the emission reductions per type of source may result from this.

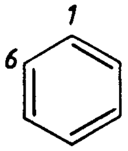
The document benzene is the first of a series of integrated criteria documents. The document has been drawn up by the National Institute of Public Health and Environmental Protection (RIVM), the Dutch Organization for Applied Scientific Research (TNO) under the auspices of the RIVM.
For various parts, such as control techniques and their costs, valuable information has been obtained from several chemical concerns. This appreciated cooperation has been achieved through the Department Environment and Environmental Planning of the Council of the Dutch Employers' Union VNO and NCW. The chapter on effects -including the appendix- has been submitted separately to industrial experts for comment. The highly dissenting views of the industrial representatives with regard to the way of extrapolation of the data on carcinogenicity of benzene has been added to the document in an addendum.

The content of this document has been checked by a Review Committee of the RIVM. Support in the preparation of this document was rendered by a Counselling group consisting of staff members of the Ministry of Public Housing, Physical Planning and the Environment, The Department of Inland Waterways (RIZA) and the Ministry of Agriculture and Fisheries.

1. PROPERTIES AND EXISTING STANDARDS

1.1. PROPERTIES

1.1.1. Structural formula and molecular structure



C_6H_6

1.1.2. Registration numbers

CAS : 71-43-2
RTECS : CY 1400000 (NIOSH, 1983)

1.1.3. Chemical names and common synonyms

Benzene	(IUPAC)
Benzeen	(NL) (NNI, 1968)
Benzene	(GB) (Pergamon Press, 1979)
Benzol	(D) (Shell Nederland Chemie, 1975)
Benzene	(F) (Hommel, 1980)

Benzol, light oil, phene, phenyl hydride, nitration of benzene (benzene of a good quality), benzene for nitration, benzol coal naphta, cyclohexatriene, pyrobenzol (English).
Krystallbenzol, Phenylwasserstoff, Reinbenzol, Pyrolsebenzin, Schwerbenzol (German).
Benzine Lourde, benzine cristallisable, benzine de houille, benzine régie, benzol hydrure phénylique (French).

1.1.4. Physical properties (Othmer, 1978)

1 $mg.m^{-3}$ = 0.31 ppm (20°C, 101.3 kPa) (Verschueren, 1983)
1 ppm = 3.2 $mg.m^{-3}$

molecular mass,	$g.Mol^{-1}$	78.11
melting point,	^oC	5.533
boiling point (101.3 kPa),	^oC	80.100
density (-3.77^{o}C),	$kg.m^{-3}$	873.7
vapour pressure (26.075^{o}C),	kPa	13.33
viscosity (20^{o}C),	mPa.s	0.6468
surface tension (25^{o}C),	$mN.m^{-1}$	28.18
critical temperature,	^oC	289.45
critical pressure,	kPa	4924.4
solubility of benzene in water (25^{o}C), $g.100g^{-1}$ of water		0.180
n-octanol-water partition coefficient (20^{o}C)		log P = 2.13 (Verschueren, 1983)

Hansch and Leo (1979) give a range of 1.56-2.15 for the partition coefficient of benzene in an octanol/water system. The coefficient depends on temperature, pressure and pH.

Benzene is a volatile, colourless, inflammable aromatic liquid with a characteristical odour. Benzene is the simplest component of the aromatics, which possess according to Hückel (4n+2) π electrons, (in which n is a whole number, for benzene n=1). These 6 π electrons are distributed along the ring and all carbon-carbon bounds have the same length.

1.1.5. Chemical properties

In the industrial production various reactions with benzene occur, such as oxidation, reduction, nitration, sulphonation, halogenation and alkylation (Othmer, 1978), which will not occur in the environment in ordinary circumstances.

The reactions with OH-radicals, which lead to degradation of benzene are environmentally relevant (chapter 3).

1.1.6. Storage and transport (Ullman, 1974)

The International Convention concerning the Carriage of dangerous Goods by Rail, the European Agreement concerning the International Carriage of dangerous Goods by Road, the European Agreement concerning the International Carriage of dangerous Goods on the Rhine and the IMO (Intergovernmental

Maritime Consultative Organization) qualify benzene as an inflammable substance, danger class 3 (Staatsuitgeverij, 1978). Every organization describes the measures to be taken and the labels to be used with regard to the transport of this substance. The transport lines and tanks should allow heating. Benzene is non-corrosive for metals, therefore steel can be used for pipelines and tanks.

1.2. EXISTING STANDARDS AND GUIDELINES

In The Netherlands and abroad standards and guidelines for benzene in relation to soil, water and air have been set up. Furthermore, demands are made in The Netherlands for chemical waste, packaging and solvents.

1.2.1. Soil

A framework of testing for the evaluation of the concentration levels in soil is indicated in the "Leidraad Bodemsanering" (VROM, 1983). The indicative guidelines mentioned there should not be seen as standards, but as a framework for evaluation. The following distinction is made: A - reference value, B - testing value for further inquiry and C - testing value for research on reconstruction. The concentrations are considered in connection with the function of the soil and the local situation of pollution.

Table 1.1. Testing framework for the evaluation of the concentration levels of benzene in soil

Matrix	*A*	*B*	*C*
Soil (mg.kg^{-1} of dry matter)	*0.01*	*0.5*	*5*
Ground water (µg.l^{-1})	*0.2*	*1*	*5*

1.2.2. Water

Table 1.2. Quality requirements for drinking and surface water (in μg.l^{-1})

Country	Type	Concentration	Remarks	Reference
Netherlands	drinking water	10 (max.)	mineral oil	VROM (1985)
	surface water	2 (median)	monocyclic hydrocarbons	
	surface water	1 (median)	benzene	
EEG	drinking water	10 (max.)	dissolved hydrocarbons mineral oil	Commission EC (1980)
WHO	drinking water	10 (max.)	benzene	WHO (1984)

1.2.3. Air

Table 1.3. MAC-values (occupational exposure limits as time-weighted averages (TWA) during 8 hours) in mg.m^{-3}

Country	Concentration	Remarks	Reference
The Netherlands	30		Nat. MAC list (1985)
U.S.	30		ACGIH (1984-1985)
	75	15 min.	(TWA)
Germany	26		MAK-Werte (1984)
Russia	5		Izmerov et al. (1982)

Table 1.4. Air quality standards ambient air in mg.m^{-3} (IDC, 1984, 1985)

Country/Province	*Concentration*	*Remarks*
The Netherlands	*0.010*	*interim limit value, annual avarage*
	0.001	*interim guideline, annual average*
Groningen	*0.03*	*annual average*
USSR	*1.5*	*maximum*
	0.8	*daily average*
East-Germany	*1.5*	*1/2 hourly average*
	0.8	*daily average*
Poland	*1.0*	*20 min. average*
	0.3	*daily average*
Czechoslovakia	*2.4*	*1/2 hourly average*
	0.8	*daily average*
Israel	*4.8*	*1/2 hourly average*
	1.6	*daily average*
China	*2.40*	*maximum*
	0.80	*daily average*
West-Germany	*3*	*1/2 hourly average; to be exceeded once per 4 hours max.*
	10	*max. 1/2 hourly average*

1.2.4. Chemical waste, packaging and solvents

According to the "Wet Chemische Afvalstoffen" (Staatsblad, 1977a) waste is considered to be chemical waste if the concentration of aromatic hydrocarbons is larger than 20 g.kg^{-1}. According to the "Warenwet" the migration value of benzene found in metallic upper layers, multiplied with a factor depending on use, should be no more than 0.05 mg.dm^{-2} for packaging and articles of use for food and drink (Staatsuitgeverij, 1983).

The use of benzene or of a product of which the content of benzene is more than 1 volume-percent (as a solvent, cleaner or dilutent) is only permitted in a closed system (Staatsblad, 1977b). The maximum content in fuel (petrol) amounts to 5 vol. % since 1-10-86 (Staatsblad, 1983).

2. PRODUCTION, APPLICATIONS, SOURCES AND EMISSIONS

2.1. PRODUCTION AND APPLICATIONS

Table 2.1. incorporates some data on the production and use of benzene. The data are based on the open literature (CID-TNO, 1985; CHEMFACTS, 1978-1981; SRI, 1983; UNITED NATIONS, 1981), and have been extrapolated to 1981 when necessary. The total production in The Netherlands in 1981 was 670 ktons (60% of the nominal capacity). 415 ktons were imported and 155 ktons were exported (CBS, 1981a). Moerover 96 ktons were present as a component of petrol (2.6% weight percentage). Thus the total amount available for use in The Netherlands was: 930 ktons + 96 ktons = 1026 ktons.

Table 2.2. illustrates the use of benzene in the United States, Western Europe, Japan and The Netherlands as a percentage of the total use (SRI, 1983).

The use of benzene as a solvent has been reduced greatly in the last few years, especially as a result of the replacement with toluene. However, benzene does occur in small quantities in various solvents on a hydrocarbon basis. An accurate estimate of the quantities involved is difficult, especially because in this case it often concerns small concentrations in large volume flows.

Table 2.1. *World production and -use of benzene in 1981 in ktons per year. Benzene in petrol is not included*

Country	Capacity	Production	Use
West-Germany	1,630	980	910
Great-Britain	1,560	800	540
The Netherlands	1,100	670	930
Italy	1,040	450	690
France	940	550	660
Belgium	190	40	270
Spain	310	210	100
Finland	120	70	50
Portugal	40	20	10
Austria	20	10	5
Other Western-European countries	-	-	35
Total of Western-Europe	6,950	3,800	4,200
USSR	3,250	1,700	1,800
Remainder of Eastern-Europe	2,590	640	440
Total of Eastern-Europe	5,840	2,340	2,240
United States	8,030	5,190	5,570
Remainder of America	1,320	960	580
Total of North- and South America	9,350	6,150	6,150
Japan	2,880	2,060	1,820
Other Asian countries	670	400	340
Total of Asia	3,550	2,460	2,160
Other countries	100	50	50
World	25,800	14,800	14,800

Table 2.2. Use of benzene in 1981 in the United States, Japan, Western Europe and The Netherlands in a percentage of the total consumption. Benzene in petrol has not been incorporated

Application	*United States*	*Japan*	*Western Europe*	*Netherlands*
Production of:				
Ethylbenzene/styrene	*51.1*	*50.4*	*48.6*	*73*
Cumene/phenol	*20.6*	*12.1*	*19.3*	*16*
Cyclohexane	*13.8*	*25.6*	*13.4*	*11*
Alkylates	*3.0*	*3.7*	*5.2*	-
Maleic acid anhydride	*2.8*	*2.5*	*3.3*	-
Nitrobenzene/aniline	*5.3*	-	*6.7*	-
Chlorine benzenes	*2.6*	*5.7*	*2.0*	-
Other products	*0.8*	-	*1.5*	-
Total	*100*	*100*	*100*	*100*

2.2. SOURCES AND EMISSIONS

2.2.1. Emissions to soil

For the pollution of the soil with benzene the following causes can be distinguished:

- deposition from the atmosphere
- leakage from storage tanks at petrol stations
- spilling at storage and handling
- transport accidents
- wash-out from polluted areas

- Deposition from the atmosphere

The total deposition on Dutch surface is estimated at about 25 tons per year (chapter 3). Since the land surface of The Netherlands is about 88% of the total surface, about 22 tons of benzene precipitates on the soil.

- Leakage of underground storage tanks at petrol stations

Based on a recent investigation (Van Deelen, 1985) it is estimated that every year about 50 of the 34,000 sub-soil storage tanks of petrol spring a leak from external or internal corrosion. As a result of this an average of about 5,000 l of petrol gets into the soil. The total loss is therefore 250,000 l per year. With a benzene content in petrol of 2.6 weight percentage and a density for benzene of 880 $kg.m^{-3}$,it can be concluded that about 5 tons of benzene end up in the soil in this way.

- Leakage of ground storage tanks

Van Deelen et al. (1986) made some calculations on the chances of leakage of overground storage tanks through corrosion of bottom plates. Based on the data of this report it can be calculated that about 4 tons of benzene per year get into the soil as a result of corrosion of bottom plates.

- Spilling at storage and handling

It is assumed that losses as the result of spilling during storage and handling mainly lead to emissions into the air.

- Transport accidents

Based on an investigation carried out in 1983 on the chances of accidents during the transport of fuel and the quantities released (VROM, 1983b), it has been calculated that during road transport of petrol an average of 1 ton of benzene ends up in the soil each year (about 0.001% of the quantity transported). During transport through pipelines about 13 tons of benzene are supposed to get into the soil every year (about 0.2% of the quantity transported).

- Wash-out from polluted areas

As a result of industrial activities from the past, rather large amounts of benzene are to be found in the soil at various locations in The Netherlands. Quantitative data on the amounts involved are not available. Based on an inventory of the various polluted areas (VROM, 1983) and the standards from the guideline on soil reconstruction (chapter 1), the number of polluted areas has been arranged in order of the amount of the concentrations found in soil and ground water (chapter 4; fig. 4.2.). In about half of the cases it concerns areas of former gas works, while garage companies and car scrap yards resp. storage yards for wrecked vehicles also constitute a source of benzene emissions into soil and ground water.

2.2.2. Emissions to water

Table 2.3. presents a survey of emissions into water per source of emission in The Netherlands (RWS, 1983; RIZA, 1982, 1983; Van der Most, 1985).
The total industrial emission into water is estimated at about 240 tons for 1981. 118 Tons were discharged in the lower rivers, 95 tons in the Southern Delta waters and 15 tons in other state-managed waters. Moreover 2 tons were discharged in non-state-managed waters. It is assumed that diffuse discharges (10 tons) are mainly emitted in non-state-managed waters.

Table 2.3. Emissions of benzene into water in The Netherlands in 1981 per source of emission in tons per year

Source	*Emission*	*Percentage*
Petrochemistry (refineries included)	*77.5*	*31.9*
Remaining chemistry	*96.3*	*39.6*
Storage and handling	*37.3*	*15.3*
Tank cleaning	*18.9*	*7.8*
Diffuse discharges	*10.0*	*4.2*
Deposition	*3.0*	*1.2*
Total	*243*	*100*

On account of transport accidents in inland navigation about 3 tons of benzene is generally emitted to surface water every year (state-managed waters excluded; VROM, 1983b) (ca. 0.35% of the quantity transported).
With accidents during road transport within built-up areas there is a risk of emission to surface water via the sewerage.
The load through deposition is difficult to quantify. Wet deposition probably plays an unimportant part (see 3.4.2.). The load of the Dutch surface through dry deposition is estimated at ca. 25 tons (chapter 3.). At a

water surface of 12% of the total Dutch surface, this entails a load of the surface water with 3 tons a year.
Based on occasional measurements (IRC, 1983) the trans-frontier emission of the Rhine is estimated at less than 5 tons (ca. 0.2 $g.sec^{-1}$).
The accuracy of the emission data is largely dependent on the fact that measurements often refer to low concentrations in large volume flows. Consequently the accuracy of the industrial data is not larger than ca. 30%. The figure related to diffuse discharges is based on very limited sampling. The possible error may be about 100%. The same counts for the contribution of deposition.

2.2.3. Emissions to air

Emissions in The Netherlands

- Production and use of benzene and petrol production

The emissions of benzene into the air from industrial sources have greatly decreased the last few years as a result of the closing down of companies or departments of companies, changes in production processes and replacement with other solvents. While in the first round of the emission registration (1974-1979) an emission of about 1700 tons was registered, this amount appears to have been reduced in the second round to 825 tons, coming from 45 companies and 77 installations. These values are based on benzene emissions and they have not been deduced from emissions of aromatics. The emissions resulting from the use in laboratories have only been registered for a small part. The total emission from this source is estimated at ca. 1 ton. During the production of petrol in refineries 37 tons were emitted (process emissions, leakage, storage and handling), while 44 tons of benzene were emitted at companies for the storage and handling of petrol (intermediate trade). The above mentioned emissions have been divided to economic activity and source of emission in the tables 2.4. and 2.5.

Table 2.4. *Industrial emissions of benzene in 1981 distributed according to economic activity in tons per year*

Activity	*Emission*		*Percentage*	
Benzene production and -use	*825**		*91*	
- chemistry and petrochemistry		*471*		*52*
- cokes- and tar processing		*107*		*12*
- foundries		*39*		*4*
- other uses		*23*		*3*
- storage and handling, cleaning		*185*		*20*
Petrol production	*81*		*9*	
- refineries		*37*		*4*
- storage and handling (trade)		*44*		*5*
Total	*906*		*100*	

** The emissions in the Rijnmond area as to storage and handling and the chemical industry are higher than estimated by VROM (1983-1984)*

Table 2.5. *Industrial emissions of benzene in 1981 divided into emission cause in tons per year*

Emission cause	*Emission*	*Percentage*
Process emissions		
- production of benzene and derivatives	*390*	*43*
- production of petrol	*37*	*4*
Storage an handling in general		
- breathing- and replacement losses (benzene)	*188*	*21*
- pumps, valves, safeties, cleaning (benzene)	*138*	*15*
- breathing- and replacement losses (petrol)	*29*	*3*
- pumps, vlaves, safeties, cleaning (petrol)	*15*	*2*
- loading	*46*	*5*
Use of benzene and derivatives	*63*	*7*
Total	*906*	*100*

Table 2.6. Emissions of benzene by road traffic in 1981 in tons per year

Source	*Emission*			
	Built-up areas	*Motor ways*	*Other roads*	*Total*
Exhaust gases from petrol engines of motor cars	*2,460*	*770*	*1,880*	*5,110*
Cold start of petrol engine	*650*	*-*	*-*	*650*
Exhaust gases of diesel engine	*430*	*170*	*240*	*840*
Vaporization from car tanks	*100*	*-*	*-*	*100*
Exhaust gases from mopeds and motor cycles	*400*	*50*	*50*	*500*
Subtotal	*4,040*	*990*	*2,170*	*7,200*
Replacement losses from car tanks				*44*
Replacement losses from storage tanks				*39*
Leakages at petrol stations				*12*
Total				*7,300*

- Road traffic

At petrol stations as well as during the use of the vehicle benzene, emissions are caused by vaporization or replacement and leakage of unburned petrol. As a result of combustion of petrol in the engine a quantity of benzene is formed. Also in diesel engines benzene is formed during combustion (the content of benzene in diesel oil is negligible). On the basis of data on fuel consumption (CBS, 1981) and emission factors, the emissions have been calculated in table 2.6. Although road traffic will increase (in the year 2000 40% more traffic), the share of improved cars will also increase under the influence of higher demands to be made in 1990 (in year 2000 35% of improved cars). Consequently the emissions will not increase (section 7.3.1.).

- Remaining traffic

Apart from road traffic, navigation, aviation and rail roads also emit benzene. Assuming that the benzene content in the hydrocarbon fraction of the exhaust gases is the same as during emissions from diesel engines in road traffic, respectively 90, 35 and 5 tons of emitted benzene can be calculated for navigation, aviation and rail roads (Emission registration 1974-1979).

- Space heating

During space heating through the combustion of coal, oil and, in a very limited degree of natural gas, benzene is emitted. During the use of coal this partly comes from the fuel itself. During the use of oil and natural gas the emitted benzene is formed by the process of combustion. On the basis of quantities of consumed fuel (CBS, 1981a) and emission factors (UBA, 1982; Herlan and Mayer, 1978), a benzene emission of 23 tons has been calculated for 1981.

- Smoking cigarettes

Benzene has also been demonstrated in cigarette smoke (section 4.4.1.). Based on the consumption of cigarettes in 1981 and the emission factors for the emission of benzene, an emission of 8 tons a year has been calculated.

- Re-emissions from water

An intense exchange of benzene between air and water occurs, as mentioned in chapter 3. Depending on the concentrations in air and water, an important part of the water emission may be re-emitted to the air.

Summary of the emissions into the air in The Netherlands

The emissions of benzene in The Netherlands are summarized in table 2.7.
It is noted that the total traffic emission of 7300 tons tallies well with the quantity of 7000 tons estimated by Guicherit and Thijsse (1982) for 1977 based on measurements made in ambient air. The total emission tallies well with the value (8000 tons) given in the "IMP Lucht 1984-1988". The distribution over the various emission sources deviates (especially for road traffic, and storage and handling of petrol) from the figures mentioned before because of changed views.

Table 2.7. Emissions of benzene into the air in 1981 in tons per year

Emission source	*Emission*		*Percentage*	
Industrial emissions	*906*		*11*	
- Production, use and transport of benzene and derivatives		*825*		*10*
- Production and transport of petrol		*81*		*1*
Emissions from road traffic	*7,295*		*87*	
- Storage and handling at petrol stations		*95*		*1*
- Evaporation from car tanks		*100*		*1*
- Exhaust gases from car engines		*7,100*		*85*
Remaining emissions	*161*		*2*	
- Remaining traffic		*130*		*2*
- Space heating		*23*		*0*
- Smoking of cigarettes		*8*		*0*
Total	*8,362*		*100*	

Frequency of the emissions and accuracy of the emission data

The production of benzene and derivatives, as well as the refinery of oil products, takes place in continuous processes. The inaccuracy in these emission figures is ca. 10% (VROM, 1983).

The breathing losses in tanks without valves occur especially between 8.00 and 14.00 hours. If valves are present, the emissions occur between 11.00 and 14.00 hours. In the months of June, July and August the emissions are a factor 2 higher than during the rest of the year. The storage at petrol stations is underground, so no breathing losses occur here. Replacement losses at storage and handling companies occur discontinuously, during the day as well as at night. Emissions resulting from the loading of tank cars and the replacement losses at petrol stations take place especially during the day. The inaccuracy of these emission data is about 35% (VROM, 1981-1983). The emissions from pumps, valves and safeties occur during the day as well as at night. The inaccuracy of these data is ca 20% (VROM, 1981-1983). The emissions from exhaust fumes of road traffic occur mostly during the day. The inaccuracy of the emission data is about 20%. The emission factors for emissions through vaporization have been based on few measurements. The inaccuracy of these data is estimated at 100% (UBA, 1982).

Emissions in Europe

The main source of benzene emissions in Western Europe is road traffic (table 2.8.). A detailed calculation of the emissions based on vehicle kilometres, consumption of fuel and benzene contents in petrol has been executed for The Netherlands, Belgium/Luxemburg, West Germany and France. The benzene emissions per inhabitant in The Netherlands, Belgium/Luxemburg, and France were respectively 0.51, 0.41 and 0.55 kg (an average of 0.50). West Germany, which has a much higher benzene content in petrol, contributes an emission of 1.00 kg per inhabitant. The emissions in other European countries have been calculated with and emission factor of 0.50 kg per inhabitant.

The distribution of the refineries over Europe is very inhomogeneous. These emissions have been calculated on the basis of data on the quantity of processed crude oil (OECD, 1983) and an emission factor of 2 tons of benzene per 10^6 tons.

For the calculation of the emissions from the remaining sources an emission factor of 75 kg per 1000 inhabitants has been calculated on the basis of the Dutch situation. The figure for the United States has been taken from an OECD report (OECD, 1981); the one for the global emission from an article of Fishbein (1984). The latter seems rather high.

Starting from an air column of 1 km, a frontage of 200 km, a wind velocity of 8 $m.sec^{-1}$ and an annual average concentration-contribution of about 1.5 $\mu g.m^{-3}$ from abroad (chapter 3.), the flux would be more than 30 ktons a year.

Table 2.8. Emissions of benzene into the air in tons per year

Country	*Road traffic*	*Refineries*	*Remaining sources*	*Total*
Belgium/Luxemburg	*4,950*	*60*	*750*	*5,760*
Denmark	*2,600*	*10*	*390*	*3,000*
West Germany	*62,000*	*200*	*11,000*	*73,200*
France	*30,000*	*200*	*4,000*	*34,200*
Greece	*4,700*	*30*	*700*	*5,430*
Great Britain	*29,000*	*150*	*4,200*	*33,350*
Ireland	*1,650*	*0*	*200*	*1,850*
Italy	*29,000*	*190*	*4,200*	*33,390*
The Netherlands	*7,300*	*80*	*980*	*8,360*
Total of EC	*171,200*	*920*	*26,420*	*198,540*
United States				*260,000*
World			*(?)*	*4000,000*

2.2.4. Emission factors

In the above mentioned, many emission figures based on emission factors have been stated. In this section the various published emission factors, such as those from the Umweltbundesamt (UBS, 1982), the Environmental Protection Agency (EPA, 1978), the Organisation for Economic Cooperation and Development (OECD, 1984) and the Department of Housing, Planning and Environmental Control (VROM, 1981-1983) are compared to each other. Because of the emission registration in The Netherlands, the emission factors are more accurate in comparison to some of the other countries and therefore they may show a deviation in some cases.

Production of cyclohexane

UBA (1982) and OECD (1984) state a maximum emission of 0.25 kg of benzene per ton of cyclohexane in West Germany. The emissions in The Netherlands

(VROM, 1981-1983) are 0.01-0.1 kg of benzene per ton of cyclohexane. The American values (EPA, 1978) are considerably higher (2.8 kg of benzene per ton of cyclohexane).

Production of cumene

The OECD (1981) mentions a maximum emission factor of 0.21 kg per ton of product in West Germany, which tallies well with the American factor of 0.25 kg per ton of product. It appears from data of the emission registration that in The Netherlands only 0.02 kg per ton of product is emitted (mainly emission from pumps and valves).

Production of ethyl benzene

The UBA (1982) indicates a maximum emission of 0.11 kg per ton of product in West Germany. The American factors are considerably higher (0.62 kg of benzene per ton of product). In The Netherlands an emission factor of 0.04 - 0.06 kg per ton of product (VROM, 1981-1983) has been determined (mainly emissions from pumps, valves, safety valves and tanks).

Production of coke

The UBA (1982) uses an emission factor of 0.035 kg per ton of coke, the EPA (1878) a factor of 0.07 kg per ton. In The Netherlands the emission registration found values of 0.028-0.046 kg per ton, tallying well with the German data.

Refineries

The emission factors from the UBA (1982) vary between 1.1 to 4.0 ton per 10^6 tons of processed crude oil. Most of the values given are between 2 and 2.5 tons per 10^6tons. For The Netherlands the emission registration determined an emission factor of 0.9 ton per 10^6 tons of processed crude oil.

Foundries

The emissions in foundries are caused by the heating of moulding sand in which binding agents are to be found. Depending on the nature of the material used 65-300 g of aromatic hydrocarbons per kg of sand is released. The average benzene content of this is estimated at 20% (Metal institute TNO, 1980).

Heating

For the emissions through heating, UBA (1982) emission factors have been used. These are:

Coal (household) : 0.2 g of benzene.kg^{-1} of coal
Coal (supply stations and industry) : 0.1 mg of benzene.kg^{-1} of coal
Oil (pulverization heaters) : 8.5 mg.kg^{-1} of oil
Natural gas : 0.1 g of benzene.joule^{-1}

Exhoust gases from road traffic

In the exhaust gases from petrol engines as well as in those of diesel engines benzene has been demonstrated (Veldt, 1980). The amounts found constitute a 4.1 weight percent for petrol and for diesel engines 2.7 weight percent of the hydrocarbon fraction. The quantity of emitted hydrocarbons has been calculted using emission factors per vehicle kilometre drafted by the CBS (CBS, 1985) and the traffic productions per type of vehicle in built-up areas, on motor ways and on other roads. These emission factors are incorporated in table 2.9.

Tabele 2.9. Emission factors of hydrocarbons in grams per vehicle kilometre

Type of vehicle	*Type of engine*	*Built-up areas*	*Motor ways*	*Remaining roads*
Motor cars	*petrol engine*	*4.4*	*1.4*	*2.0*
	diesel engine	*1.1*	*0.25*	*0.3*
Vans	*petrol engine*	*5.7*	*1.6*	*2.4*
	diesel engine	*1.7*	*0.1*	*0.7*
Lorries	*diesel engine*	*11.0*	*2.5*	*3.7*
Buses	*petrol engine*	*10.0*	*3.2*	*4.0*
	diesel engine	*9.5*	*1.8*	*3.4*
Motorcycles		*6.0*	*6.0*	*6.0*
Mopeds		*5.0*	-	*5.0*

Evaporation of petrol from cars

The available information on evaporation from car tanks and carburettors is scanty. Based on a German inquiry (UBA, 1985) an emission of 10 g of hydrocarbons per vehicle a day is estimated. However, this is possibly higher (20 g).

Storage and transport of petrol at petrol stations

The emission factors which the Umweltbundesamt (UBA, 1982) and the Environmental Protection Agency (EPA, 1979) use tally well. These values have been used in this document. For replacement and breathing losses at storage tanks an emission factor of 0.17 volume percent (0.14 weight percent) is used. For replacement and breathing losses during the filling up of car tanks a factor of 0.175 volume percent (0.142 weight percent) is used.

The benzene emissions have been calculated on the basis of a weight percentage of 2.6 percent in the fluid (Den Tonkelaar, 1982) and 0.6 percent in the vapour (announcement of refineries). The emissions through replacement and storage losses at petrol stations have been taken from the study "Vapour-recycling along the petrol-handling chain" (VROM, 1985).

Smoking of cigarettes

As emission factors for the main stream and side stream 0.018 (Baggett et al, 1974) and 0.39 mg (Jermini et al., 1976) respectively per cigarette have been chosen (chapter 4., section 4.4.1.).

2.3. SUMMARY AND CONCLUSIONS

Natural sources are negligible.

In 1981 1026 ktons of benzene were available for use, of which 96 ktons were present as a component in petrol in The Netherlands. The emissions in The Netherlands per environmental compartment have been summarized in table 2.10. Emissions from abroad are negligible for water (5 tons a year), but they are important to the air compartment (> 30 ktons a year).

Table 2.10. *Survey of benzene emissions in The Netherlands per environmental compartment in 1981 (in tons per year)*

Compartment	*Quantity (*)*	*Source*
Soil	*22*	*indirect emission through deposition*
	14	*transport accidents*
	9	*leakage of storage tanks*
	unknown	*wash-out in polluted areas*
Water (fresh)	*240*	*industry*
	3	*transport accidents*
	3	*indirect emission through deposition*
Air	*7295*	*road traffic*
	906	*industry*
	130	*remaining traffic*
	23	*space heating*
	8	*smoking*
	unknown	*indirect, re-emission from water*

** for indirect emission one is referred to chapter 3*

The survey shows the emission to air to be the largest one, with road traffic as the most important source. The emission from abroad is also determined primarily by road traffic: the total emission to air in the EC is about 200 ktons, of which more than 170 ktons are contributed by road traffic.

3. DISPERSION AND TRANSFORMATION

3.1. BEHAVIOUR IN SOIL

3.1.1. Dispersion

Benzene only adsorbs in a limited degree on the soil (Karickhoff et al., 1979; Rogers et al., 1980; Korte et al., 1982). In field experiments it was determined that evaporation and degradation are the most important processes (0-40 cm); very low (bound and dissolved) residues were found (Scheunert et al, 1985). Also on the basis of evaporation data with a water column (MacKay and Leinomen, 1975) it seems probable that evaporation is an important removal mechanism in the top centimetres of the soil. Assuming a deposition of 22 tons a year, a load occurs of about 1 $\mu g.m^{-2}$ a day. Due to evaporation and biological decomposition the concentrations will not or hardly be measurable in soil and ground water.

Another situation may occur in local cases of soil pollution. The distribution of benzene over the solid phase (soil material) and the liquid phase (ground water) can be described as a standard partition coefficient: $K_{oc} = K_d$ / %OC (K_d = partition coefficient soil/water and % OC = percentage of organic carbon in soil material). For benzene this value is relatively low and varies between 80-100 (Karickhoff et al., 1979; Rogers et al., 1980). This indicates that benzene in the liquid phase can rapidly sink into the soil. At a high load of benzene it will be transported to deeper soil due to the force of gravity. The data obtained from soil pollution research in The Netherlands confirm this in most cases. It should be kept in mind, however, that this research took place mostly on sandy soils. Also around pump islands and petrol filling locations high benzene levels have been found in soil to the level of the ground water in some cases (Riemens, 1985). Hydrologic research at one of the stations demonstrated that the pollution dispersed in the ground water to a small extent, as result of the low ground water flows in the examined situations. At a few accidents with tank cars, benzene was even found in the soil at a distance of 400 m from the place of the accident (Brinkmann, 1985).

In houses in the neighbourghood of leaking storage tanks and in homes built on former dumping sites, the indoor air can be increased with a few dozens of $\mu g.m^{-3}$(see 4.4.1.).

3.1.2. Transformation

Abiotic transformation

Considering the physical and chemical properties of benzene a nucleophile substitution in natural circumstances can be ruled out. Therefore hydrolysis does not occur. Neither will oxidation occur in natural circumstances in the soil. This process only takes place in extreme conditions (increased temperature and pressure, use of catalysts) (Howard and Durking, 1974).

Biotic transformation

Compounds containing a benzene ring often occur in nature. Consequently many micro-organisms are present in soil, which are able to grow on these kind of compounds. Various investigators (Zobel, 1950; Claus and Walker, 1964; Gibson, 1976) demonstrated that certain bacteria, isolated from soil material, can use benzene as a single source of hydrocarbon.

A clear decomposition of benzene as single source of hydrocarbon could be observed to a benzene concentration of 0.1% in 68 of the 200 isolated bacteria decomposing hydrocarbons. It is therefore assumed that higher benzene concentrations will not or hardly be decomposed. It should be born in mind that the isolation of specific bacteria which can grow in laboratory conditions on e.g. benzene as sole hydrocarbon source, may lead to misleading conclusions. In general the substratum concentration in a laboratory study will be higher than in natural circumstances. In natural conditions enzymes, which are essential to decomposition, cannot be induced. Apart from that, other hydrocarbon sources which may influence the induction of enzymes negatively as well, are also present in natural circumstances. The degradation of benzene is thus greatly dependent on the environmental conditions. For instance, Helfgott et al. (1977) stated that benzene is rather persistent, while Korte and Klein (1982) concluded on the basis of (labelling) experiments that benzene is highly degradable. Walker and Colwell (1975) demonstrated that bacteria, in a creek polluted with oil, decomposed benzene only in the presence of dodecane in itself, or if dodecane and naphtalene both were present. The degradation of benzene could possibly be attributed to co-oxidation or to the fact that the concentration of benzene was much lower than to which the bacteria decomposing oil were exposed.

An investigation into the behaviour of benzene passing the soil of an infiltration area in the dunes showed a removal of 72-99% after a time of 7-49 days (benzene concentration of inflitration water: 50-100 $ng.l^{-1}$) in aerobic conditions (KIWA, 1981). However, the latter results are difficult to interpret: the removal percentage was at its highest (99%) after 7 days, after which the benzene content increased again. Moreover, diluting effects (about 20%) and evaporation played a not unimportant part.

It is concluded that benzene can be decomposed (completely) biologically, if aerobic circumstances occur, sufficient nutrients are present and the benzene concentration (< 0.1%) or the concentration of other (toxic) substances is not too high.

Various researchers examined the removal routes of benzene (Van der Linden and Thijsse, 1965; Raymond and Jamison, 1967; Gibson et al., 1968-1977; Lee, 1976; Chapman, 1979). On the basis of these investigations a survey of the most probable routes of removal has been given in fig. 3.1. The final products (succinate and acetyl coA, pyruvate and acetate) which are caused via the catecholic splitting can be used via various cycles, such as the tricarbonic acid cycle (TCA), during which degradation to CO_2 occurs.

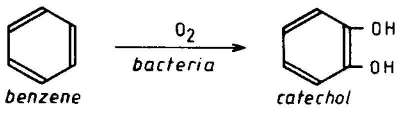
3.2. BEHAVIOUR IN SURFACE WATER

3.2.1. Dispersion

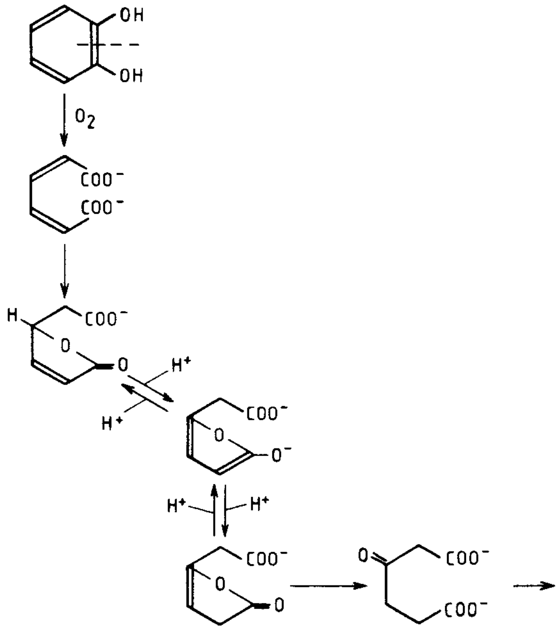
Benzene is hydrophobic (log K_{ow}= 2.13). A small part of the benzene present in surface water is associated with the organic fraction of solid material. The dispersion in water itself is therefore mainly determined by the transport of water itself.

Henry's constant is $5.55 \times 10^{-3} atm.m^{-3}.mol^{-1}$ at 25°C (MacKay et al., 1979). From this value and the concentrations in air it can be deduced that an equilibrium exists between benzene in air and in surface water. Locally increased concentrations in air or in water may cause disturbances of the equilibrium. Thus it can be calculated from Henry's Law that in the case of relatively high concentrations of benzene in water (such as during catastrophes) the evaporation to air will have a half-life of ca. 5 hours per metre of water depth (EPA, 1979). In view of the benzene levels in Dutch surface water (chapter 4) an important part of the benzene emissions in water will be re-emitted to air.

I Hydroxylation of an aromatic hydrocarbon ring



II Ortho-fission of catechol



III Meta-fission of catechol

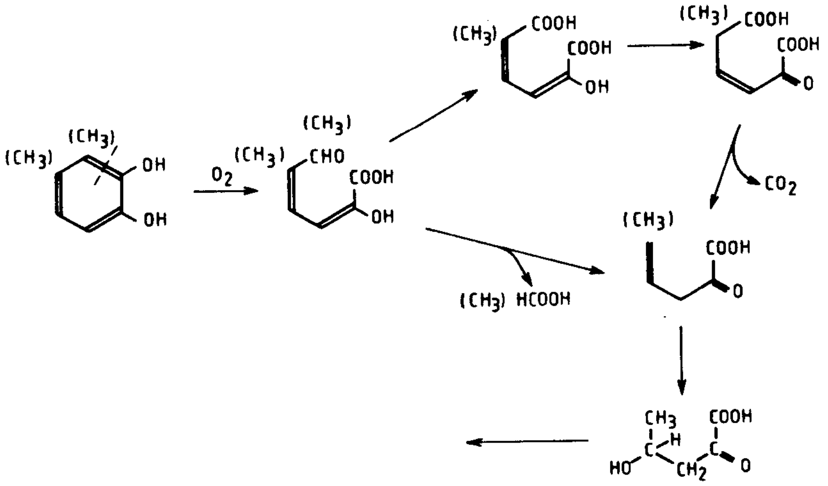


Figure 3.1. Biological degradation routes of benzene

3.2.2. Transformation

Abiotic transformation

Benzene has, on the basis of its molecular structure, a limited number of possibilities for transformation. Only sunlight induced reactions will occur. Transformations resulting from absorption visually observable light may be excluded on the basis of the absorption spectrum of benzene. Based on the acceptor properties of benzene, processes transferring energy and electrons can be excluded as well. The radicals formed by sunlight in surface water may lead to transformation of benzene, however. Among these radicals alkoxy- and alkyl peroxy-radicals are negligible because of their low reactivity (k is resp. $10^4$and 1 $M^{-1}s^{-1}$) (Hendry et al., 1979).

The OH-radical is the only demonstrable cause for the transformation of benzene. Immediately below the water level the half-life is about 80 days calculted for the reaction with $[OH^{\cdot\cdot}]$ = $10^{-17}M$ (Mill et al., 1980; Korte et al., 1982) and k = $10^{9.5}M^{-1}.s^{-1}$(Anbar and Neta, 1976). The half-life increases linearly with depth (decreasing light intensity). The singulet oxygen formed in surface water does not contribute to the transformation because of the low reactivity ($k < 10^3$ $M^{-1}.s^{-1}$) (Wilkinson and Brummer, 1981). There is no reason to suppose that benzene reacts with the hydrogen peroxide formed in surface water. Algae may play a part in the light induced transformation of organic micropollution. Probably this is an unimportant process for benzene since a numer of polycyclic aromates are little reactive (Zepp and Scholtehauer, 1982).

The nature of the products depends on the presence of oxygen. It is expected that partly formation of phenol and partly incorporation of aromatic fragments in the DOC occur.

Biotic transformation

Information on biodegradation in surface water is limited and mainly refers to seawater.

The transformation rate in estuarine, coastal and open ocean water depends on the season and the possible previous exposure to petroleum hydrocarbons (Lee, 1976). The highest velocities were registered in estuaries, possibly caused by a relatively high number of bacteria. For initial benzene concentrations of 6-24 $\mu g.l^{-1}$ the half-life was 15-38 days and it increased linearly with the initial concentration levels. Wakehan et al. (1983) observed the course of benzene concentrations in mesocosms (depth of 5.5 m,

diameter of 1.8 m) in the sea. At 0.2-4 $\mu g.l^{-1}$ half-lives of 23 (at 8-16°C) and 3.1 (20-22°C) days were determined in 1980; in 1982 a half-life of 13 days was found at 3-7°C. In winter and spring evaporation would be the main process, while in summer the reduction of benzene was attributed partly to biodegradation. At larger depths the half-lives increase proportionately.
With reference to the behaviour in biological waste water purification plants, Thom and Agg (1975) classified benzene as a substance which is degraded, taking the adaptation of the sludge for granted. In a experimental installation for water purification of the conservancy board ("Hoogheemraadschap") of West-Brabant at Bath, a removal of benzene of 99% occurred (1% via aeration) (Kamerling, 1985).
For a survey of the degradation routes one is referred to 3.1.2.

3.3. BEHAVIOUR DURING THE PRODUCTION OF DRINKING WATER

References to the behaviour during dune infiltration and biological water purification are to be found in 3.1.2. and 3.2.2. Benzene can be removed effectively by treatment with ozone or active carbon. E.g. a treatment of surface water containing benzene (80 $\mu g.l^{-1}$) with 2.8 $mg.l^{-1}$ of ozone resulted in a removal of 97% (Hoigné and Bader, 1979). O'Brien et al. (1981) reported a removal by active carbon: at a depth of the bed of 2.9 m a break through of 10 $\mu g.l^{-1}$ occurred for 5 $mg.l^{-1}$ of benzene in water at a load of 3030 $(m^3.m^{-3})$.

3.4. BEHAVIOUR IN AIR

3.4.1. Dispersion

Dispersion of benzene can be distinguished in:

- dispersion on a local scale (in streets and along roads by emission of exhaust gases, petrol stations etc.);
- dispersion on a regional scale (in the vicinity of large industrial sources and in towns; maximum cross section of the area of a few dozens of kilometres);
- dispersion on a national scale (maximum cross section of the area of a few hundreds of kilometres).

Dispersion on a local scale

Table 3.1. gives an impression of the concentration contributions to be expected from exhaust gases of cars. The amounts have been deduced from values for NO_x (Van den Hout et al., 1983) For which a NO_x : benzene relation of 14 has been assumed.

Table 3.1. *Increase of the annual average concentration of benzene in and near streets and roads through exhaust gases*

Type of road	*Increase ($\mu g.m^{-3}$)*
Busy street in a big city	*14*
Busy street in a small town or village	*11*
Quiet street	*7*
Busy motorway (wayside)	*7*
Ibid. (at a distance of 100 m)	*3*

At petrol stations benzene is emitted (table 2.6.). Average concentrations resulting from leakage and replacement losses were estimated at medium sized petrol stations during opening hours (12 hours per natural day).
The average source strength amounts circa 4.4 x 10^{-7}kg.s^{-1} per station (during the emission period). The resulting concentration levels (isopleths) are illustrated in fig. 3.2. The estimated average concentration at a distance of 10 m is 20 $\mu g.m^{-3}$. So, the contribution of these sources to the average local concentration is small.

Measured levels in cars in forensic trafic (about equal to those in streets) averaged 66 $\mu g.m^{-3}$ (Den Tonkelaar and Van der Tuin, 1982). Yearly averages will be lower naturally.

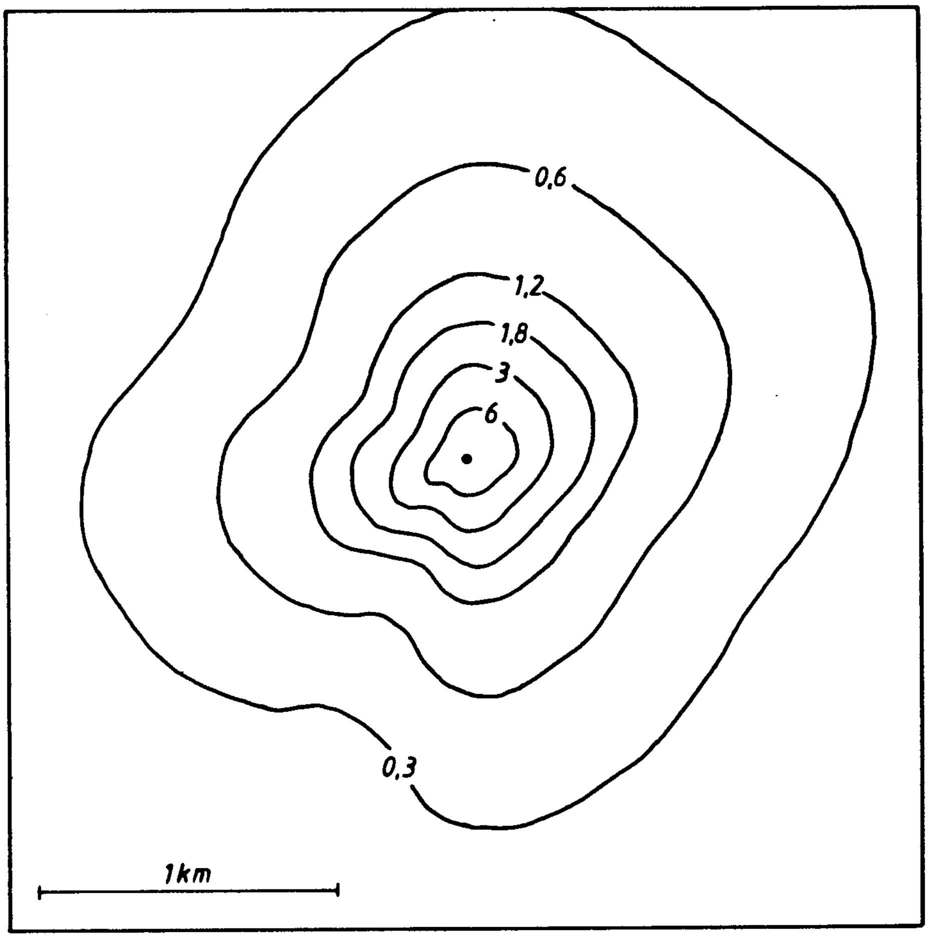


Figure. 3.2. *Average concentration contributions (12 hours per natural day) of benzene (in ng.m^{-3}) at a petrol station of an average size. Climatology Schiphol; scale 1:25,000*

- Dispersion on a regional scale

The largest emission of benzene from industrial sources occurs in the Botlek area (315 tons per year). The sources are situated in a roughly rectangular area of 5 x 3 km. In order to calculate the annual average concentrations in the vicinity of this area, the area has been divided into 15 squares of 1 km^2. It was assumed that the emission originated from 15 point sources with a height of 20 m, situated in the central points of these squares, with a source strength of 1/15 x 315 tons a year. The calculated contributions to the annual average concentrations outside this area are about: 1 μg.m^{-3} at 3 km, 0.5 μg.m^{-3} at 5 km, 0.3 μg.m^{-3} at 7 km and 0.2 μg.m^{-3} at 9 km from the centre. It is noted that a calculation based on the actual location coordinates and the (non-public) emission figures from the individual companies shows a similar result; locally the isopleths are shifted for about 0,5 km.

Urban background levels may be deduced from the results of previous calculations of NO contributions of traffic (Van den Hout et al., 1983). For this an emission relation NO_x : benzene for traffic resp. within and outside the built-up area of 14 and 60 is taken for granted. The levels are illustrated in fig. 3.3. Together with the contributions of foreign sources (fig. 3.4.) the urban background level will be about 3 $\mu g.m^{-3}$ according to this calculation. Calculated and measured annual averages may differ a bit (see chapter 4). These differences may be caused by a deviating frequency of the wind direction and/or choice of the measurement location (see table 3.1.).

Fig. 3.3. *Contribution of traffic, the most important source of benzene, to annual average benzene concentrations ($\mu g.m^{-3}$) at 5 x 5 km scale. In the vicinity of big cities the concentrations increase relatively strongly. In Amsterdam and Rotterdam the concentrations run to ca 1.4 $\mu g.m^{-3}$*

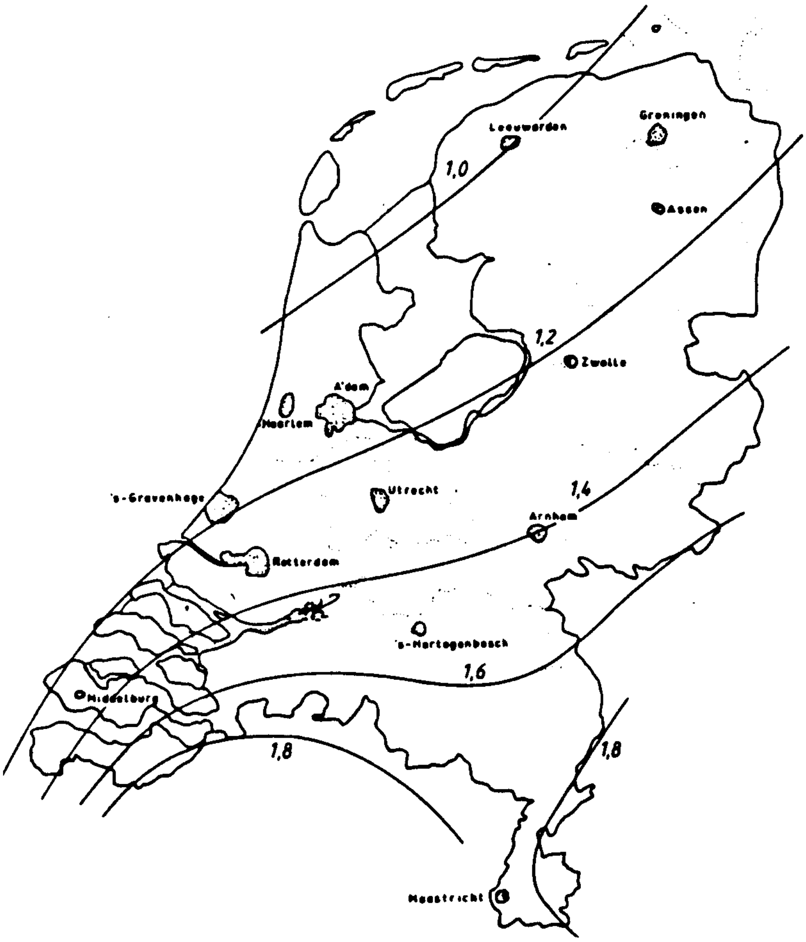


Fig. 3.4. The contribution of foreign sources to the annual average benzene concentrations deduced from measurements ($\mu g.m^{-3}$)

- Dispersion on a national scale

In 1981 the total emission of benzene into the air in The Netherlands was more than 8,360 tons (table 2.10.). Largescale calculations which were compared with empirical data (van Egmond and Huygen, 1979) demonstrate that an emission of a 1000 tons per year into air by a large amount of sources distributed over a large area will increase the national annual average with roughly 0.05 $\mu g.m^{-3}$. From this it might be concluded that the annual average concentration of benzene at a national scale is 0.4 $\mu g.m^{-3}$. This estimate tallies reasonably well with the result of more detailled calculations on the contribution of traffic (fig. 3.3.). The contribution of sources outside The Netherlands has been estimated with a characteristical residence time of 5 days (4.3. x 10^5s). Based on the emissions from Belgium and West Germany (79 ktons per year, R = 100 km, R

= 300 km) and those of the rest of Western Europe (about 106 ktons per year, R = 300 km, R = 800 km), contributions of respectively 0.18 μg.m^{-3} and 0.08 μg.$^{-3}$ were found; together 0.3 μg.m^{-3}. This estimated foreign contribution is lower than the one which follows from the contribution which foreign traffic in itself makes to the NO_x -concentration (15 μg-.m^{-3}) in The Netherlands (Van den Hout et al., 1983). At an average NO_x : benzene relation of 35 the foreign contribution is 0.4 μg.m^{-3} of benzene (or somewhat higher, considering the longer residence time of benzene). The foreign contribution deduced from measurements is again higher (ca. 1.5 μg.m^{-3}, fig. 3.4.).

3.4.2. Deposition

Dry deposition

Data on the dry deposition of benzene are lacking, but the deposition velocities of a few other gaseous compounds have been measured. An investigation of Judeikis (1982) shows that saturation at the soil occurs rapidly, while Kotzias et al (1981) discovered that deposition occurs through the decomposition at the soil. Thus it has to assumed that benzene is adsorbed at the earth's surface until saturation occurs and that further transport from air to soil/water is determined by transformation and transport in soil/water. This indicates that it is difficult to estimate the deposition velocity (v_d). Assuming v_d= 10 cm.s^{-1}, (about the same as the one of aceton above clay, Judeikis, 1982), the removal constant will then be k_d=v_d/h, in which h is the height of the mixing layer. At h = 1000 m, T1/2 = ln2/k_d= 2 years.

At v_d= 10^{-3}cm.s^{-1} the annual load of The Netherlands at an average concentration of 2 μg.m^{-3} is ca. 25 tons.

Wet deposition

The average measured concentration of benzene in rain-water is circa 30 ng.l^{-1} (Van de Meent et al., 1985). This means that the benzene concentrations in air and water are in proportion according to Henry's Law (H = 5.55 x 10^{-3} atm.m^{3}.mol^{-1}; MacKay et al., 1979). At an ambient air concentration of 2 μg.m^{-3}(chapt. 4) it can be concluded from H = p/S, in which p is the ambient air concentration and S is the concentration in water in mol.m^{-3}, that S = 10 ng.l^{-1}. At an annual rainfall of 760 mm and a concentration of 10-30 ng.l^{-1}, about 0.3-0.9 ton a year is removed by wet deposition.

3.4.3. Transformation

Degradation of benzene may occur in the atmosphere under the influence of various mechanisms such as the reaction with OH-, H_2O-, alkoxy- and peroxy radicals, oxygen atoms and ozone. However, on the basis of the rate constant of the reaction and the concentration, only the reaction with hydroxyl radicals is important. A large numer of authors measured the rate constant of the reaction (table 3.2.):

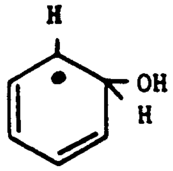
Table 3.2. *Measured rate constants of the reaction with hydroxyl radicals* (k_{OH}), ($ppm^{-1}.min^{-1}$)

Relative rate constant of the reaction	*Reference*
< 5,700	*Doyle et al. (1975)*
1,200	*Cox et al. (1980)*
3,100	*Barnes et al. (1982)*
Absolute rate constant of the reaction	
2,350 ± 200	*Davis et al. (1975, 1977)*
1,830 ± 180	*Hansen et al. (1975)*
1,780 ± 200	*Perry et al. (1977)*
1,830 ± 150	*Tully et al. (1981)*
1,300 ± 100	*Wahner and Zetsch (1981,1983)*
1,800 ± 300	*Witte and Zetsch (1984)*

Especially with the determination by relative methods large deviations are found. The determinations of the absolute rate constant show much less divergence. The average and most found value is 1,800 ppm^{-1}.min^{-1}. The half life at an average concentration of hydroxyl radicals above The Netherlands is:

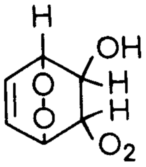
$$T_{1/2} = \frac{\ln 2}{1800 \times 5 \times 10^{-8}} = 5.3 \text{ days}$$

Kinetic and mechanistic research from Perry et al. (1977), Hoshino et al. (1978), Tully et al. (1981) and Kenely et al. (1978 and 1981) demonstrated that benzene reacts principally under formation of the additive product (I):

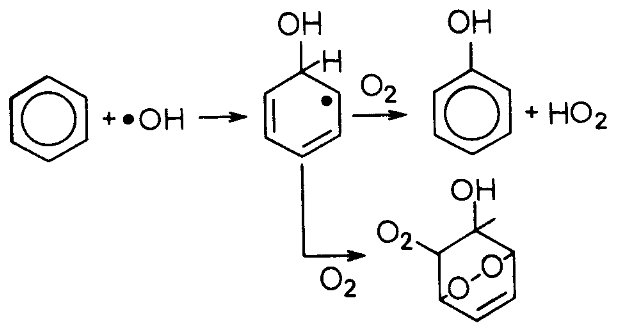


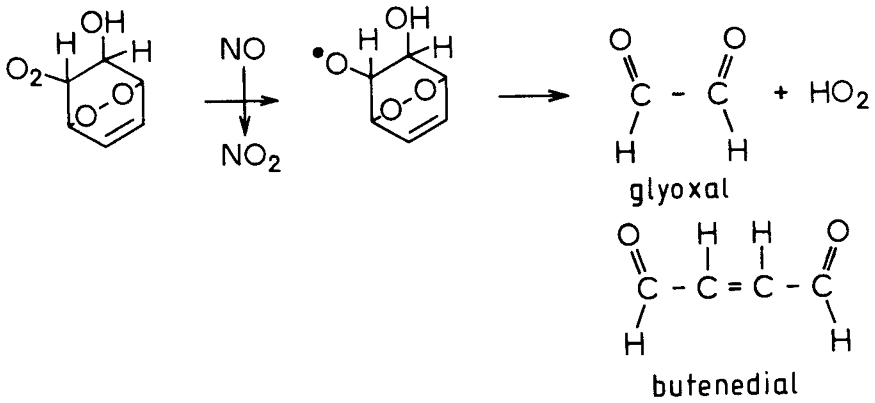
I

This intermediate may continue to react in several ways viz. to benzene or to phenol, nitrobenzene and ring opening products such as glyoxal and formaldehyde (Heuss and Glasson, 1968; Nojima et al., 1975). Moreover it has been demonstrated that during the degradation of benzene in atmospheric circumstances NO is being transformed into NO_2 and that O_3 may be formed.
In view of the fact that a.o. methyl glyoxal and butenedial originate from toluene (Atkinson et al., 1980; Besemer, 1982; O'Brien and Dumdei, 1984) it is assumed that the intermediate may lead to the formation of a socalled endoperoxide



which continues to react to butenedial and glyoxal.
The following mechanism is in accordance with the observations described above:





Besemer (1982) made it plausible that reaction of butenedial under the influence of light may lead to the formation of formaldehyde and acroleine. Apart from that, the formation of glyoxal from butenedial under the influence of OH-radicals should be taken into account. Glyoxal photolyses forming CO and formaldehyde.

The formation of nitrocompounds is probably negligible because in those cases in which formation was observed a high NO_x-concentration in relation to the open air concentration was also present. Apart from the formation of formaldehyde, NO_2, followed by ozone, also appear to be formed. In view of the low reactivity of benzene in relation to other hydrocarbons this only entails a small contribution.

3.5. **BEHAVIOUR IN BIOTA** (See chapter 5 for details)

3.5.1. Absorption and distribution

Via the inhalatory and oral route benzene is quickly absorbed by man and mammals to 55 and ca. 100% respectively; absorption via the skin does probably not occur. Benzene is distributed through the whole body; the highest concentrations occur in fatty tissue and marrow.

Water organisms absorb benzene rapidly. Bioaccumulation is low (usually factor 1-10).

3.5.2. Transformation and excretion

Of the absorbed quantity of benzene in man and mammals 40 respectively 50% is excreted unchanged via the lungs; a fraction of benzene leaves the body unchanged via the urine. Transformation takes place through the P450 mixed-function oxydase (m.f.o.)-system, during which phenol is formed as the most important metabolite. A small part of this is metabolized further: 60-80% of the absorbed dose is excreted via the urine as phenol conjugate.
In (higher) water organisms benzene is probably partly metabolized by the present m.f.o-system as well; excretion occurs via gills and faeces. Also in higher plants benzene is degraded. Some studies mention a complete degradation (to CO_2) in all parts of the plant. One is referred to 3.1.2. and 3.2.2. for microbial degradation.

3.6. MULTICOMPARTMENTAL DISTRIBUTION

The distribution of benzene over the compartments of air, water, soil and sediments may be estimated on the basis of the emissions with the aid of the fugacity model developed by MacKay (1985). This (stationary) model has been illustrated schematically in fig. 3.5.

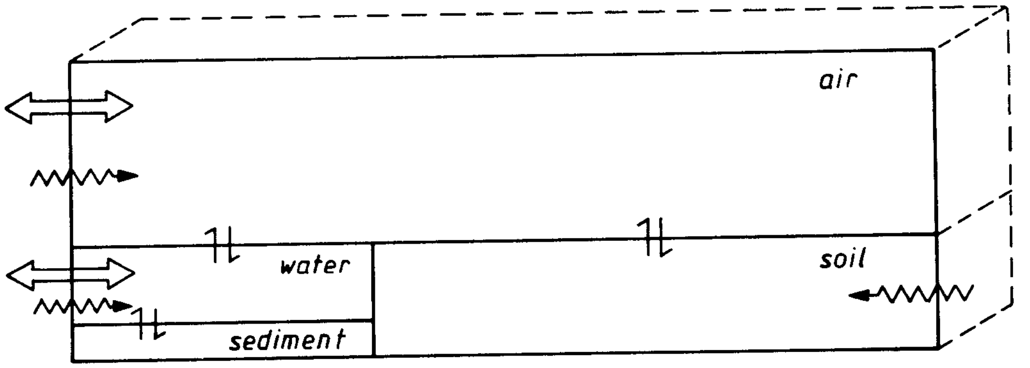


Fig. 3.5. Schematical representation of the MacKay-model, in which:

- *transport over the boundaries of the compartments*
- *advective transport*
- *emission*

Ideally mixed compartments and photolysis (water and air) and biodegradation (water) as important degradation mechanisms are assumed. Especifically for the Dutch situation the following model parameters have been estimated:

- total surface : 41,000 km^{-2}(88% soil/12% water)
- height of air column : 1,000 m
- height of water column (fresh) : 2.5 m
- height of sediment column : 0.03 m
- height of soil column : 0.15 m
- residence time air : 2.3 days
- air supply and -concentration : 55% sea air (NW), 0.1 μg.m^{-3}; 45% land air (South East; Belgium, Germany), 1.8 μg.m^{-3}

For the remaining parameters reference is made to MacKay (1985); for the used emission data to chapter 2. The outcomes of this arithemetric model are given in table 3.3.

Table 3.3. Distribution of benzene in The Netherlands over environmental compartments (yearly average) bases on Dutch and trans frontier emissions

Distribution	*Air*	*Water (Fresh)*	*Soil*	*Sediment*
Concentration	*2.1 μg.m^{-3}*	*58 ng.l^{-1}*	*12 ng.kg^{-1}*	*130 ng.kg^{-1}*
Distribution (%)	*99.0*	*0.9*	*0.1*	*< 0.1*
Removal by reaction (%)	*4.6*	*0.2*	*n.c.*)*	*n.c.*
Removal by advection (%)	*95.2*	*<0.1*	*n.c.*	*n.c.*

**) not calculated*

These data show that removal by transportation through the air (advection) is the most important removal mechanism. As a result the retention time and the concentration level of the (imported air among others determine the concentration level of the ambient air in The Netherlands.

At a longer retention time of for instance 5 days, the concentrations in air, water, soil and sediment measure 3.4; 68; 25.5 and > 100, respectively. If, in this case, "clean" sea-air is imported, those values are 2.6; 65; 20 and > 100. If only air is imported from Belgium and Western Germany (1.8 $\mu g.m^{-3}$) these values are 4.2.; 71; 32 and > 100, respectively.

3.7. SUMMARY AND CONCLUSIONS

Because emission of benzene mainly takes place in the air (chapter 2), its relatively high vapour pressure, the poor solubility in water and the little adsorption to soil, most of the benzene is found in the atmosphere (99%). Removal too mainly takes place in the air compartment. With respect to this, removal in other environmental compartments is negligible small. Removal in air mainly (ca. 95%) takes place by advection, but in fact it may very well be negative because of the benzene loading of the imported air (chapter 2). Removal by degradation especially takes place by a reaction with hydroxyl readicals (half-life ca. 5 days). The behaviour of benzene in other environmental compartments can be important on a local or regional scale because of the generally higher concentrations. Deposition to soil usually leads to evaporation and biodegradation of benzene. At higher loading levels (for instance discharge, calamities) high concentrations in groundwater can develop, because of the high mobility of benzene in soils. As a result, certain functions (such as water catchment areas) can be threatened. Opposite to this, benzene is readily removed in drinking water processing by treatment with ozone or active carbon. Emissions of benzene to surface water are mainly re-emitted to the air. Additional removal takes place by biodegradation (half-life a few days up to weeks) and by reaction with mainly hydroxyl radicals (half-life a few weeks up to months). In biological effluent water treatment plants benzene is removed effectively. Benzene is quickly absorbed by biota and excreted partly unchanged, partly metabolized. Benzene does hardly or not bioaccumulate. During both biotic and abiotic transformations of benzene, potentially harmful (intermediate) products can be formed like phenol and formaldehyde. The formed quantities cannot be estimated approximately.

4. ENVIRONMENTAL CONCENTRATIONS AND EXPOSURE LEVELS

4.1. NATURAL SOURCES AND BACKGROUND CONCENTRATIONS

Natural sources are amongst others emanation from oil which ends up in the environment through cracks in the earth (Fishbein, 1984), and volcanic eruptions and vegetation (Graedel, 1978). Apart from that, 35 $\mu g.m^{-3}$ of benzene was measured in the plume of a forest-fire at a distance of ca. 6 km of the seat of the fire (Westberg et al., 1981). These emissions, however, are low in comparison with anthropogenic emissions, as is shown by the measurements of Rasmussen and Khalil (1983) and Rudolph et al. (1984) above the Pacific, the Atlantic Ocean and in rural areas. The benzene concentrations in the Northern and Southern Hemisphere differ considerably (fig. 4.1.). Especially the higher concentrations (ca. 0.5 $\mu g.m^{-3}$) between 30^o and 70^o N indicate an anthropogenic emission (Japan, United States, Europe). Fig. 4.1. also demonstrates a correlation in occurrence between benzene and acetylene; both substances are emitted to an important degree by traffic, while the residence time does not differ much.

In a survey of the rural areas by the OECD, concentrations of 0.1-3.6 $\mu g.m^{-3}$ are mentioned.

4.2. OCCURRENCE IN SOIL

In areas which had not been classified as polluted, benzene concentrations of < 0.005 - 0.03 $\mu g.l^{-1}$ were found in Dutch ground water (Zoeteman, 1981). As a part of the issue on soil pollution an inventory was made of the seriousness of a number of chemically polluted sites in The Netherlands (see also 2.2.1.). On the basis of this inventory and the standards from the guideline on Soil Reconstruction (Staatsuitgeverij, 1983), the number of polluted sites has been classified to the concentrations found in the soil and ground water in fig. 4.2. Although data on the concentrations in soil are limited, it can be concluded from the figure that the levels of benzene in ground water are generally considerably higher than those in soil material (see also 3.2.1.).

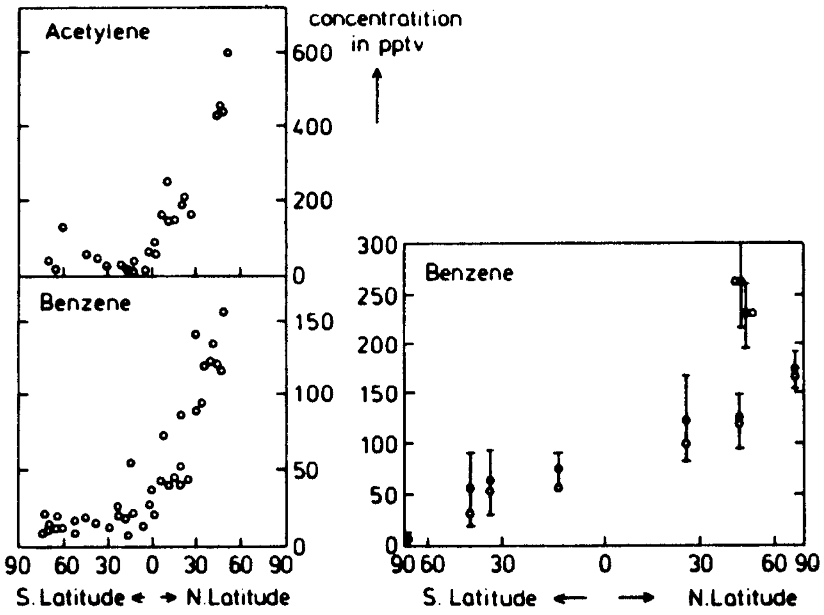


Fig. 4.1. *Benzene and acetylene concentrations in the Southern and Northern Hemisphere (at the right: the Pacific, according to Rasmussen and Khalil, 1983; at the left: the Atlantic, according to Rudolph et al., 1984). Dark circles illustrate seasonal average concentrations of levels above the detection limit (≥ 5 pptv); the open circles illustrate all measurements. Vertical lines illustrate the 90% confidence limits.*

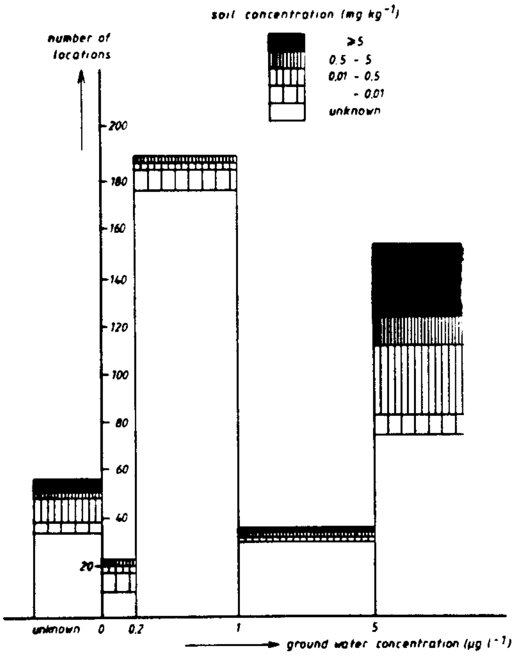


Figure 4.2. *The number of sites containing benzene according to the standards for soil- and ground water pollution from the guideline on soil reconstruction (1983)*

4.3. OCCURRECNCE IN SURFACE WATER

In 1978 and 1979 the benzene concentration of the water of the Rhine was < 0.1 $\mu g.l^{-1}$ (Morra et al., 1979; Linders et al., 1981). In the period of August 1984 - April 1985 a median concentration of 26 $ng.l^{-1}$ was determined in the Rhine (Jutphaas) (Hrubrec, 1985). In the water of the Meuse usually less than 0.1 $\mu g.l^{-1}$ was found in 1982 and 1983 (RIWA, 1982; 1983). In Lake IJssel (Andijk) too the average level of benzene was less than 0.1 $\mu g.l^{-1}$ (Meijers, 1984). A recent investigation of sea water in the coastal area of the North Sea indicated a concentration of < 5-20 $ng.l^{-1}$; in the central part of the North Sea average concentrations of ca. 5 $ng.l^{-1}$ were found (Van de Meent et al., 1985).

4.4. OCCURRENCE IN AIR

4.4.1. Indoor air

- Occupational exposure

Occupational exposure mainly occurs during the production of benzene and derivatives, the maintenance of equipment, unloading and at laboratories.
According to Brief et al. (1980) the time weighted average concentration over a working day of 8 hours (TWA) in an industrial unit will seldom be higher than 160 $mg.m^{-3}$. In oil refineries, during ordinary operation, the chances of the TWA exceeding the value of 3.2 $mg.m^{-3}$ are less than 5% and the chances of exceeding 16 $mg.m^{-3}$ are nil. At petrochemical plants the chances of exceeding a TWA of 16 $mg.m^{-3}$ are ca. 8%. This larger risk of transgression of the limit is due to higher benzene concentrations in the process flows and in the products of the petrochemical industry.
Air concentrations to 4.8 $mg.m^{-3}$ during maintenance of equipment containing a liquid with benzene concentrations to 15% have been reported (Weaver et al., 1983). Exposure to high benzene concentrations (up to 170 $mg.m^{-3}$) may occur during trans-shipment in tank lorries and -boats, especially during the socalled open trans-shipment. This peak load is generally of short duration and leads to a TWA between 1.3 and 34 $mg.m^{-3}$, with an average of 13 $mg.m^{-3}$. During "closed" trans-shipment the TWA is about 10 times lower. The TWA for tank lorry drivers is between 0.06 and 3.2 $mg.m^{-3}$ and the TWA for people involved in trans-shipping is about 9 $mg.m^{-3}$ (Weaver et al., 1983).

For the personnel of petrol stations the TWA is generally lower than 3.2 mg.m^{-3} (Lehmann, 1984; CONCAWE, 1981). During trans-shipment of larger quantities of petrol, concentrations may occur that are considerably higher (table 4.1.). The scene of action, however, is at a large distance of residential areas.

Table 4.1. *Benzene concentrations in air during trans-shipment of benzene in mg.m^{-3} (UBA, 1982)*

Occupational group	*Av. exposure over 8 hours*	*Av. max. exposure 45 min.*	*Range of max. exposure*
Petrol pump attendant	*0.22*	*0.37*	*0.10- 2.76*
Tank lorry drivers	*0.54*	*2.47*	*0.03 98.5*
Crew of a tanker	*4.18*	*19.44*	*2.17-170.0*

Increased exposure also occurs in laboratories where several activities are performed with benzene (or benzene containing mixtures). In two laboratories of refineries concentrations up to 13 mg.m^{-3} were found (Weaver et al., 1983). At laboratories where benzene (compounds) had been used, the exposure was between 0.3 and 52 mg.m^{-3} (Hertlein, 1980).

Benzene as a solvent has practically completely been replaced by other agents. However, exposure is possible because benzene is present in various substances as a pollutant. E.g. in rubber industry concentrations up to 2 mg.m^{-3} were found (Cocheo et al., 1983; Jones, 1981). Increased concentrations may also occur in garages, but the TWA will generally not exceed 3 mg.m^{-3} (CONCAWE, 1981; Jonsson and Berg, 1980).

A few recent published surveys include a summary of the literature concerning occupational exposure (Fishbein, 1984; Weaver et al., 1983; Umweltbundesamt, 1982).

All data above mentioned are taken from foreign publications. No data have been found concerning the Dutch situation. The MAC-TWA in The Netherlands is 30 mg.m^{-3} at the moment (chapter 1).

- Non-occupational exposure

On the basis of single measurements in 96 recently built (within the last 6 years) and in 134 pre-war homes in Ede and in 89 pre-war homes in Rotterdam, during the winter months in 1981/82 and 1982/83 average indoor air concentrations was 5-7 $\mu g.m^{-3}$ were found; the maximum concentration was 148 $\mu g.m^{-3}$. The factor in/out (average concentration in indoor air/average concentration in outdoor air) was 2 (Lebret, 1985). During the period of July 1982-february 1983 benzene concentrations were measured in 4 homes for 1 week per 2 weeks; the median and maximum concentrations varied respectively 3-6 and 7-11 $\mu g.m^{-3}$(Boleij et al., 1985). Abroad the average indoor air concentrations varied between 6 and 52 $\mu g.m^{-3}$ and the in/out factors between 0.6 and 3.9 (Johansson, 1978; Seifert and Abraham, 1982; De Bortoli et al., 1984; Hartwell et al., 1984; Wallace et al., 1984).

As a result of local soil pollution the benzene concentration can be increased occasionally in the living space of homes. In homes near petrol station with leaking petrol storage tanks one should reckon with a contribution to the indoor air of a few dozens of $\mu g.m^{-3}$ (maximum value measured: 58 $\mu g.m^{-3}$; Kliest and Fast, 1985). In houses built on former dumping sites an occasional increase of the benzene concentration in the living space occurs as a result of the pollution of the soil. In Lekkerkerk (Van de Wiel et al., 1981) such a contribution was not found. This did happen in Dordrecht (Van Esch et al., 1981): in the space beneath the floor and in the living space the concentrations were respectively 230 and 34 $\mu g.m^{-3}$. In houses built on sites of former gasworks, polluted with aromatics benzene included, no increase of the indoor air concentration of benzene has been determined so far (Van de Wiel, 1985).

The benzene concentration in cars is generally determined by the concentration in ambient air, but it may be increased by evaporation of petrol. During commuter traffic the benzene concentration was measured in petrol cars of different make during a good 4,000 drives (Den Tonkelaar and Van der Tuin, 1982). The average concentration was 66 $\mu g.m^{-3}$; the maximum 2,700 $\mu g.m^{-3}$. During 86 drives on motor ways an average concentration of 27 $\mu g.m^{-3}$ was found. In Germany the average concentration during rides in the city was between 55 and 560 $\mu g.m^{-3}$ (Umweltbundesamt, 1982; Mücke and Rudolf, 1984).

- Exposure through smoking

In table 4.2. the benzene concentrations in cigarette smoke are illustrated, as well as the quantities of benzene in the main stream (the inhaled smoke) and side stream (the indirectly inhaled smoke) of cigarettes. In public spaces where smoking occurs, the benzene concentrations were 0.020-0.150 $mg.m^{-3}$, with a maximum of 3.17 $mg.m^{-3}$ (Badre et al., 1978). Inhalation of cigarette smoke leads to a benzene intake of 0.010 mg (Brief et al., 1980) to 0.031 mg (Weaver et al., 1983) per cigarette.

Table 4.2. Benzene concentrations in cigarette smoke and quantities of benzene in the main- and side stream of cigarettes

Cigarette smoke	*150- 205 $mg.m^{-3}$*	*(Lauwergijs, 1979)*
Main stream	*0.018 mg per cig.*	*(Baggett et al., 1974)*
	0.010-0.100 mg per cig.	*(US. DHEW, 1972)*
	0.012-0.091 mg per cig.	*(Feron et al., 1979)*
	0.050-0.100 mg per cig.	*(Klus and Kunh, 1982)*
Side stream	*0.390 mg per cig.*	*(Jermini et al., 1976)*
	0.488 mg per cig.	*(Klus and Kunh, 1982)*
	0.050-0.360 mg per cig.	*(Feron et al., 1979)*

4.4.2. Open air

Benzene has been measured at a large number of locations all over the world. An extensive survey of measurements in rural areas, in cities and in the vicinity of industrial sources up to 1980 has been given by the OECD (1981). In cities the following concentrations were found: Canadian cities 19-318 $\mu g.m^{-3}$; German cities 7-670 $\mu g.m^{-3}$; Dutch cities 2-185 $\mu g.m^{-3}$; Zürich (Switzerland) 80-239 $\mu g.m^{-3}$; London (England) an average of 156 $\mu g.m^{-3}$ with maxima up to 600 $\mu g.m^{-3}$ and American cities 2-185 $\mu g.m^{-3}$.
In table 4.3. additional data on concentration levels abroad after 1980 are mentioned.

Table 4.3. Survey of benzene concentrations in air in foreign countries after 1980

Location/ Country	Period	Concentration ($\mu g.m^{-3}$)	Duration and period of sampling	References	Remarks
Houston	5/80	18.4	period of 2 weeks 12 samples/ day 15-60 min.	Singh et al. (1982)	Min.concentration ca. 0.2 $\mu g.m^{-3}$ Max. concentration ca. 200 $\mu g.m^{-3}$
St. Louis	5-6/80	4.5			
Denver	6/80	14.0			
Riverside	7/80	12.3			
Staten Island	3-4/81	13.4			
Pittsburgh	4/81	15.9			
Chicago	4/81	8.2			
Oslo Norway	3/80	40-120 40 SS	period of 3 days, duration of sampling 2 hours - 1 day	Wathne (1983)	SS: "street station" (12,000 cars/day RS: reference station at a distance of 200 m from SS; no direct influence of traffic maxima to 114 g.m
	8-9/80	20 RS			
New Jersey, USA	1-2/82		24 hours 30 samples	Harkov et al. (1984)	
Newark		8.4			Newark is an industrialized area a.o. petrochemical industry; residential area at the same time
Elizabeth		10.0			Elizabeth is situated in the vicinity of petrochemical and other industries
Camden		9.0			Camden is influenced by various industries

Table 4.3. Continued

ibid. Newark	8/81	3.1	38 samples		
Elizabeth		3.2			
Camden		3.6			
Los Angelos "Downtown"	9-10 11/81	38-93	sampling 3-5 min. 23 days	Crosjean and Kung (1977)	Samples gathered at 8 o'clock in the morning or as an average of the period between 6-9 a.m.
Rhine/Ruhr area Germany	4/81 3/83	4.6-22.4	weekly 40 sampling stations Monday-Friday 10 samples half-hourly values	Bruckman et al. (1983)	
Black Fores ("Reinluft-gebiet")		2.0	802 samples 1 week 6 samples		
England	1983		20 minutes during 4 weeks May-August 1983 average of ca. 200 samples	Clark et al. (1984)	
London		23 (2 -85)			
Motor way (4 lanes)		9 (0.2-40)			
Background 45 km from London		6 (0.7-16)			

Around sources the concentration levels are clearly increased in comparison with background levels (OECD), 1981). In the vicinity of chemical industries 10-30 $\mu g.m^{-3}$ are found. Occasionally higher concentrations may occur up to a few hundreds of $\mu g.m^{-3}$; once a value of 75,000 $\mu g.m^{-3}$ was reported.

Also in The Netherlands benzene concentrations have been measured at several locations. Jeltes and Burghardt (1975) found levels of 2 $\mu g.m^{-3}$ with a maximum of 25 $\mu g.m^{-3}$ in Delft; in the Hague 15 $\mu g.m^{-3}$ at a distance of traffic routes and 42 $\mu g.m^{-3}$ in the centre (max. 93 $\mu g.m^{-3}$); in Rotterdam near the Meuse tunnel 87-108 $\mu g.m^{-3}$ (15-120 minute averages). Goudena and Guicherit (1980) found similar levels in the Hague and Rotterdam. Den Hartog (1981) measured a number of hydrocarbons at the measurement locations Terschelling, Hellevoetsluis, Vlaardingen and Delft during the period of 1979-1981 and he ascertained that benzene was always present. Quantitative statements are not possible due to the sampling method applied.

The most recent measurements have been taken by Thijsse (1985) during the period 1982-1983 (table 4.4.).

Table 4.4. *Annual average concentration levels of benzene measured at five stations in The Netherlands during the period 1982-1983 (duration of sampling 24 hours, 80 samples) (Thijsse, 1985)*

Measurement station	*Concentration (av.) ($\mu g.m^{-3}$)*	*Maxima*) ($\mu g.m^{-3}$)*
Vlaardingen	*9.0*	*59.4*
Biest-Houtakker	*2.4*	*8.1*
Rekken	*2.0*	*5.3*
Witteveen	*1.6*	*6.5*
Bilthoven	*2.8*	*10.4*

**) These maxima mainly occur in winter*

The concentration depends amongst others on the wind direction (fig. 4.3.). This can be observed especially at the station Vlaardingen, for which Rotterdam (east wind), industry (south wind) and the motor way (north wind) can be recognized as sources.

The annual average largescale concentration level in The Netherlands is ca. 2 $\mu g.m^{-3}$. Since most inhabitants of The Netherlands are working and living in towns, the average exposure to benzene via the atmosphere is a factor 2-10 higher. An important point for attention is the introduction of leadless petrol, as a result of which the aromatic content of petrol will increase and therefore the benzene emission will increase as well (table 4.5.).

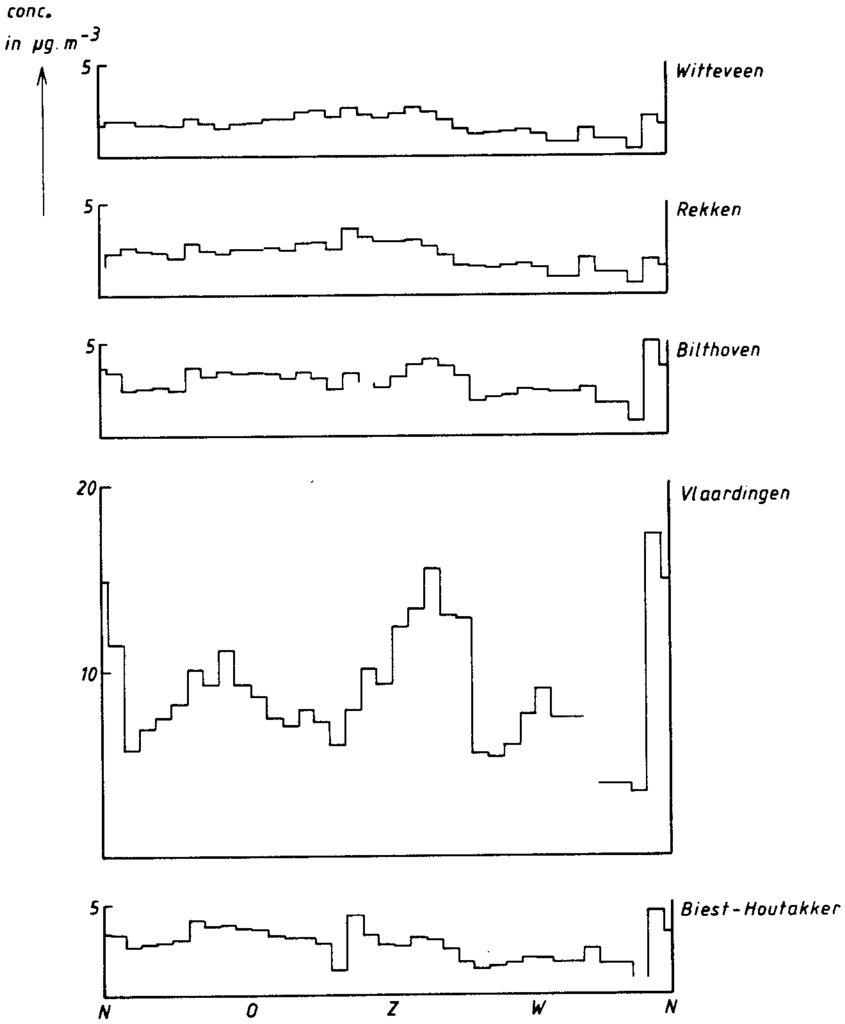


Fig. 4.3. Three-point average benzene concentration at five Dutch stations (Thijsse, 1985)

Table 4.5. Influence of the change to leadless petrol on the benzene concentration in ambient air (Seifert and Ullrich, 1978)

Period	*Benzene conc. in ambient air* ($\mu g.m^{-3}$)	*Pb-content in petrol* ($g.m^{-3}$)	*Number of Samples*
Nov/Dec '75	*49.0*	*3.1*	*60*
Nov/Dec '76	*68.9*	*1.0*	*48*

In rain water a median benzene concentration of ca 0.03 $\mu g.l^{-1}$ was dtermined (Van Noort, 1985).

4.5. FOOD AND DRINKING WATER

Few quantitative data are available on the occurrence of benzene in food products. Benzene forms a natural part of certain products viz. vegetable products such as potatoes, vegetables and fruit (Mara and Lee, 1978). A report of the NCI (1977) refers to data on the benzene load in food. Products that are mentioned are eggs (2100 $\mu g.kg^{-1}$). Jamaica rum (120 μg-$.kg^{-1}$, radiated beef (19 $\mu g.kg^{-1}$) and heated or tinned beef (2 $\mu g.kg^{-1}$). In the United States it is estimated (on the basis of these relatively poor data) that the daily intake can be 250 μg a day (National Research Council, 1980; National Toxicology Program, 1983). In The Netherlands the contents are assumed to be smaller than 100 $\mu g.kg^{-1}$; exact data are lacking. The fact that non-identified sources (food?) might contribute to the total benzene load might appear from high benzene concentrations in expired air from persons not specifically exposed (24-60 $\mu g.m^{-3}$: Fishbein, 1984; 3.5-16.0 mg a day as phenol: Elster et al., 1978).

Benzene may occur in food naturally, through migration from metallic covering layers of the packaging material (see 1.2.4.) or through contamination via an environment loaded with benzene. In respect to the latter, one should be reminded of the fact that benzene is hardly bioaccumulative: concentration factors are generally between 1 and 10 (chapter 5). On the basis of concentration levels in ground water and surface water of resp. 0.03 and 0.10 $\mu g.l^{-1}$ the contribution of the environmental load to the benzene content in fish and vegetable food is < 1 $\mu g.kg^{-1}$. If a benzene intake of 250 μg per day and a food intake of 1,850 g per day was to be assumed (Verhoeven and Compaan, 1980), the benzene contents of food would be 135 $\mu g.kg^{-1}$ on average of which more than 90% would be present due to natural occurrence and migration from metallic covering layers of packaging material. It is taken for granted that in The Netherlands (partly because of a different cultural pattern with respect to packaging of food and drink and the fact that benzene is no longer used in plastic packaging material) the benzene content is lower than 135 $\mu g.kg^{-1}$ (250 μg per day); possibly lower than 100 $\mu g.kg^{-1}$.

Benzene concentrations in drinking water are maximally 0.005 $\mu g.l^{-1}$ (detection limit) in The Netherlands (Kool et al., 1979).

4.6. EXPOSURE LEVELS

On the basis of the previously mentioned concentrations (see also table 4.7.) the exposure levels for man and (parts of) ecosystems can be estimated.

Concerning the human exposure the following is assumed: an intake of 0.05 l of surface water and 50 mg of soil material a day (Duggan, 1980; Van Wijnen, 1981); a daily intake of 2 l of drinking water (Van Wijnen, 1981; Zielhuis, 1981; Rosenblatt et al., 1982) and an average breathing air of 12 m^3 (Rosenblatt et al., 1982). Moreover it is assumed that smokers smoke an average of 10 cigarettes a day and stay in places where smoking takes place for 10 hours a day. For passive smokers a sojourn of 2 hours is assumed. Participation in traffic is estimated at 1 hour; the daily intake of food at ca. 1,850 g for which a content of 100 $\mu g.kg^{-1}$ (worst case) is assumed. For staying in indoor- and open air a distribution of 75/25 is used and and in/out factor of 2 (only for rural areas). In table 4.6. a rough approximation has been given for the daily intake of benzene of the population, divided to residential area, car use, participation in rush hour and the degree of exposure to cigarette smoke. An absorption via the oral and inhalatory route of resp. 100 and 50% is assumed (section 5.1.1.) for the determination of the absorbed quantity of benzene. It should be noted that this estimate knows large uncertainties. For example, the contribution of food to the total daily load may be substantially (e.g. a factor 10) lower.

As a result of this, the relation between voluntary and non-voluntary exposure levels may change considerably. In conformity with table 4.6. the non-voluntary intake is about 200-455 μg per day, while due to the voluntary exposure (smoking) the intake levels are increased 2-3 (urban areas) or 2-6 (rural areas) times. It is assumed that the actual contribution of voluntary exposure is relatively considerably larger.

A separate focus of attention is the exposure level at the work place; the daily intake amounts to $4 \times 10^3 - 8 \times 10^6$ μg in various (foreign) situations.

With regard to the aquatic ecosystems the exposure level may be equated with the concentration in surface water (< 0.1 $\mu g.l^{-1}$), while with respect to terrestrial ecosystems the exposure level may vary greatly from species to species, depending on e.g. way of life (underground, overground, combination) and feeding pattern (nature and quantities).

4.7. SUMMARY AND CONCLUSIONS

In table 4.7. a summary has been given as far as possible of the benzene concentrations and -contents found in various environmental compartments.

The concentration in soil (nationally) has been derived from the one in ground water, based on an average OC-percentage of 2% (Scheele, 1980) and a K_{oc} value of 100 (see 3.1.1.). On the basis of this relationship the proportion of the A-, B- and C-values (see 1.2.1.) between soil material and ground water used at present seems inaccurate.

There are no or insufficient data available on the benzene levels in food and at the work-place for the Dutch situation. This entails that the daily quantity of benzene absorbed by man cannot be determined. As a result of voluntary exposure (smoking) the daily intake of benzene is considerably increased; with respect to the non-voluntary exposure this intake is at least a factor 2-3 higher. Because of working at certain work places the daily intake can be multiplied by ten to a thousand.

Table 4.6. A rough estimate of the daily individual intake (µg) by the Dutch population (in millions) divided to residential area, participation in traffic and active/passive smoking. A high load via food was assumed (185 $\mu g.d^{-1}$). Intake in the work place has not been included.

Residential area	Car use/ rush hour		Smoking behaviour/ passive smoking		Daily intake
Rural area (5)	-	(2.9)	-	(1.3)	200- 270
			2 hours of passive smoking	(0.8)	210- 340
			10 cig. day and 10 hours of passive smoking	(0.8)	290-1110
	1 hour a day	(2.1)	-	(0.9)	215- 285
			2 hours of passive smoking	(0.6)	225- 355
			10 cig. day and 10 hours of passive smoking	(0.6)	305-1125
Urban area (9)	-	(5)	-	(2.2)	200- 440
			2 hours of passive smoking	(1.4)	210- 495
			10 cig. day and 10 hours of passive smoking	(1.4)	290-1205
	1 hour a day	(4)	-	(1.8)	215- 455
			2 hours of passive smoking	(1.1)	225- 510
			10 cig. day and 10 hours of passive smoking	(1.1)	305-1220

Table 4.7. *Summary of levels of benzene concentrations and -content in various environmental compartments in The Netherlands*

Soil			
- *ground water (national)*		*0.005-0.03*	$\mu g.l^{-1}$
- *ground water (local)*		*5*	$\mu g.l^{-1}$
- *soil material (national)*		*0.01 -0.06*	$\mu g.kg^{-1}$*
- *soil material (local)*		*5,000*	$\mu g.kg^{-1}$
Surface water			
- *fresh*		*0.01 -0.1*	$\mu g.l^{-1}$
- *salt*		*0.005-0.02*	$\mu g.l^{-1}$
Air			
ambient air	- *rural*	*1.1 -8.1*	$\mu g.m^{-3}$
	- *urban area*	*2 -42 (max. 93)*	$\mu g.m^{-3}$
	- *national (annual av.)*	*2*	$\mu g.m^{-3}$
	- *rain water*	*0.03*	$\mu g.l^{-1}$
indoor air	- *living space*	*3 -7 (max. 148)*	$\mu g.m^{-3}$
	- *ibid. on poll. soil*	*3 -58*	$\mu g.m^{-3}$
	- *space where people smoke*	*20 -150 (max. 3,170)*	$\mu g.m^{-3}$
	- *car/rush hour*	*66*	$\mu g.m^{-3}$
	- *smoking*	*10 -100*	$\mu g.cig^{-1}$
	- *work place (various)***	*60 -34,000 (max.170,000)*	$\mu g.m^{-3}$
Food (average)		*100 (?)*	$\mu g.kg^{-1}$
Drinking water		*0.005*	$\mu g.l^{-1}$

**) Deduced from data on ground water*

***) Foreign data*

5. EFFECTS

This chapter contains a summary of data on the effects of benzene, including a risk-estimation. More detailed information is given in the Appendix (Knaap et al., 1987)

5.1. HUMAN TOXICITY

5.1.1. Chemobiokinetics and metabolism

By inhalation 30-50% of benzene is rapidly absorbed (37-55% in animals). No human data are available on absorption in the gastro-intestinal tract, but animal data suggest ca. 100% absorption. There are indications that absorption via skin does not occur.

Following absorption, benzene is widely distributed throughout the body, independent of the route of administration. Levels fall rapidly once exposure stops.

It would appear from the available data that metabolism of benzene in humans is very similar to the general pattern observed in animal experiments. It is generally accepted that benzene is being metabolised by the P-450 mixed function oxidase system. One of the main metabolites is phenol. A small part of phenol is metabolised to hydroquinone and catechol. An even smaller part is transformed to phenylmercapturic acid or to trans-trans-muconic acid. Of the absorbed dose 12 - 40% is exhaled unaltered (in animals up to 50%). Elimination can be described by a three compartment model. The first phase corresponding to elimination from blood and well vascularised tissue, the second to elimination from less perfused tissue like muscle and skin and the third phase corresponding to elimination from fat tissue. A small part is excreted unaltered in the urine; 60 - 80% dose is excreted in urine as phenol conjugates.

5.1.2. Animal experiments

Benzene has low acute toxicity to animals (LC50 2-8h: 15-60 $g.m^{-3}$; LD50: 1-10 $g.kg^{-1}$ b.w.).

No clinical signs of toxicity in the rat were seen at or below 1600 $mg.m^{-3}$.

The principal toxic effect following repeated exposure to lower (150 $mg.m^{-3}$) levels of benzene is in the blood and blood forming tissues.

Benzene is carinogenic in rats both by oral and inhalation administration, and in mice by inhalation.

Benzene is non-mutagenic in all of the point/gene mutation test systems in which it has been tested so far. Benzene can induce chromosome damage in plants and in mammalian somatic cells in vitro and in vivo. The clastogenic potential of benzene is partly due to its hydroxylated metabolites. It has been suggested that benzene and its metabolites interfere with the formation of the mitotic spindle and perhaps do not interact directly with DNA. However, binding of benzene to nucleic acids has been reported.

Benzene is not teratogenic at doses lower than those which produce maternal toxicity.

Several compounds may enhance or inhibit the toxicity of benzene.

5.1.3. Observations in man

Acute exposure to 65 g.m^{-3} may cause death. In fatal cases extensive hemorrhages have been oberved. Exposure to 2,275 mg.m^{-3} during 30 minutes produces signs of disturbances of the central nervous system.

Chronic exposure to high but ill-defined concentrations (about 400 mg.m^{-3} and higher) causes damage to the haematopoietic system. This includes anemia, leucopenia and trombocytopenia, in severe cases aplastic anemia. Adverse effects (anemia, leucopenia) have been observed in workers probably exposed to 130 - 260 mg.m^{-3}.

Exposure to 3.25-97.5 mg.m^{-3} causes a transient reduction in red blood-cell counts. This phenomenon was not regarded as clinically significant. Enzyme changes within the leucocytes have been observed after exposure to 32.5-81 mg.m^{-3} during at least a three years period.

There is considerable evidence that exposure to high concentrations (ca. ≥ 325 mg.m^{-3}) of benzene may eventually result in leukemia. In many cases leukemia was preceded by pancytopenia or aplastic anemia, but a relation could not be determined for all cases. Exposure to benzene and acute myeloid leukemia was found to be correlated, to a lesser extent this has been shown for erythroleukemia and other leukemias and lymphomas as well.

The studies by Aksoy et al. (1972), Ott et al. (1978) and Rinsky et al. (1981) are the only epidemiological investigations of humans exposed to benzene which also attempt to characterise the exposure situation in some detail. The EPA (1984) has accepted and used all three studies for the elaboration of a risk-estimation. The present report (see Appendix)

concludes that the Aksoy et al. (1972) and the Ott et al. (1978) studies cannot be used for a risk-estimation.
With regard to environmental exposures no direct relation has been shown between exposure to benzene and hematological disorders. In two studies minor hematological changes have been observed among persons living in an area polluted - among other substances - with benzene (in one area 50 $\mu g.m^{-3}$). However, these studies do not prove a causal relationship between benzene exposure and blood changes. In several studies no relation was obeserved between (possible) increased environmental exposure to benzene and the occurrence of leukemia among the general population. However, these results cannot be accepted as a proof against a leukemogenic action of benzene in environmental concentrations. There is sufficient evidence for a strong correlation between a clear benzene hemopathy in human subjects (exposure to high levels of benzene) and chromosome aberrations in bone marrow cells or peripheral lymphocytes. Available data are insufficiently consistent to establish a dose-response relationship. Occupational exposure to low levels of benzene (0.6-40 $mg.m^{-3}$) causes chromosomal abnormalities (bases on studies with apparently healthy workers).
An immunotoxic action of benzene has been shown in occupationally exposed men. No teratogenic effects of benzene have been observed. However, limited research has been done on this subject.
Although exposure to low concentration of benzene has not been shown to be leukemogenic, several reports do conclude that the existence of a threshold has not been established.
Concentrations above 10 $mg.m^{-3}$ may cause odour annoyance.

5.2. ECOTOXICITY

5.2.1. Uptake, metabolism, bioaccumulation and elimination

Equilibrium between uptake and elimination is reached readily (within 6-24 hrs in fish). The log n-octanol/water partition coefficient is low (2.13), indicating restricted bioconcentration (BF expected: 20) in aquatic organisms. Measured bioconcentration factors are low indeed: 30 for *Chlorella sp.* (Algae), 153-225 for *Daphnia sp.* (Crustacea) and 1-135 for different life stages of fish species, most values being between 1-10. For higher plants an average BF of 200 (fat base) is reported. No data are reported on biomagnification. Accumulated benzene burdens in organisms are cleared rapidly when the external contamination is removed.

5.2.2. Toxicity to aquatic organisms

The short-term toxicity to micro-organisms (Bacteria, Algae and Protozoa), invertebrates and fish ranges for each taxonomical group from 10 $mg.l^{-1}$ to concentrations at saturation (~ 800 $mg.l^{-1}$). No major differences in sensitivity between freshwater and marine species are observed. Fish seems to be the most susceptible group of aquatic organisms, most LC50 values ranging from 5-50 $mg.l^{-1}$. Adequate data on chronic exposure on aquatic species and ecosystems are lacking.

5.2.3. Toxicity to terrestric organisms

No reliable data are available on the toxicity to terrestrial invertebrates and higher plants. All investigations have been carried out before 1965. Toxic doses, ranging from 10-1,000 $mg.l^{-1}$, are difficult to compare or to interpret. For mammals the acute LC50 en LD50 are 15-60 $g.m^{-3}$ and 1-10 $g.kg^{-1}$ b.w. respectively. No serious effects were observed at ≥ 1600 $mg.m^{-3}$.

5.3. EFFECTS ON MATERIALS

Benzene is non-corrosive to metals.
Organic polymers such as PVC, polystyrene, acrylonitrile-butadiene-styrene (ABS), polycarbonate, are unstable in the presence of liquid benzene. Deposition of aromatic hydrocarbons on the metal surfaces of electrical contacts eventually causes malfunctioning of electronic equipment.

5.4. GLOBAL EFFECTS

In view of its degradability no concentration build-up of benzene in the atmosphere is expected to occur. Therefore and because of its low IR-absorbance benzene will exert no important global effects.

5.5. RISK EVALUATION

5.5.1. Humans

From the preceeding paragraphs it can be concluded that:

- Benzene did not induce mutations in bacteria, *Drosophila* or mammalian cells in vitro, but can cause chromosomal effects (aberrations, micronuclei or SCE) in mammalian cells both in vitro and in vivo. Cytogenetic effects in peripheral lymphocytes are observed in human subjects with benzene hemopathy but not in apparently healthy persons exposed to relatively low benzene levels.
- Animal experiments indicate that benzene is tumorigenic for rats and mice.
- Many case-reports, several case-control-studies and some cohort-studies have shown a correlation between exposure to benzene and the occurrence of leukemia, particularly acute myeloid leukemia (only at high dose levels, occupational exposure).

Based on these data benzene is considered to be carcinogenic to humans. However, the mechanism by which it produces leukemia is not known. The question arises whether or not a threshold value exist.

Extrapolation model

Arguments in favour of the existence of a threshold value are:

- Since several leukemia cases were preceded by aplastic anemia, some authors believe that aplastic anemia must preceed leukemia. As aplastic anemia likely does not occur following exposure levels below 32.5 $mg.m^{-3}$, a threshold value for the occurrence of leukemia may exist.
- Benzene itself did not induce point/gene mutations, both with and without metabolic activation. The postulated potent mutagenic intermediate benzene epoxide may be very short-lived and its presence restricted to the liver m.f.o.-system. Further the clastogenic effects observed are not transmissible and may not survive through the first mitosis. Also the occurrence of chromosome damage does not necessarily correlate with carcinogenesis. Therefore some scientists (see addendum) consider benzene as not genotoxic, implying not to use the one-hit model for risk-estimation.

Arguments against the use of a threshold value model:

- Many leukemia cases are not distinctly related to preceding severe hematological disorders. Therefore there is no evidence to support the idea of the existence of a threshold level below which no adverse health effects would be expected to occur.
- No reliable dose-response relationships from animal studies nor from epidemiological studies of the general population are available.
- Benzene and its metabolites can induce cytogenetic damage; binding of benzene to nucleic acids has been observed. Therefore there is no evidence to support the idea that benzene (or metabolites) is not genotoxic.

In the absence of firm data, in the present report risk estimation is based on an extrapolation model without a threshold value, using data from occupationally exposed workers.

Risk estimation

In table 5.1. risk estimations for benzene are given as determined by different authors and organizations, using different data bases. White et al. (1981) used data from Rinsky et al. (1981), Ott et al. (1978) and Aksoy et al. (1972). The RIVM (1984) based its calculations by means of the linear extrapolation on data of the IARC (1982b: workers exposed for their entire life for 2 hours a day to 325 $mg.m^{-3}$ had an increased risk of developing leukemia of 140-170 per 1,000 subjects) and the OECD (1983), based on EPA-data (1979: 58-90 leukemia cases would occur per 110 million persons exposed to 3-13 $\mu g.m^{-3}$ in urban areas on a year base). Based on the existing literature (table 5.1.), it may be concluded that a life-time exposure to 0.05-0.6 $\mu g.m^{-3}$ would result in one additional leukemia case per 10^6 individuals. In the present document the study of Rinsky et al. (1981) is the only epidemiological investigation including data on exposure situation that can be used for a risk estimation, indicating a life-time concentration of 0.12 $\mu g.m^{-3}$ to be inhaled to pose a risk of 1 : 10^6.

Table 5.1. *Risk estimations for benzene as determined by different authors and organizations*

Author(s)	*Risk factor (life-time propability of developing leukemia.mg.m^{-3})*	*Lifetime concentration to be inhaled to pose a risk of 1 : 10^{6} (µg.m^{-3})*	*Reference*
EPA (1984)	*0.0067*	*0.147*	*Federal Register (1984)*
Hattis and Mendez (1980)	*0.00788*	*0.127*	*OECD (1984)*
Luken and Miller (1979)	*0.00177*	*0.565*	*OECD (1984)*
White et al. (1981)	*0.0083*	*0.12 (0.06-0.24)*	*White et al. (1981)*
RIVM, based on data of IARC (1982b)	-	*0.5 - 0.6*	*VROM (1984)*
RIVM, based on data of EPA (1979)	-	*0.05- 0.35*	*VROM (1984)*

No dose-response-relations are available on oral intake of benzene and subsequent risk of leukemia. Therefore, a dose-response-relation is being derived from inhalation studies. As the mechanism by which benzene produces leukemia in humans is not known, equal amounts of benzene that are being taken up in the body, whether by oral intake or by inhalation are supposed to have the same effect.

A lifetime leukemia risk of 1:10^{6} has been calculated for continuous inhalation of 0.12 (0.05-0.6) µg.m^{-3}. Based on a daily inhalation of 12 or 20 m^{3}, this corresponds to an intake of 1.44 (0.6-7.2) and 2.4 (1-12) µg per day respectively. With an absorption rate of 50% this corresponds to a daily uptake of 0.72 (0.3-3.6) and 1.2 (0.5-6) µg respectively. Assuming 100% absorption in the gastro-intestinal tract, an oral intake of ca. 1 (0.3-6) µg a day would pose a leukemia risk of 1:10^{6}.

As a consequence of the above transposition from inhalation to oral intake, it is possible to determine the total leukemia risk from oral intake and from inhalation by adding the respective risks.
Admittedly, these values are based on conservative extrapolation methods, which could be criticized. Starting point is, however, that it cannot be excluded that prolonged exposure to low concentrations give rise to leukemia among human beings.
No data are available to evaluate the effects of exposure to peak levels of benzene during short periods of time. Since benzene is considered as carcinogenic to humans such exposures should be avoided.

5.5.2. Ecosystems

Aquatic life

Recently, different evaluation methods have been proposed to arrive at a "safe" concentration in the aquatic environment based, among others, on acute toxicity data. Based on literature data on acute, chronic single-species toxicity as well as on effects on (model)ecosystems, Slooff et al. (1986) found the following relationships:

$\text{Log NOEC}_{(\text{single species})} = -1.28 + 0.95 \log \text{lowest LC50}$ ($r = 0.89$ and an uncertainty factor (UF) of 25.6

$\text{Log NOEC}_{(\text{ecosystem})} = -0.55 + 0.81 \log \text{lowest LC50}$ ($r = 0.77$) and an UF of 85.7

Kooyman (1987) suggested to use an interspecies safety factor of a^{α}, in which $a = (1 - 1/2^{1/n})^{-1/1.6}$; n is the number of species to be protected in a certain environment (e.g. 1,000) and α is the standard deviation of the ln LC50 values (acute) experimentally determined. This factor is applied on the median value of the LC50's.
Applying the first method on the lowest LC50 value observed (5 mg.l^{-1}), the $\text{NOEC}_{(\text{single-species})}$ and the $\text{NOEC}_{(\text{ecosystem})}$ is 0.24 and 1.04 mg.l^{-1} respectively. Dividing these values by the UF's, as "safe" concentration levels 0.009 en 0.012 mg.l^{-1} can be proposed respectively. However, since benzene is considered as a non-specific acting compound (narcotic mode of action), the UF-values will be lower. Therefore the "safe" concentration will be between 0.01-1 mg.l^{-1}.

Using the second proposal, application of the safety factor (440.95) on the median LC50 (48 $mg.l^{-1}$) results in the calculated lowest LC50 among 1,000 species of 0.11 $mg.l^{-1}$. It should be noted, however, that the scatter in the toxicity data is at least partly the result of using actual or nominal concentrations for the LC50 determination. Hence, the actual value will be < 0.11 $mg.l^{-1}$. Therefore the "safe" concentration will be between 0.01-1 $mg.l^{-1}$.

Comparing the results of both extrapolation methods 0.1 $mg.l^{-1}$ is tentatively proposed as a safe level for the aquatic environment. It should be noted, however, that non-specific acting compunds at low concentrations are additive.

Short-term exposure (< 24 h) to peak levels of ca. 1 $mg.l^{-1}$ does not likely result in ecological damage.

Terrestrial life

On the basis of the very few data, no estimate of ecologically acceptable levels of benzene to terrestrial biota can be made (see also 8.2.1.).

5.5.3. Other risks

Environmental concentrations will not affect organic polymers, nor will they exert to important global effects.

6. MONITORING METHODS AND MEASUREMENT STRATEGIES

6.1. MONITORING METHODS

Monitoring method is a collective notion for sampling method, storage method, conservation, sample preparation and method of analysis to determine the substance concentration in the sample. The emphasis of the monitoring issue may vary along this chain per environmental compartment.

6.1.1. Sampling methods

- Soil

Sampling of soil material close to the surface (0-2m) can be done with a spade or hand drill. For sampling of deeper layers various drilling systems are on the market such as auger boring, wash boring, reversed circulation running system, and coring by means of augers (Van Duijvenbooden et al., 1985). Coring by means of augers is preferred, because it is usually not yet clear which soil fraction contains the most benzene (see table 6.1.).
The relatively high mobility of benzene in soil should be taken into account: an important part will be situated or below the ground water level (see section 3.2.). For this reason the sampling tube and Begemann bore are preferred to the other coring methods. Moreover these two methods allow for anaerobical sampling. Coring by means of augers has the additional advantage of rather accurate determination of the sampling depth.
For sampling the water bottom the mudsampler offers the least risk of disturbances in the composition of the grain size.
Sampling of ground water (saturated zone) is best done via teflon or other high quality plastic filters (Petty John et al., 1981; Barcelona et al., 1985).
Most boring systems are suitable for the installation of stand pipes from which the ground water can be sampled. If no working water is used during boring, three times the content of the tube should be pumped out before sampling. For boring systems using rinsing or working water, the quantity of used working water should be pumped out, followed by three times the content of the tube before sampling.

Table 6.1. Survey of flat drilling methods and their application

Coring method	*Suitability in soil*				*Suitable to a depth of (m)*	*Diameter of the hole (cm)*
	soil with stones, solid clay	*clay, peat, loam*	*sand above groundw.*	*sand below groundw.*		
Sampling tube (Ackerman bore)	*+/o*	*+++*	*++*	*+*	*75*	*4- 7*
Begemann-bore	*o*	*+++*	*++*	*+++*	*10-30*	*3- 7*
Gouge bit	*+/o*	*+++*	*0*	*0*	*5-10*	*2- 6*
Vibrating coring system	*++*	*+++*	*+++*	*+*	*3-10*	*4- 8*
Gravel bailer (v.d. Staay)	*o*	*+/o*	*o*	*+++*	*5-15*	*3-10*

Key: +++ very favourable
++ reasonable
+ moderate
o (very) bad, or not practicable

In cases of deeper boring (more than 10 m), it is recommended to excercise a waiting time of one month after pumping the hole clean. Because of the volatile character of benzene, sampling should be very careful. Turbulence is to be avoided, so that reversed circulation pumps should not be applied. Hose pumps or the auger tube (poorly impermeable soil) are preferred or the more expensive methods with a submersible pump or the pressure method developed by the Institute for Cultural technology and Water management (ICW) for depths of more than 7 m. The sampled ground water should be injected along the wall of the bottle. The glass bottles (content 1 litre) have to be filled completely and cooled down in order to avoid evaporation losses. For more detailled information one is referred to the preliminary practice guideline for sampling and analysis for soil pollution research.

- Surface water

During sampling the risk of loss should be taken into account due to the volatility of benzene. After, or if possible, during sampling, the sample should be passed into a glass bottle with a well-fitting (PTFE) cap as soon as possible. The bottle should be filled to the brim.

Benzene is not perceptibly associated with suspended matter in water (section 3.1.1.). Therefore no attention need be paid to suspended particles when sampling. Benzene should be sampled preferably below the water surface with a bailer.

- Air

Sampling of air occurs continuously or in badges; the latter method with or without the application of an enrichment method. The choice of sampling is mainly determined by the benzene concentrations to be expected. For continous measurement mass spectrometry and infra-red spectrometry are available (section 6.1.3.).

If the sample is not enriched, the benzene content is measured by the direct injection of ca 1 ml of air into a gaschromatograph (section 6-.1.3.). Enrichment of the sample occurs with the aid of adsorbents. Air is sucked for a certain time (average time) at a constant flow through a tube filled with an adsorbent. Benzene adsorbes quantitatively; the main components of air do not or hardly adsorb. Various researchers tested the formation of volatile organic compounds as a result of the action of ozone, nitrogen oxides and halogenes in air on TENAX (Vic et al., 1977; Bunch and Pellizzari, 1979; Hanson et al., 1981; Pellizzari and Krost, 1984; Pellizzari et al., 1984). Benzaldehyde, acetophenon and phenol were found as volatile main components. The installation of a filter impregnated with sodium thiosulphate eliminates the influence of the oxidating substances (Pellizzari et al., 1984). None of the volatile substances mentioned is expected to disturb the chromatographical analysis of benzene. The influence of ozone and halogen on adsorbed aromatics is little or not demonstrable (Bunch and Pellizzari, 1979; Venema et al., 1983).

For strong adsorbents desorption occurs with the aid of carbon disulphide or thermically for moderately strong adsorbents. Both desorption methods allow for a gaschromatographical analysis with the help of capillary columns.

Since the volume of the adsorbent is too large (0.1 ml to a few ml) for a direct flash injection in a capillary column, the sample is focussed again after desorption. This happens at a lowered temperature in a volume of a few μl (cryofocussing). Usually, the front part of the capillary column is used for this. For the sake of completeness it is noted that sampling methods have been described during which the measurement component condenses cryogenically or adsorbs on the wall of the sampling tube or on glass beads with which the tube is possibly filled te create a large surface (Rudolph and Jebsen, 1983; McClenny et al., 1984; Riggin, 1984).

Adsorption/thermal desorption

TENAX GC amd TENAX TA (polyphenylethers) are applied most (good thermostability; small background concentration). In the literature breakthrough volumes of 28 (Krost et al., 1982), 30 (Clark et al., 1982), 31 (Brown and Purnell, 1979) of air per of adsorbent are mentioned. In commercially available equipment (Hurrell, 1981; Dooper, 1983) tubes filled with ca 0.15 g of TENAX are used. This corresponds with sampling volumes of about 4.5 1 of air. The adsorption isotherm is straight up to the ppm-area, consequently the breakthrough volume will little depend on the benzene concentration (Brown and Purnell, 1979). Clark et al. (1982) found a difference of 20% in breakthrough volume with dry and humid air. Also the dependence on the suction rate is small (Brown and Purnell, 1979). Long sampling times are not possible in view of the low air flow belonging to it and the demonstrable migration of benzene. Several authors (Ciccioli et al., 1976; Kebbekus and Bozzelli, 1982; Krost et al., 1982; Clark et al., 1982) reported an adsorption/desorption efficiency of ca 100%. Desorption is possible from 100°C (Brown and Purnell, 1979) to a maximum of 300°C.

For the adsorption of relatively volatile substances such as benzene, polymers adsorbing more strongly of the styrene-divinyl benzene type are also applied (XAD-2; Porapak N). The breakthrough volume is indeed larger, but the thermal stability is less. With thermal desorption more background pollution occurs. The action of nitrogen oxides results in the formation of many volatile compounds (Hanson et al., 1981). The corrosion of the adsorbed compounds is not essentially worse than with TENAX (Bunch and Pellizzari, 1979).

Inorganic adsorbents which are used more or less specifically for the adsorption of benzene are: Spherosil (Ball, 1976; Kager and Rascheeff, 1979). carbon layer on glass beads (Manns and Nitz, 1981) and carbon moleculars sieve (Riggin, 1984). All have a larger affinity to benzene than the organic adsorbents.

Adsorption/solvent desorption

Adsorption on activated carbon followed by desorption using carbon disulphide has been described by NIOSH (1977). For use at the work place an air volume of ca 10 l is prescribed. The desorption is 95% or more if 100 mg of carbon are added to ca 1 ml of carbon disulphide (White et al., 1970; Meller and Miller, 1974; Colenutt and Davies, 1980; Otsen et al., 1983). The influence of moisture in the sampling air on the desorption efficiency is small (Kalab, 1982).

The adsorption isotherm of benzene on activated carbon is highly curved: the partition coefficient (C solid/C gas) for low concentrations is much higher than for high concentrations. Compared to the work place the concentrations in ambient air are low. This offers the possibility to draw hundreds of litres of air without breakthrough (Van de Wiel et al., 1981; Van de Wiel and Bos, 1984). A suction rate of a few litres per minute without breakthrough is possible at low relative humidities. At high relative humidities and high suction rates the chances on breakthrough are considerably increased (Van de Wiel and Bos, 1984). At an increase of the duration of sampling the breakthrough volume will decrease as a result of migration of benzene in the sampling tube (Saalwaechter et al., 1977). Sampling of 1 m^3 of air during two weeks is possible without the occurrence of breakthrough. The accuracy of the method can be compared with or is perhaps even better than the accuracy of the thermal desorption technique. A method based on the above mentioned data has been determined in the preliminary standard NVN 2793 (1985).

Comparison of the most common adsorption/desorption techniques

TENAX	CARBON
- small air sample, (very) short sampling duration	- large air sample, short to very long sampling duration
- one analysis per sample	- many analyses per sample
- no solvent peak	- a solvent peak
- no preparation of air sample	- blending carbon and CS, possibly shaking

Passive sampling

With passive sampling the flow of the component to be measured is determined by diffusion over a stagnant layer of air. The driving force is the concentration which is on the one hand identical to the air concentration to be measured and on the other hand it is negligible due to a layer of strongly adsorbing material (activated carbon). Comparison to other techniques within one laboratory lead to an estimate of 25% for the inaccuracy of the passive sampling technique (Purnell et al., 1981; Hickey and Bishop, 1981). In an investigation on indoor air pollution an underestimate of ca 40% was found at a concentration level of a few dozens of $\mu g.m^{-3}$ (De Bortol et al., 1984). The cause of the deviation could not be found.

Various pieces of equipment have been developed for passive sampling at the work place (Nguyen et al., 1984). The cause of the divation could not be found.

Various pieces of equipment have been developed for passive sampling at the work place (Nguyen et al., 1983; Dräger, 1985). This equipment is portable (personal samplers).

6.1.2. Methods for storage and conservation

- Soil

Samples (minimally 500 g) should be stored coolly immediately after sampling preferably in glass jars (0-4^{o}C) in view of the possible loss of benzene through volatilization. Analysis should take place as soon as possible and at least within 48 hours. If analysis is timed for a much later time (a few days to weeks), the benzene may have been transformed due to microbiological processes thus causing an underestimation of the benzene level. The way in which soil material is to be conserved in order to keep the loss of volatile organic compounds (benzene included) to a minimum is still a subject of study. Possibly immediate freezing of the soil sample offers good possibilities.

Ground water samples should be stored coolly in glass jars (0-4^{o}C); samples are to be analyzed within 48 hours. Also in this case evaporation losses during the handling of the sample and biological degradation with long storage times should be taken into account. Degradation can be limited by the addition of bactericides.

- Surface water

What has been stated for the storage of ground water samples also goes for the storage of surface water samples.

- Air

That which has been written about the storage of soil samples also goes for the storage of loaded adsorbents, as well as for internal checks.

6.1.3. Preparation of the sample and methods of analysis

- Soil

For the determination of benzene in soil material no standard and/or recommended methods are available. In principle the following methods can be used:

- the soil sample is mixed with water to a slurry and subsequently extracted with an organic solvent for benzene, or the sample is directly extracted with an organic solvent for benzene in a Soxhlett apparatus. The extracts obtained are analyzed on benzene with the aid of a gaschromatograph (GC). A disadvantage of this method is the loss of benzene during evaporation. This drawback can be overcome by the appication of an azeotropic destillation (Kozloski, 1985).
- at high concentrations (ppm-range) after mixing with water to a slurry, direct water injection into the GC is possible. Generally a large insecurity on the recovery exists with this method; the impression is that a considerable fraction of benzene still adsorbed on soil is not determined.
- static headspace technique: a sample is mixed with water and heated. After the equilibrium adjustment between the solid/liquid phase and the vapourous phase a gas sample is extracted (e.g. 0.5 ml) for injection in the GC (Hachenberg and Schmidt, 1977; Ramstad and Nestrick, 1981). The suitability of this method decreases with the increase of the organic carbon content of the soil.
- purge and trap technique: a gas (N or He) is passed through a heated sample mixed with water, and via a cooling system lead to an adsorbent. Subsequently the components bound to the adsorbent are desorbed thermally (6.1.1.) and separated and detected with the aid of a GC, possibly in combination with a mass spectrometer (MS) (Kolb et al., 1984; Luijten et al., 1983).

Since the instrumental measurement boils down to the detection of ng to μg quantities, this corresponds with a sampling quantity to be processed in the order of magnitude of 1 g of soil material. To avoid non-representative

sub-sampling a thorough mixture without large evaporation losses has to be achieved (Slingerland and Luijten, 1985).
With regard to ground water at high concentrations (ppm range) it is sufficient to use a direct water injection into the GC. At lower concentrations one should make use of a suitable organic solvent to extract the benzene from water, after which the extract is analyzed with the GC. Nowadays the static head-space or purge and trap method are often used.

- Surface water

For the determination of benzene in surface water one is referred to the methods described for ground water (section 6.1.3.); extraction, static head space and purge and trap.

- Air

The measurement methods of the last ten years have been mainly based on gaschromatography in, or not in, combination with mass spectrometry. Chromatographical methods are discontinuous. For continuous measurements in air, mass spectrometry and infra-red spectrometry are available.

"Test tubes"

For the determination of benzene in air, tubes can be bought with a measurent area between 1.5 and 1,375 $mg.m^{-3}$ (Dräger, 1985). Homologous aromatics (toluenes, xylenes etc.) cause some interference according to the operating instructions.

Infra-red spectrometry

Benzene has adsorption bands in infra-red; this adsorption can be measured with a one-channel spectrometer from 500 $\mu g.m^{-3}$. With the aid of microelectronics more components can be measured at the same time and there is a possiblility to eliminate the interference of compounds that absorb the rays at the wavelength for benzene (3.3 μm). The response time at a suction rate of 20 $l.min^{-1}$ is less than a minute.

Gaschromatography

The benzene content can be measured by directlty injecting a volume of ca 1 ml of the gaseous phase into a GC, with a packed column and a flame ionisation- (FID) or photo ionisation detector (PID) (Hester and Meyer, 1979; Leveson and Barker, 1981; Clark et al., 1984). An important criterium for determination is the selectivity. In relation to the large number of hydrocarbons in the environment the separating capacity of packed columns leaves a few things to be desired. In order to limit the interfering influence of hydrocarbons selective columns and detectors are applied.

- Columns with a highly polar stationary phase slow down the elution of polarizable substances such as benzene, so that these eluate together with highboiling hydrocarbons (Cl_1-,Cl_2-isomers). Such highboiling hydrocarbons usually occur in air in very low concentrations (Stuckey, 1969; Supelco, 1976; Hester and Meyer, 1979).
- The PID is much more sensitive to benzene than to alkanes. On a weight basis the sensitivity factor in relation to hexane, heptane, undecane and dodecane is resp. 70, 40, 7 and 6 (Langhorst, 1981; Nutmagul et al., 1983). The previously mentioned improvement of the selectivity through the application of polar columns is partly or perhaps completely undone by the increased response of lhigher hydrocarbons. This argument does not apply to the FID, which has a practically equal sensitivity to benzene and alkanes on weight basis.

The PID is not only more selective but also more sensitive than the FID. Hester and Meyer (1979) and Clark et al. (1984) mention a limit of detection for air samples of 0.9 $\mu g.m^{-3}$; from the results of Leveson and Barker (1981) a value of 0.6 $\mu g.m^{-3}$ can be deduced. The limit of detection when using a FID is at least an order of magnitude higher (Rudolph and Jebsen, 1983). The absence of auxiliary gases for the application of photo ionisation detection makes a chromatograph with PID suitable for portable applications (Leveson and Barker, 1981; Clark et al., 1984). However, with a large humidity of the air this method is not suitable for quantitative sampling (Barsky et al., 1985). Compared to IR-spectrometry and MS the GC/PID is able to measure (much) lower concentrations of benzene at less cost. On the other hand, only a momentary analysis per 10 to 15 min is possible. Therefore the direct GC-method is less suitable for the determination of the time average concentration.

The selectivity is increased when a MS is used as detector. As a check on the selective elution Rudolph and Jebson (1983) and Driscoll et al. (1978) proposed the relation between the response of various detectors (FID/PID). In general however, the capillary separation technique is used in combination with a FID, because of its uniform sensitivity of many organic matters in the same concentration area.

The inaccuracy of a chromatographical analysis for air samples including sampling, storage and desorption is estimated by Krost et al. (1982) for a GC/MS system at least 10% (standard deviation). For a GC/FID or GC/PID this might be a bit better if the influence of co-eluting substances is small. The inaccuracy for soil- and water samples is considerably larger through sampling and/or preparation of the sample.

Mass spectrometry

Quadruple mass spectrometers are often used in combination with GC. This separation technique can be abandoned for direct measurement in air, albeit with a loss of selectivity. Since the air input of the intake can be no more than a few ml per min, low analysis limits at direct suction are ruled out. For organic compounds the limits of analysis may be reduced considerably by incorporating in the inlet circuit a Llewellyn separator of SIM. The principle is based on the large difference in permeation between organic and inorganic compounds in dimethylsiloxane-polymer. With the aid of a three-stage system an enrichment of 10^6 has been obtained for some substances (Evans and Arnold, 1975; Meier, 1978). The authors mentioned a detection limit for benzene of ca 3 $\mu g.m^{-3}$ for the Multiple Ion Detection Mode.

An apparatus for the simultaneous detection of maximally 15 masses in stationary and mobile applications has been described by Ottley (1980). The response time is ca 2 seconds; the detection limit according to the producer is ca 12 $\mu g.m^{-3}$. No data are available on the selectivity. Ottley (1980) confines himself to the remark that it is better than the selectivity of infra-red equipment.

6.2. MEASUREMENT STRATEGIES

The aim of a measurement strategy is to draw up a measurement plan that is intended to provide the required results with as little effort (cost) as possible, and of which the results should have an acceptable accuracy. For this issue a distinction can be made between measurement for the determination of the levels in the environment (locally, regionally and nationally) and of the origine (source). The choice of the measurement plan and further completion of that plan is largely determined by data on sources (ch. 2), dispersion and consequent exposure levels (ch. 4) and the risks to be expected from this for man and ecosystems (ch. 5).

The achieved accuracy of the measurement results depends on the number of samples in space and time, the variablility in space and time of the value to be determined (average, percentiles) and on the measurement method.

6.2.1. Soil

With regard to soil and ground water only measurement plans on a local level are important. When drawing up a measurement plan one should take the heterogenicity of the soil into account: variation in physical-chemical soil characteristics occurs within a distance of 1 m. Preknowledge of the geological nature of soil is therefore indispensable for good sampling, because a difference in soil structure clearly influences e.g. the adsorption behaviour of benzene (Rogers et al., 1980).

A general survey of sampling strategies is given by Cochran (1977) and Obdam (1984).

As far as measurement strategies are concerned, a distinction should be made between already existing cases of soil pollution and potential (more benzene specific) situations of pollution. In the first case an investigation in stages will have to be made into the nature, quantity and location of the pollution, into the transport of pollutions in the soil and into the effects of the pollutions and of the reconstruction measures (to be taken). The measurement strategy to be pursued with regard to benzene depends therefore partly on the seriousness of the pollution with other substances, the use planned of the zone in question and the chances of dispersion. Considering this dependence no general measurement strategy can be given; each situation demands a specific measurement plan. For the underground storage tanks it is indicated in 7.1. that leakages through corrosion can be prevented practically completely by the use of improved material and maintenance. If these measures were to be taken, monitoring could be limited to the checking of benzene levels in soil and ground water in the direct vicinity of the (new) storage tanks, for which the measurement frequency and -distances should be chosen with regard to the kind of soil and ground water level. For the emissions to soil at petrol stations an AMvB (order in council) is in preparation.

6.2.2. Surface water

In view of the benzene concentrations in surface water and the levels at which ecotoxicological effects are to be expected (a difference of more than a factor 1,000) only measurements of the effluents of the most important sources may be important for the checking and determination of the accuracy of possible measures.

6.2.3. Air

Aim of the measurement is not only the determination of the levels but also of the source of the pollution in order to estimate beforehand the effectiveness of possible measures. In the following, foreign countries, industry and traffic will be considered as source categories.

National background

For the determination of the benzene concentrations on a national scale and of the contribution of foreign sources to those concentrations, a measurement network of a few locations with a spatial representativity of a few dozens of km will be sufficient. Some of the macro stations of the National Network are sufficiently representative. This is shown by experiences obtained in the AEC-project (AEC = Airpollution by Emission of Coal-fired installations) (Thijsse and Huygen, 1985). For the determination of the annual averages and the source contributions with an accuracy (standard deviation) of about 10% a few dozens of samples per measurement location per year are sufficient. In this case dispersion models for the selection of measurement days (stratification, see appendix C) and for the extrapolation of the measurement results in space and time will have to be used. To determine the contribution of traffic, typical traffic pollutants will have to be measured at the same time (lead, acetylene).

Industrial sources and traffic

Annual average concentrations in the vicinity of reasonably constant, isolated point sources can be measured with an accuracy of 10% if a few hundreds of 24-hours samples are taken and analyzed according to the Fett-Lahmann network (see appendic C). In the case of benzene the already present background level will certainly have to be taken into account.

Consequently the needed monitoring effort will possibly increase with factor 1.5. Monitoring effort will possibly increase with factor 1.5. Monitoring costs may be limited by application of passive sampling methods, after the determination of the suitability of those methods (section 6-.1.1.). The required monitoring effort will double more or less compared to the effort for a point source if various plants emit in each other's neighbourhood. A measurement location between the various emission locations is therefore essential. Fingerprinting companies or departments of companies with short-term samples and the determination of the source contributions with systematically taken 24-hours samples is in this case an alternative to be considered. For the determination of source contributions it is necessary to determine several volatile organic compounds in the samples.

In the AMvB's (orders of council), in which air quality demands for lead, CO and NO_2 will be made, methods for the checking of those demands will be described as well. In this context a project which is to come up with a measurement strategy for traffic pollutions has been started (Huygen et al., 1985). This strategy could also be used for the measurement of benzene near traffic.

The possibility to use CO, which can easily be measured continuously, as a tracer for benzene is especially noted. In this case benzene measurements are performed in parallel to the CO measurements at a limited number of locations with different traffic patterns (e.g. 10) and at different times (e.g. a total of 100). Subsequent model calculations will probably give a sufficiently complete picture of the air pollution by benzene emissions in traffic.

6.3. SUMMARY AND CONCLUSIONS

Benzene can be measured well; depending on the used analysis techniques the limits of detection are in soil material 10 $\mu g.kg.^{-1}$, in (ground-, rain-, drinking- and surface-) water 0.005 $\mu g.l^{-1}$ and in air 0.01 $\mu g.m^{-3}$. In table 6.2. a survey has been given of the enrichment methods, analysis techniques and detection limits of benzene in soil, water and air.

With regard to measurement strategies only measurement plans at a local level are important for soil and ground water, with a clear distinction between already existing cases of soil pollution and potential, more benzene specific pollution situations. The measurement strategy to be taken in the former situation partly depends on the seriousness of the pollution with other substances, the use planned for this zone and the chances on dispersion. With regard to the more specific sources (e.g. storage tanks) monitoring can be limited to checking the levels in the direct vicinity. For surface water only measurements of effluents of the most important sources matter. For air measurement plans are given for the source categories: foreign countries, traffic and industry. In all cases dispersion models are required for the measurement planning and interpretation of data.

Table 6.2. Analyseis methods and detection limits of benzene in soil, water and air (see text)

Sampling method	Quantity of sample	Sample treatment	Method of analysis	Detection limit
Soil				
< 2m: spade, hand drill > 2m: sampling tube, Begemann bore, Gats auger, vibrating coring system, gravel bailer	min. of 500 g	- mixing with water, then extraction with org. solvent	GC	*
		- direct extraction with Soxhlett appar.	GC	$200\ \mu g.kg^{-1}$
		- mixing with water, then direct water-injection	GC	*
		- static head space	GC/GC-MS	*
		- purge and trap	GC/GC-MS	$10\ \mu g.kg^{-1}$
Groundwater				
< 7m: hose pump	min. of 1 l	- direct water inj.	GC	
auger tube		- extraction with org. solvent	GC	
> 7m: ICW pressure method		- static head space	GC/GC-MS	$10\ \mu g.l^{-1}$
submersible pump		- purge and trap	GC/GC-MS/GC-FID	$0.005\ \mu g.l^{-1}$
Surface water				
min. of 1 l		- direct water inj.	GC	
		- extraction with org. solvent	GC	
		- static head space	GC/MS	$10\ \mu g.l^{-1}$
		- purge and trap	GC-MS/GC-FID	$0.005\ \mu g.l^{-1}$
Air				
- direct		---	GC/MS	$12\ \mu g.m^{-3}$
- direct		---	IR	$500\ \mu g.m^{-3}$
- direct	ca 1 ml	---	GC-FID/GC/PID	$6\ \mu g.m^{-3}/0.6\ \mu g.m^{-3}$
- TENAX	ca 4.5 ml	thermal desorption	GC-FID/GC-PID	$0.1\ \mu g.m^{-3}/0.01\ \mu g.m^{-3}$
- XAD, Porapak	ca 0.5 ml	thermal desoption	GC-ECD	
- activated carbon	ca 10 l	carbon disulphide desorption	GC-ECD	$0.1\ \mu g.m^{-3}$

* are not supposed to come up with reliable results

7. EMISSION CONTROL

In this chapter technical measures to control the emissions of benzene to soil, water and air are indicated. The cost and economic aspects of emission control will be briefly discussed in connection with, amongst others, the lead-, hydrocarbons- and the acidification issue.

7.1. CONTROL OF EMISSIONS TO SOIL

Although it appears that the scale of the pollution of soil and ground water near petrol stations is limited (section 2.2.1.), it is desirable, in view of the seriousness of the pollution, to keep paying attention to control measures. This is motivated by the measured high concentrations, the large number (34,000) of underground storage tanks at petrol stations and the location in often vulnerable areas, such as water catchment areas. Leakage, which can occur at underground storage tanks for petrol, is the result of internal and external corrosion. Internal corrosion can be limited by maintenance (regular removal of water and sludge from the tank) and by increasing the frequency of internal inspection. External corrosion can be prevented by increasing the criterium at which cathodic protection is appied, by increasing the frequency of checking the cathodic protection system and the condition of the external coating. The emission through leakage (5 tons a year) can be controlled practically completely with these measures. Through protective measures and a better inspection leakage of tanks above the ground may also be virtually stopped (4 tons a year). Recently the oil companies have decided to apply overflow securities at all tanks to be installed in the future. To prevent damage and breakage of pipelines several measures may be taken, such as restricting the crossing of pipelines, the application of connections with a double bends, the prevention of overground load and keeping the distance between tank and pump as small as possible (Riemens, 1985). In so far as a part of the spilling and leakage losses at petrol stations would still end up in the soil or sewer, this can be controlled by jointless pavement in combination with petrol separators (Riemens, 1985; De Boer and Riemens, 1985).

To reduce the emission to the soil at petrol stations an AMvB (order of council) is in preparation. Moreover the government has plans to reconstruct other stations and private storage.

The cost in relation to the more intensive checking of storage tanks will lead to a higher cost of inspection. The cost in relation to the reduction of emissions to soil and sewer are more than Dfl. 4,000 per kg of non-emitted benzene, for a maximum of 10 tons a year. For this an investment cost for the application of jointless pavement in combination with petrol separators of about Dfl. 8,000 per pump is necessary, which boils down to a maximum of 200 million guilders. On an annual basis the cost are maximally 40 million guilders. The petrol price could rise about 1 Dfl. 0.01 per litre as a result of this measure.

Insufficient data are available on the possible soil emission of benzene at the storage of car wrecks.

Soil reconstruction techniques are available for the cleaning of soil containing benzene. Thermal methods (defumigation, incineration) are available for all cases. The costs are more than Dfl. 150 per ton of soil material. Depending on the type of soil a biotechnological approach, possibly in situ, may be considered. The development in this field, however, is still in full swing.

7.2. CONTROL OF EMISSIONS TO SURFACE WATER

The most important technologies for the removal of benzene from waste water flows are:

- strips in combination with cleaning of air (adsorption). With steam strips recovery is easier; this technology is especially applicable to low discharges;
- phase separation, which should be mainly considered as pre-cleaning and recovery for benzene, but it is also applicable to discharges of petrol;
- adsorption on activated carbon
- biological purification for which, apart from strips, the biological degradation plays an important role. The degree in which benzene is released into the air is in this case mainly dependent on the concentration and on the load of the water purification plant. In a test installation with an influent concentration of 1 $mg.l^{-1}$ of benzene it appeared that benzene hardly adsorbed on sludge, for ca 1% it ended up in air and for ca 98% it was degraded (see 3.2.2.);
- extraction with oil, which can be used as fuel later on.

A planned biological purification at the chemical industry will reach a removal efficiency of 80% for benzene according to the expectations of the company. Considering the concentration (a few mg.l^{-1}) it is expected that a part of this (ca 23 tons a year) will be emitted to the air. This air emission can be partly prevented by choosing for treatment of a partial flow with a higher benzene concentration by means of steam strips. The cost of this depends on the degree of difficulty with regard to the accessibility of the source (high concentration, low flow). The investment will be Dfl. 2,000,000 at a maximum; the annual cost will be about the same. Extraction with oil is possibly more attractive but insufficient data from the actual practice are available on this. Emission reductions by the application of phase separation at storage and transport, just as the cost of this, cannot be indicated on the basis of the available data.

Table 7.1. Control of benzene emissions to surface water (tons/year)

Source	*Emission*	*Measure*	*Reduction*	*Rest-emission*	*Remarks*
Petro-chemistry	*78*	*out of operation*	*6*	*22*	
		biol. purification	*50*		*to air: 23*
		(+ steam strips)	*-*		*resp. 13 (see text)*
Remaining chemistry	*96*	*steam stripping*	*75*	*21*	*Dfl. 30.kg^{-1}*
Storage and handling	*37*	*(phase separation)*	*?*	*37*	
Tank cleaning	*19*	*(phase separation)*	*-*	*19*	
Diffuse sources	*10*	*petrol separators*	*?*	*10*	
Total	*240*		*131*	*109*	

7.3. CONTROL OF EMISSIONS TO AIR

7.3.1. Traffic

Exhaust gases

The exhaust gases of petrol engines constitute the largest source of benzene. Apart from benzene also NO_x, lead, CO, soot and other hydrocarbons are emitted into the environment via exhaust gases. Many measures to control the emissions are especially aimed at other components than benzene. Frequently an effect on the benzene emission can be expected as well. Possible control measures of the emission via the exhaust pipe are:

- Adapted design of petrol engine

  Optimization of the design of the engine and in the control of the engine (ignition and fuel metering) may lead to lower emissions of hydrocarbon. Moreover such measures entail a higher efficiency (Rijkeboer, 1985). The attainable reduction of the benzene emission remains limited.
- Exhaust purification

  This measure is in discussion at this moment. The EEC ministers concerned with the environment have reached an advanced agreement on sharpening the limit values. To comply with these requirements adaption of the engine will certainly not suffice for cars with an capacity of the engine of more than 1.4 l. After-treatment of the exhaust gases with an oxidation- or threeway catalyst will be necessary. For smaller cars (ca 50% of the European fleet of cars) one has not yet reached an agreement). In this way hydrocarbons (also benzene) are removed with a fairly high efficiency (70-80% in the test period with a cold start). The emission with catalyst technology depends on the temperature. Immediately after the start the efficiency is less than after heating up. This explains that the test results with a heated-up engine and catalyst (efficiency ca 90%) are better than can be expected in actual practice.
- Different fuel (composition)

  In this case one might think of leadless petrol. LPG, alcohol and hydrogen.

  Leadless petrol has become the policy in the meantime, while LPG has already been used for a longer time and the consumption increases. In the case of leadless petrol the knock rating of the petrol (octane content) should be kept at an acceptable value. This can be done with MTBE (methyl tertiary butyl ether, which is expected to be produced on a limited scale for economic reasons), with branched aliphatics, but especially with the increase of the aromatic content with max. 10%. It is noted that the benzene emission (traffic) is, for more than half, the result of transformation out of other higher aromatics. Also evaporation plays a part, for which there is a linear proportion with the benzene content (Tins, 1983). The benzene content can increase more strongly than the aromatic content. The present benzene content is ca 2.6 vol %.

- Different type of engine

  In principle the Stirling-engine, the electric driving, the gas turbine engine and the diesel engine are suitable. In practice the latter is much used and it has a much lower benzene emission than petrol engines (table 2.9.). Disadvantages are, however, the higher emissions of soot and of polycyclic aromatics. With respect to the engine types mentioned earlier, there are no indications that these will largely figure in the next twenty years.

  In table 7.2. the most important measures concerning the approach to petrol engines are given, as well as the effects on the emission of benzene and other components.

Table 7.2. *Reduction of the present-day emission to air of exhaust gases from petrol cars in % (Rijke boer, 1983)*

Measure	*Reduction of emission*	*Effect on the emission of other substances*
Replacement of cars built in '70-'80 with cars of '80-'85	*15-20*	*Decrease of CO and* C_xH_y*, increase of* NO_x
HCAM-engine	*20-30*	*Decrease of CO,* C_xH_y *and* NO_x
HCAM-engine with oxidation catalyst	*70-80*	*Decrease of CO (stronger than just HCAM),* C_xH_y*,* NO_x*, no Pb*
Threeway catalyst	*70-80*	*Decrease of CO,* C_xH_y*,* NO_x*, no Pb*

The mentioned measures may not be regarded separately. Often combinations are necessary in order to achieve optimum results. For example, leadless petrol is a prerequisite for the application of a catalyst. The higher benzene content in leadless petrol might influence the benzene emission. However, for the use of leadless petrol an adapted design of the engine is needed, which in its turn compensates for this effect. Another example of the interweaving of the measures and effects is the application of the three-way catalyst. In this case an optimum regulation of the oxygen content is required, which can be achieved with electronic fuel injection. The change from petrol to LPG or from petrol engine to diesel engine can be realized to a limited extent in practice. LPG is obtained during oil extraction and refinery and much more use of LPG might lead to larger amount of superfluous heavier fractions. For similar reasons the availability of diesel fuel is limited. Therefore only a restricted change is possible. Application of LPG in the centre of town (buses, taxis) might deserve recommendation. Apart from that other developments have to be taken into account. The following developments are expected with an unchanged policy by the Institute for Environmental Affairs (1983):

- an increase of car traffic with 40% between 1981 and 2000;
- a decrease of the use of petrol of cars with petrol engines resulting from an increase of LPG and diesel engines; the number of traveller kilometres with petrol cars decreases with 3%, although the use in town increases with 15%;
- a decrease of the petrol consumption with 10% to ca 4.1×10^9 litre in 2000;
- a replacement of the present day fleet of cars with new cars which will meet the requirements of the EC standards of 1985 (ECE 15-04), as a result of which the emissions of hydrocarbons will be reduced with ca 35%, which is even more than the replacement mentioned in table 7.2.

When the relative influence on the emission of hydrocarbons and of benzene are supposed to be the same, it is possible to estimate the development in the benzene emissions with exhaust gases for the future. In table 7.3. situtations have been worked out for a short term (1990) and for a bit longer term (2000) on the basis of the developments mentioned above. These situations are:

A Present situation
B Development of engines (situation around 1990)
C Development of engines and threeway catalysts and oxidation catalysts for large resp. medium-sized cars (50% in number, 60% of the emission).
D Scenario 2000 (described above, LPG and diesel doubled).
E Scenario 2000 with threeway- or oxidation catalysts for all cars.
G Scenario 2000 with an increase of only LPG and threeway- or oxidation catalysts for all cars.

Table 7.3. Benzene emissions (tons/year) in short and longer term according to various scenarios (see explanation text)

Scenario	*Total*	*Petrol cars*	*Diesel cars*	*Other traffic*
A	*7,200*	*5,700*	*840*	*635*
B	*6,100*	*4,600*	*840*	*635*
C	*3,900*	*2,400*	*840*	*635*
D	*5,900*	*3,700*	*1,540*	*635*
E	*4,100*	*1,900*	*1,540*	*635*
F	*3,100*	*900*	*1,540*	*635*
G	*2,400*	*900*	*840*	*635*

In this table the costs of the application of these measures have not been included, since these are hard to separate from the total development, also in regard to other substances. The following may serve as elucidation. At a further optimization of the HCAM-engine a fuel economization of an expected 15% can be achieved. The production of cars with similar engines will be approximately Dfl. 350 more expensive than of cars according to the EC guideline. That is to say, the purchase price will be ca Dfl. 1,000 higher. As a result of fuel economization, however, driving a car might be Dfl. 300 a year on average cheaper for the consumer (price per litre Dfl. 2.-) than in the case of ECE-1504 cars.

When the exhaust gases of the HCAM-engine are cleaned with an oxidation catalyst the economization on fuel as a result of leadless petrol will be a bit lower (ca 10%) in comparison with the ECE-1504 car. The catalyst costs about Dfl. 250 per car. The purchase price will therefore be ca Dfl. 800 higher than the price of a car according to the ECE guideline. As a result of economization on fuel driving this car will be about as expensive for the consumer.

As apposed to the fuel economization for HCAM-engines the use of leadless petrol in engines with a threeway catalyst connected to them will demand extra fuel (0-5%) in comparison with the ECE-1504 car. The application of a threeway catalyst will increase the production costs with ca Dfl. 600 per car. The purchase price will rise ca Dfl. 1,800. In this case a possible price-rise of the required noble metals at a largescale application of the threeway catalyst has not been taken into account.

A reduction of the benzene emission with a few dozens of percents at the most is possible through changing to LPG. The fuel costs are ca 35% lower when using LPG. On the other hand, the purchase price is higher so that an actual economization is only attainable at more than 15,000 kilometres a year.

Losses

Apart from the emission with exhaust gases benzene is also emitted in air with petrol as a result of replacement-, breathing- and evaporation losses (chapter 2). It is estimated that from this a total of 100 tons can be ascribed to replacement losses (bulk storage, transport, storage at petrol station and car tank). This emission can be completely controlled by vapour recycling systems.

This entails a total investment of ca 200 million guilders, or 50 million guilders annually. The cost effectiveness is ca Dfl. 500 per kg of non-emitted benzene. Consequently the petrol price might rise with 1 cent per litre maximally. Respiration losses from storage tanks above the ground are relatively small. These might be controlled by isolation and painting the tanks white. The respiration of car tanks constitutes a larger contribution. This can also be controlled by isolation. In this case also a small carbon filter can be applied per tank. The benzene emission will be reduced approximately 90 tons a year. The production costs are ca Dfl. 100 per filter. Installation included the purchase price of cars will rise ca Dfl. 300. The cost effectiveness is a good Dfl. 1,650 per kg of non-emitted benzene, for which it should be noted, that benzene is only a small fraction of the petrol vapour. In so far as losses occur by evaporation from the carburettor, these can be reduced by the application of active carbon filters. Leakage losses from pumps and valves may be reduced with 7 tons a year by an intensivation of checking and maintenance.

In table 7.4. the measures mentioned are summarized.

It should further be noted that the mentioned benzene emissions are proportional to the benzene content in the fuel. E.g. the change to leadless petrol, apart from changes in the combustion efficiency and consequently the through-flow, might lead to a larger emission. Assuming a benzene emission of 3.5% (may be higher), the emission will increase with a factor 1.35 or 85 tons a year.

Table 7.4. Emission control (in tons/year) of activities related to traffic and relating cost (in mln of guilders)

Source	*Emission*	*Measure*	*Emission reduction*	*Rest emission*	*Invest-ment*	*Annual cost*
Petrol production	*37*		*25*	*12*		
Storage and handling	*29*	*Vapour recycling system*	*25*	*4*	*200*	*50*
Tanks at the pump	*39*		*39*	*0*		
Car tank (repl.)	*44*		*44*	*0*		
Car tank (resp.)	*100*	*Activated carbon*	*90*	*10*	*1,000*	*150*
Pumps/valves etc.	*15*	*Checking/ maintenance*	*7*	*8*	-	*15*
Leakage, spilling	*12*		-	*12*	-	-
Total	*276*		*230*	*46*	*1,200*	*215*

7.3.2. Industrial sources

In an absolute sense the contribution of the industrial sources is small compared to the contribution of traffic. However, around a few point sources the contribution to the concentration of the neighbourhood may be important. That is why especially the large industrial sources have been considered. There are various technical possibilities to reduce the emission of benzene:

Purification of gaseous emissions:

- thermal combustion with a high efficiency and transformation to CO_2 and H_2O; this technology is especially suitable if the gaseous effluent contains various organic components with a high heat of combustion and in fairly high concentrations;
- catalytic combustion is well possible, but demands more knowledge on the specific composition of the exhaust gas streams;
- condensation with the possibility of recycling, which is especially suitable with low exhaust gas discharges and high concentrations;

- adsorption on activated carbon with the possibility of recycling;
- scrubbing, at which an oil compound is used as washing liquid; the oil enriched with benzene can be used elsewhere.

Process integrated measures:

- changes in process(ing) (since the consequences of such measures can usually be estimated only by the companies themselves merely the suggestions of the companies have been included);
- closed system (vapour recycling systems);
- replacement with other types of valves and pumps with a lower emission (factor);
- internal floating roofs and isolation for storage tanks;
- white-washing of tanks.

In the light of table 2.5., in which the emissions have been divided to source, the possibilities for emission control are considered in practice.

Process emissions

As a result of the putting out of use of some process installations, the benzene emissions have already been reduced with 19.6 tons a year. For some sources thermal after-burning seems to be the most suitable technology. This concerns air polluted with a mixture of hydrocarbons and sometimes carbon monoxide. Four sources, three of which still have rather large air discharges, may result in a reduction of the emission with 123 tons a year in total.

An emission reduction of 76 tons a year can be expected from a radical process change, which has allowed for the replacement of benzene as a solvent. It is true that as the result of all these changes different emissions occur, but these are lower and easier to control.

Sealing of process installations at coke and tar processing in combination with a better maintenance may lead in two situations to a reduction of the emission with approximately 29 tons a year. A cost estimate for this appeared to be not possible. In the case of a process installation with various sources of benzene there is a possibility to control the most important of these together. This demands, however, a rather complex system of inlets of the purification, in this case a combustion installation or a condensation system allowing for recovery. The benzene emission can be reduced with this with 21 tons a year.

Finally, a washing water stream can be mentioned which, together with several other streams, ends up in an industrial waste water purification plant. The first step in this plant is the stripping of the volatile compounds, which include benzene. The small saturated washing water stream can also be treated separately in a small stripper, after which benzene can be removed from the air in an adsorption/desorption unit with activated carbon. The emission to air can be reduced in this way with 10 tons a year.
The reduction of the re-emissions to air from waste water after this has been discharged by the company has been discussed in 7.2.

<u>Storage and handling of benzene</u>
Emissions are caused by the respiration of tanks, replacement- and loading losses and cleaning of tanks.
A distinction can be made between storage and handling activities at companies that produce or process benzene or benzene containing products, and the specific storage and handling companies. The latter companies cause ca 60% of the air emissions at all storage and handling activities.
In the first case it concerns a limited number of clearly demonstrable tanks. From these a considerable part has been put out of use, which has lead to a reduction of 68 tons a year. Because of the increase in processing at different locations, an extra emission of 5 tons a year has to be taken into account apart from that. A number of tanks already has specific provisions such as condensors, scrubbers, isolation or floating roofs. A reduction of the emission with 8 tons a year is still possible by providing 4 tanks with floating roofs, which have a single valve, with a double sealing.
At storage and handling companies the content of a tank depends on the supply. There are tanks with specific provisions for substances as benzene (heating), but benzene may also end up in other tanks. This hinders a straightforward approach. Bases on the approximation that ca 80% of all benzene is stored in a limited number of known tanks, the following tank directed measures (which are not so much concerned with the substance stored) can be taken:

- Isolation of tanks with poly urethane foam and aluminum coating reduces the breathing losses. This results at 39 tanks in a reduction of the emission of 25 tons a year in all.
- If moreover 43 (partly the same) tanks will be provided with an (internal) floating roof, a reduction of the benzene emission with

another 32 tons a year will be the result. According to the manufacturer this entails an investment of ca kDfl. 30 per tank.

Loading

At benzene producing or -processing companies the emission during loading can be reduced by means of a vapour recycling system with e.g. adsorption on activated carbon or a condensor. The receiving company should not be the only one to take such measures, but also, for instance, the supplying ships should be suitable for such tasks. An emission reduction of 7 tons a year has been realized in the mean time with a condensor. A further reduction with 6 tons a year can be expected, within reason, at another location with a similar system (without adjustment of ships).

A further reduction (2 tons a year) can be realized by stopping the pumping from one tank into another. Three possibilities can be mentioned in this case: (a) simply stopping the pumping, which from the point of view of conduct of business will be at the expense of the flexibility and capacity, (b) expansion of the tank farm with an extra 3 tanks, which would entails an investment of ca 1.5 million guilders and (c) the adaption of a number of the 50 to 200 tanks per storage and transit company with an internal floating roof (30 kDfl. per tank).

Vapour recovery systems can be realized with a number of tanks but they are very costly if applied on a large scale. At many tanks, ships, tank cars and wagons such provisions would be necessary. This would be a matter of an investment of a few hundreds of millions of guilders.

The putting out of use of installations for loading has lead to a reduction of 12 tons a year. By replacing valves with a rising stem by valves with a rotating stem the emission can be reduced with 25 tons a year. The cost of this included in table 7.5. refers to the surplus value of this type of valves at replacement in the future. A faster replacement will lead to much higher cost. The figures mentioned have been based on emission factors. It is further conceivable that an intensified programme of checking and maintenance of valves and pumps will lead to an extra emission reduction. In a first estimate the efficiency involved can be put at 50% which is 15 tons a year.

Cleaning

On the basis of the available data hardly anything sensible can be said on the quantitative influence of measures to reduce the emission during the cleaning of tanks.

Use of benzene and derivatives

In foudries during the process of binding of moulding sand benzene is emitted. This is a matter of large air discharges with low benzene concentrations. Measures cannot be very effective. The same goes in general for companies which use benzene.

In table 7.5. a summary has been given of the discussed measures and the effects achieved with these. The effects of the mentioned measures for the emissions per company has been illustrated in figure 7.1.

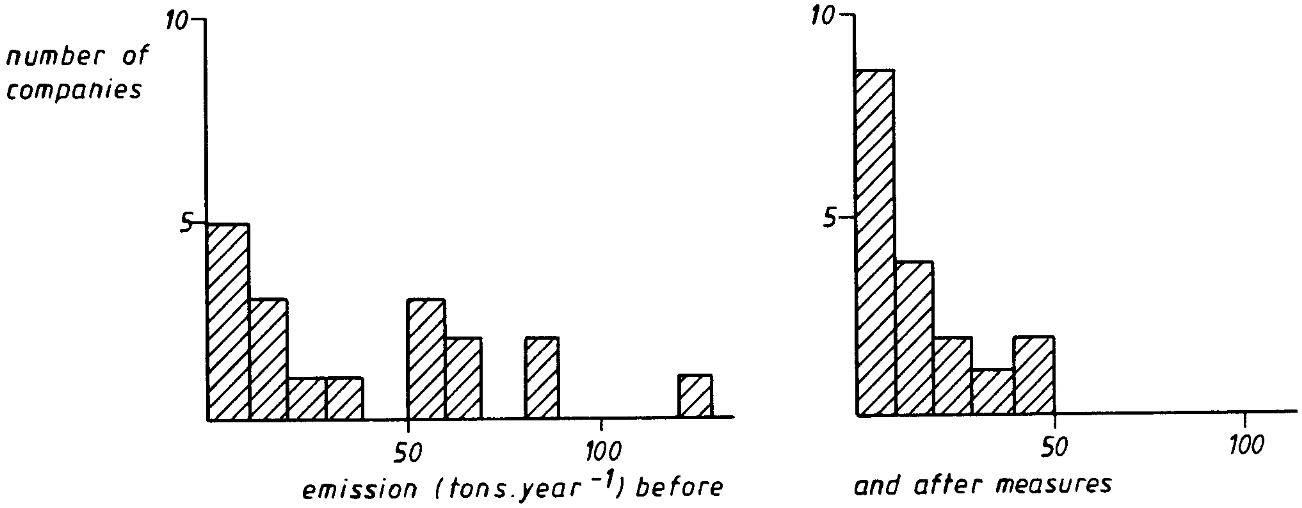


Figure 7.1. Emissions of companies (originally > 5 tons a year) before and after the proposed measures

7.4. SUMMARY AND CONCLUSIONS

Soil protection measures may prevent especially local problems with soil pollution (15 tons), of which 10 tons is emitted to air. Apart from the investment (200 million guilders) inspection costs play a part. With regard to reconstruction the costs are estimated at a good Dfl. 150 per ton of soil material.

To reduce benzene emissions to surface water a few measures at large point sources are conceivable, of which in one case the application of biological purification has already been planned. With steam strips further reductions may be attained (Dfl. 30 per kg), so that more than 100 tons still remains from the initial emission of 243 tons a year. Further reconstruction will be considerably more expensive per kg of benzene. For that matter possible emissions to air during the treatment of waste water should be reckoned with.

Practically 90% of the more than 8,300 tons of benzene which is emitted to air each year comes from traffic or traffic related activities. The emission control concerning exhaust gases (7,200 tons) cannot be regarded independently from the policy aimed at reduction of NO_x, CO, lead and other hydrocarbons. In the year 2000 a further improvement of the engine and the application of threeway- and oxidation catalysts on respectively large and medium-sized cars will lead to a rest emission of 3,900 tons a year via exhaust gases. An increase in the consuption of LPG and the application of catalysts on all cars might lead to a further reduction of the emission to 2,400 tons a year.

In general, the application of HCAM-engines would lead to a fuel economization and therefore it is cheaper in use compared to the ECE-1504 car. Application of oxidation catalysts will undo this advantage. The combination leads, for the consumer, to more or less similar costs as with the ECE-1504 car. The use of leadless petrol in engines combined with a threeway catalyst entails extra purchase and fuel costs.

During storage and handling of petrol the replacement losses can be reduced with ca 133 tons of benzene a year by vapour recovery systems at 1 or 2 guilders per kg of petrol. Breathing losses from car tanks can be treated with small active carbon filters, which is very expensive though.

In view of the developments in industry it is expected that the emission (a good 900 tons a year) will be reduced with almost 200 tons. Moreover a reduction of almost 300 tons can be achieved by measures such as afterburning, condensation and better closed equipment (average cost Dfl. 20 per kg).

Table 7.5. Survey of possible emission control techniques at industrial sources (emissions in tons of benzene a year; cost in thousands of guilders; price level 1984), petrol production and -use exluded (81 tons)

Source	*Emission*	*Control measures*	*Emission reduction*	*Investment*	*Annual cost*	*Cost per kg*
Process emissions	*390*	*Revisions in process*	*76*	-	-	-
		Thermal after combustion	*144*	*10,000*	*2,700*	*20*
		Stripping/ adsorption	*10*	*700*	*200*	*20*
		Sealing of coke chambers	*29*	*4,000*	*1,500*	*50*
Breathing- and replacement losses	*188*	*Double sealing*	*8*	*60*	*15*	*2*
		Internal floating roofs	*32*	*1,300*	*300*	*10*
		Isolation tanks	*25*	*2,000*	*100*	*15*
		Conduct of business	*3*	*1,500*	*100*	*30*
Loading	*46*	*Vapour recovery/ condensation*	*7*	-	-	-
		Vapour recovery/ condensation	*6*	*600*	*200*	*30*
Cleaning	*71*	-	-	-	-	-
Valves and pumps	*67*	*Different type of valves*	*25*	*1,250*	*340*	*15*
		Checking and maintenance	*15*	-	*350*	*25*
Other use	*63*	-	-	-	-	-
Total cost				*21,410*	*6,105*	*16*

Table 7.5., continued

Source	*Control measures*	*Emission reduction*
Process emissions	*Putting out of operation*	*20*
Breathing- and replacement losses	*Putting out of operation*	*63*
Loading	*Putting out of operation*	*2*
Valves and pumps	*Putting out of operation*	*12*
Total emission reduction		*477*

8. EVALUATION

8.1. RISKS AND GROUPS AT RISK

In order to determine the risks of the present benzene levels the concentrations in the environment (chaper 4) have to be compared to the concentration levels which are considered to be hazardous for man, (parts of) ecosystems, materials or which might give rise to problems on a global scale (chapter 5).

8.1.1. Hazards for man

Benzene is considered to be carcinogenic without any real proof for the existence of a threshold value. Because of this, exposure of man to benzene should be avoided as much as possible and should be zero in principle. Therefore a linear extrapolation model was applied and it is assumed that the risks can be added up if exposure via various exposure routes occurs simultaneously. By means of a deduction from inhalation data and information on the degree of absorption via the oral and inhalatory route, it was determined that a lifelong intake of ca 1 μg (0.3-6) a day would entail a risk of a maximum of one extra case of leukaemia per 10^6 people. It is difficult, however, to estimate the daily benzene intake. It will strongly depend on smoking habits, (possibly) the food pattern and to a less extent on car use and residential area. A stubling-block for a good evaluation is in this case the lack of data on benzene levels in the food-parcel for the Dutch situation. In table 4.6., in which a rough estimate of the daily benzene intake is given, a maximum of 185 $\mu g.day^{-1}$ via food has been assumed, which boils down to ca 37 cases a year on the total Dutch population maximally. Contributions from other sources included (but the working place is excluded) this might amount to ca 47 to 124 cases annually at a maximum (fig. 8.1., deduced from data of table 4.6.). If apart from that the insecurity of the risk estimate would be taken into account the benzene load, as is assumed, might lead to 16-744 cases of leukaemia a year for the Dutch population at the most (the part of the population which is exposed occupationally to higher benzene levels is excluded). Such a risk is higher than that which is considered to be acceptable (1 at 10^6; IMP Environment conservation 1986-1990).

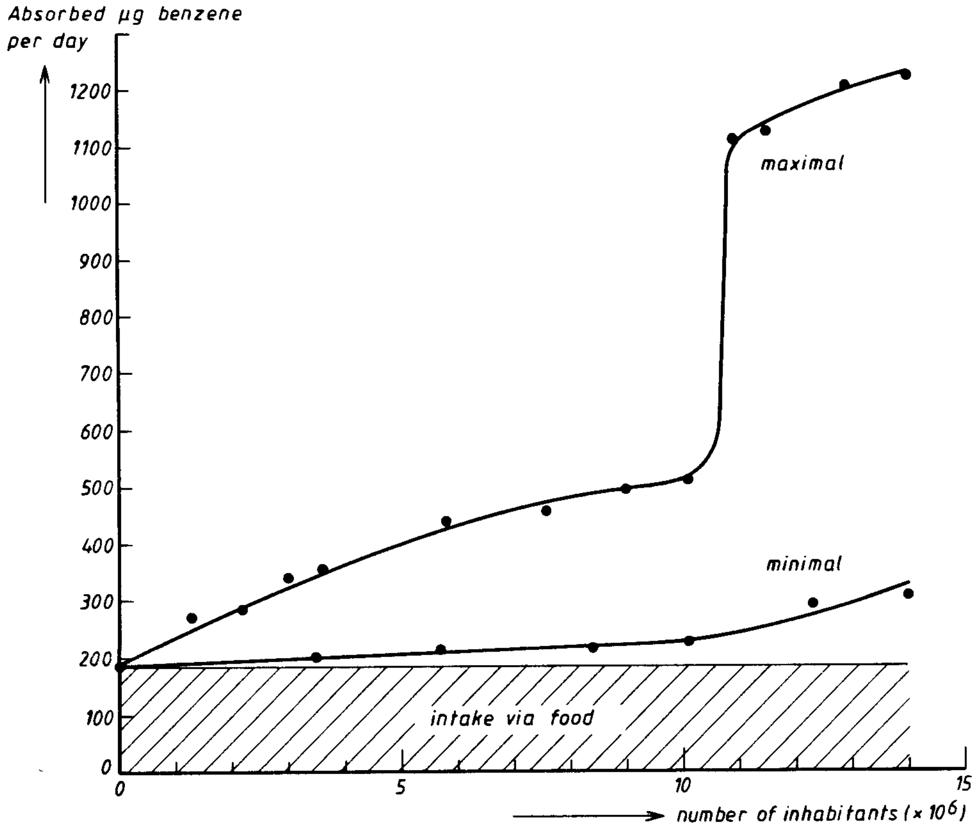


Fig. 8.1. *Distribution in the daily individually absorbed quantity of benzene by the Dutch population, occupational exposure excluded (histogram). The high increase is caused by the smoking behaviour. The absorbed quantity via food may be considerably lower*

With regard to the groups at risk a distinction should be made first between groups which are occupationally exposed to benzene and the rest of the Dutch population. Although hardly any quantitative data are available for the Dutch situation on benzene levels at the work place (professional drivers, agents, laboratory personnel, pump attendants, workers in petrochemical industry, refineries, storage and handling companies etc.) the exposure levels are expected to be considerably higher than for the rest of the Dutch population.

Of the non-occupationally exposed individuals those who expose themselves voluntarily to benzene by smoking consitute an obvious risk group; the risk may be increased by smoking with a factor 4. Average car use, living in an urban area and passive smoking during a limited time are considerably less hazardous (factor 2). It should be noted in this case that these factors will be higher as the contribution to the daily benzene load via food is less than has been supposed in table 4.6. For example, if no contribution via food would take place, the risk will be increased (maximally) with a factor of ca 2, 3 and 11 by driving a car or participation in rush hour (1 hour a day) or passive smoking (2 hours a day), living in cities and smoking (10 cigarettes and 10 hours of passive smoking a day) respectively. Possibly individuals with a certain food pattern may constitute a group at risk.

It can be deduced from table 8.1. that the environmental load with benzene (contributions via the work place, food and active and passive smoking excluded) entail a risk of a maximum of 0.3-3 cases of leukaemia a year per one million inhabitants of The Netherlands and therefore it is estimated to contribute with a maximum of 0.4-4% to the total numer of cases of leukaemia (920 cases). This risk can be compared with that which is considered to be maximally acceptable (IMP Environment conservation 1986-1990).

Table 8.1. *Maximum annual number of cases of leukaemia on the total Dutch population with the exclusion of several forms of exposure to benzene*

Exposure	*Number of cases of leukaemia in The Netherlands each year*
Total, work place excluded	*47-124*
Total, work place and food excluded	*10- 87*
Total, work place, food and smoking excluded	*4- 40*

8.1.2. Risks for ecosystems

Carcinogenic properties, such as have been determined for benzene, are evaluted differently in this report for the determination of the risk for ecosystems than for man: with reference to the ecotoxicological approach it is assumed that carcinogenicity does not play any other part than different forms of toxicity which might lead to deterioration of the structure and/or function of ecosystems. In the light of these facts, carcinogenicity is usually of minor importance.

The benzene concentrations in a fresh and salt water environment are 0.01-0.1 $\mu g.l^{-1}$ and < 0.005-0.02 $\mu g.l^{-1}$ respectively, while the level at which ecotoxicological effects are to be expected has been estimated at 100 $\mu g.l^{-1}$. Considering this difference (factor > 1,000) benzene does not consitute any danger to the aquatic environment.
With regard to terrestrial ecosystems insufficient data are available to support an ecotoxicological guideline. However, in view of the large differences between actually observed toxic concentrations for invertebrates and plants (10^4-10^6 $\mu g.l^{-1}$) and nationally occurring concentrations in ground water (< $5x10^{-3}$- $3x10^{-2}$ $\mu g.l^{-1}$) as well as between LC50 values for mammals ($1.5x10^7$- $6x10^7$ $\mu g.m^{-3}$) and nationally occurring concentrations in air (2 $\mu g.m^{-3}$), and also in view of the limited bioaccumulation capacity of benzene and the observed LD50 values for mammals (10^6- 10^7 $\mu g.kg^{-1}$), it does not seem probable that benzene in the now occurring concentration levels constitutes a danger to terrestrial ecosystems.

8.1.3. Other risks

In view of the low IR-absorption of benzene no climatological effects can be expected at the present-day concentrations in the environment, while damage to materials will be limited to corrosion of organic polymers and a possible disturbance of electric contacts at very high benzene concentrations exclusively.

8.2. FEASIBILITY OF ENVIRONMENTAL QUALITY DEMANDS

8.2.1. Comparison of existing standards and guidelines with concentration in the environment

In a number of cases the present-day environmental quality demands are not met. With regard to the soil the test values are exceeded locally. These transgressions are the result of past emissions. As far as the air is concerned the fixed interim guideline (1 $\mu g.m^{-3}$) is exceeded nationally with on average a factor of ca 2 and locally at a few locations (urban area, around sources) the interim limit value (10 $\mu g.m^{-3}$) is exceeded with a factor 4, for which road traffic constitutes the main source.

8.2.2. Autonomous developments

With regard to the soil a policy network is already available (the nuisance act licence) which is aimed at the control of leakages from storage tanks. Although at the moment there is still some delay in the granting of licences, it is expected that in 1990-1995 the emission through leakage will be controlled practically completely by control measures and checking (reduction of ca 9 tons a year). For the compartment of water a decrease of 6 tons a year has already been realized as a result of putting out of order. A further decrease is expected within the next few years of 50 tons a year by the application of biological purification at the petrochemical industry (total reduction ca 56 tons a year).

In regard to the air compartment autonomous developments are to be expected for traffic and industry. In 7.3. a number of scenarios have been worked out for road traffic, in which the situations B and C are considered to be autonomous developments, and possibly D and E as well. As a result of this the annual benzene emission could be reduced from 7,200 to ca 4,000 tons.

Starting from the expectation that no growth of any importance will occur at the industrial branches concerned, alterations in the process (76 tons) and application of vapour recovery/condensation systems (7 tons) will cause a reduction of 83 tons a year, while the putting out of use has realized a decrease of 97 tons (total reduction ca 3,380 tons a year).

Regarding the foreign emissions (see table 2.8.) a proportionally similar reduction of the emission from road traffic (possibly a bit more favourable in Germany) and the remainig constant of the other emission sources are assumed (reduction 35% in all).

On the basis of the above mentioned data the following concentrations in the Dutch environment are to be expected according to calculations with the MacKay model (see 3.6.): air 1.3 $\mu g.m^{-3}$; water $ng.l^{-1}$; soil 7 $ng.kg^{-1}$. On a local scale only road traffic is important in civilized areas. It is assumed that the 45% reduction of the benzene emission from road traffic will lead to a lowering of the concentration levels in urban areas of about 40%, making allowance for the temperature dependence of the working of catalysts.

The reduction of benzene emissions by autonomous developments is therfore still insufficient to achieve the interim guideline, but it will lead to a situation in which the interim limit value will only be exceeded very locally in urban areas (traffic). The risk in this situation is at the most

0.3-1.7 extra cases of leukaemia per year per million inhabitants through exposure to air.

8.2.3. Measures

The emissions to water can be reduced at relatively low cost with another 75 tons to 115 tons a year. If regarding road traffic scenario G (year 2000 with an increase of only LPG and threeway- or oxidation catalysts for all cars) is worked out for the EC, the emission to air would be reduced with about 1,600 tons a year in The Netherlands. These reductions would lead to a further decrease of the concentrations in the environment at a national scale: air 0.9 $\mu g.m^{-3}$, water 27 $ng.l^{-1}$and soil 6 $ng.kg^{-1}$. In an urban area the emission reduction resulting from road traffic would decrease the maximum concentration levels with a good 70%. In this situation the interim guideline will not be exceeded nationally, while locally (urban area) the interim limit value will seldom be exceeded. The risk in this case is less than 1 extra case of leukaemia per year per million inhabitants at a maximum.

Further emission control is possible, although at high cost. An emission reduction of the activities related to road traffic of 230 tons a year can be achieved, which would entail 1,200 million guilders in investments and annual costs of 215 million guilders (table 7.4.). Also at industrial sources further reduction is possible: 380 tons a year, for which the (lower) investment- and annual costs are resp. 21.5 and a good 6 million guilders (table 7.5.). If these measures were to be taken as well, the concentrations, according to model calculations, would only be reduced a little: air 0.8 $\mu g.m^{-3}$, water 27 $ng.l^{-1}$ and soil 5 $ng.kg^{-1}$. At a local scale in urban areas this emission reduction will not or hardly lead to a further decrease in the risk on the occurrence of extra cases of leukaemia resulting from benzene:

- It has been determined that due to the location of the emission and the properties of benzene about 99% of the emitted benzene ends up in air (chapters 2 and 3). Because of the important role of advective transport this means that, even if the benzene emissions at a national scale were to be reduced to zero, the benzene concentrations in ambient air at a national scale would only decrease a little (present-day average is about 2 $\mu g.m^{-3}$ with an estimated contribution from abroad of about 1.5 $\mu g.m^{-3}$).

Consequently international agreements will be necessary for an effective decrease of the national annual average.

- Since road traffic is the most important source it would be plausible to take measures especially on this issue. It should be noted, however, that there is a possibility that, if the measures were to halve the emission of road traffic, this would result in only a very limited decrease of the total incidence of leukaemia (see Clemmesen et al., 1980; Van Raalte, 1982: chapter 5).
- Consequently it is not known in how far the proposed measures will actually be effective on the annual number of cases of leukaemia. Mentioned measures are directly aimed at the reduction of the benzene concentrations in the environment and they are not explicitly aimed at lowering the exposure levels of groupsat risk, such as the occupationally exposed part of the population and that part of the population which exposes itself to high concentrations by smoking. With regard to indoor air further measures to avoid passive smoking in public areas could be pointed out too.
- Beside the mentioned measures the benzene emission from road traffic in urban areas might be reduced by the stimulation of the continous traffic flow at through roads by the installation of a wave of green traffic lights (about 50% reduction in fuel consumption) and/or the improvement of town and country planning, in which connection one may think of measures to reduce the use of cars in town centres.

8.3. RECOMMENDATIONS

- Research on sources in the indoor environment (apart from smoking).
- Research on benzene contents in food in The Netherlands.
- An investigation of the benzene concentrations in ambient air in town centres, aimed at the determination of the relation(s) between benzene levels and traffic planning.
- The emitting of benzene is only one of the many environmental aspects which are connected with road traffic. An internationally integral source oriented policy, such as this is now being developed for traffic in connection with the various issues of environmental policy, is preferred, on the basis of effectiveness (cost and benefits), to the formulation of policy measures for the reduction of emissions of the separate pollutants, such as benzene.

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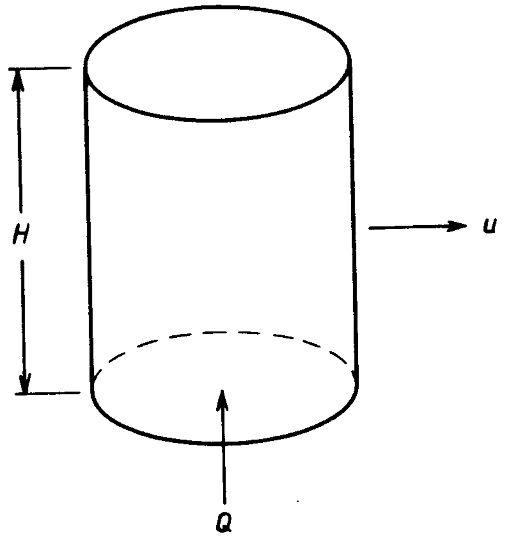
APPENDIX A

AMPLIFICATION OF CHAPTER 3.4., BEHAVIOUR IN AIR

In cases where detailed calculations of the contribution of foreign emissions to the concentrations on a national scale in The Netherlands are not useful (e.g. because the emission data are inaccurate), a simple estimate may be sufficient. A possibility is then to assume that the source distribution, dispersion and the removal of the pertinent component from the atmosphere are analogous to those of SO_2 (of which the foreign emissions and the contributions to the concentrations are known). It may further be assumed that also the concentration/emission ratio of the substance is the same as the one of SO_2. For the dispersion such an assumption seems reasonable. For the removal, however, significant differences may occur. In order to take these differences into account the following approach was adopted:
It is assumed that (see figure below) the per time unit emitted mass Q (on average over a longer period of time) is dispersed to all sides on an effective mixing height H by the average horizontal wind velocity.



The annual average concentration $\bar{c}$ (R) at a horizontal distance R of the source (R> 100 km) is estimated

$$\bar{c}\ (R) = f.\frac{Q}{2\ \pi\ R.\ u.\ \mathrm{II}}\ e^{-\alpha R} \qquad (1)$$

in which the factor $e^{-\alpha R}$ accounts for the removal of the substance from the atmosphere and f is a correction factor to be determined later. The removal constant α is related to the residence time γ of the substance in the atmosphere as follows:

$$\alpha = (u\ \gamma)^{-1} \qquad (2)$$

From the previous expressions the contribution of a homogenously emitting ring to a receptor in the centre can be calculated:

$$\bar{c} = \frac{fQ\gamma}{\pi\ (R_2^2 - R_1^2)H}\ (e^{\frac{R_1}{u\gamma}} - e^{\frac{R_2}{u\gamma}}) \qquad (3)$$

where R_1 = the inner radius of the ring
R_2= the inner radius of the ring

For $R_1/u\gamma \ll 1$ and $R_2/u\gamma \ll 1$(3) will become:

$$\bar{c} = \frac{fQ}{\pi\ u\ H\ (R_1 + R_2)} \qquad (4)$$

The value of f in (3) can be determined from the data available for SO_2. For the emissions from Western Europe R_1 and R_2 have been estimated at resp. 100 and 800 km. From Q = 800 $kg.s^{-1}$, γ = 24 hours, H = 1000 m, u = u (H/2) = 8 $m.s^{-1}$ and a concentration contribution $\bar{c}$ = 15 $\mu g.m^{-3}$ substitution in (3) gives: f = 0.8. The fact that this is close to 1 gives some confidence in the approach taken.

The assumption of similar source distribution to SO_2 is not always fulfilled. In cases where the source distance is larger or smaller, the value of R_2 should be adjusted accordingly.

APPENDIX B

ILLUMINATION OF CHAPTER 5.5., RISK EVALUATION

Example of a risk estimate

As an example the risk estimate of White et al. (1981) will be described in detail. The investigations of Rinsky et al. (1981), Ott et al. (1978) and Aksoy et al. (1972) will be used.

The authors use the formula $\beta = P_o(R-1)/x_w$, in which β equals the expected increase in the occurrence of leukaemia resulting from lifelong exposure to 1 ppm (3.26 $mg.m^{-3}$) of benzene, P_o is the chance on dying from leukaemia for the population in general which has not been exposed or hardly exposed to benzene, and R is defined as the relation of the number of observed cases of leukaemia or death through leukaemia of the labourers population to the number of expected cases and x_w is the level of exposure to benzene in the workplace, calculated as a lifelong average.
In the investigation of Rinsky et al. 7 cases of leukaemia were observed, against the expected number of 1.25, which entails R= 5.6; for acute myelogenic and monocytic leukaemias the observed and expected numbers were 6 and 0.7 respectively, which results in R=8.5. This entails, for the population as a whole, a lifelong risk of non-lymphatic leukaemia of P_o=0.0045.
With regard to the exposure levels the authors agree with the EPA that the best estimate to be made is that generally the labourers in the cohort had been exposed to benzene levels which were allowed according to the existing agreement, or to benzene levels which had been determined for the duration of the investigation in government standards. In order to determine a stretch of possible exposure levels, it was assumed that the labourers had been exposed to a bottom limit equal to half of the standard determined for working conditioms and to a top limit of twice that standard.
This resulted in the following for 1940-1971:

	Low exposure value	Intermediate value	High exposure value
Time weighted average over 36	20 ppm (65.2 $mg.m^{-3}$)	40 ppm 1) (130.4 $mg.m^{-3}$)	80 ppm 2) (260.8 $mg.m^{-3}$)

1) average of standards for working conditions
2) 1 ppm = 3.26 $mg.m^{-3}$

It is assumed that the average duration of exposure to benzene was 5, 10 and 15 years for resp. the low, intermediate and high exposure level (based on data from plastics- and rubber industry).
From this (with the intermediate value of 40 ppm) the following lifelong average level of exposure can be concluded:

$$40 \text{ ppm} \times 8/24 \text{ h.day}^{-1} \times \frac{240 \text{ working days.y.}^{-1}}{365 \text{ days.year}^{-1}} \times \frac{10 \text{ y. exp. to benzene}}{70 \text{ years per life}}$$

= 1.2. ppm as a lifelong average benzene level (= 3.9 $mg.m^{-3}$)
Thus one finds β = 0.0045 (8.3*-1)/1.25 = 0.027. For the estimated low and high levels of exposure one finds β = 0.009 and 0.109 respectively.
This formula is applied to the data of Ott et al. (1978) and those of Aksoy et al. (1972). The calculated risks vary little; for the intermediate values there is a variation of a factor smaller than 5. Nevertheless White et al. (1981) use the data of Rinsky et al. as the best estimate because, according to White et al., the research of Rinsky et al. was the best of the three, and because it gives a result that is close to the mathematical average for the three intermediate values from the three investigations.

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* Adjusted to the difference between non-lymphatic and myelogenic and monocytic leukaemia?

APPENDIX C

AMPLIFICATION OF CHAPTER 6.2., MEASUREMENT STRATEGIES

Measurement strategy is aimed at the drawing up of a monitoring plan that comes up with the required results at the lowest possible effort (cost). Moreover the results should have an acceptable accuracy. The accuracy achieved will depend on the number of samples (in space and time), the variability in space and time of the quantity to be determined (averages, percentiles) and on the way of sampling.
A suitable measure of accuracy is the confidence interval, i.e. the interval within which the probably actual value will be with an efficiency of e.g. 95%. A possible measure for the variability of the quantity to be measured is the standard deviation or the coefficient of variation deduced from this (the relative standard deviation in %). If no data (model) are available on the expected value of the quantity to be determined one will have to take random samples.

Figure C.1., taken from Stalker and Dickerson (1962), gives an example of the relation between the number of samples, the desired accuracy of the average and the variability. An ordinary, often occurring, variability (spatial or in time) corresponds with a coefficient of variation of 100%. To achieve an 80% efficiency interval about a 100 samples are needed. This is e.g. the number needed for the determination of an average large-scale level in The Netherlands. If information on the differences between the various parts of the country are desired as well, five times as many samples will soon be necessary.

Figure C.2. gives a similar relation as figure C.1., this time, however, of percentiles and a single population. The number of samples is inversely proportional to the square of the accuracy required and roughly inversely proportional to the root of the transgression chance.

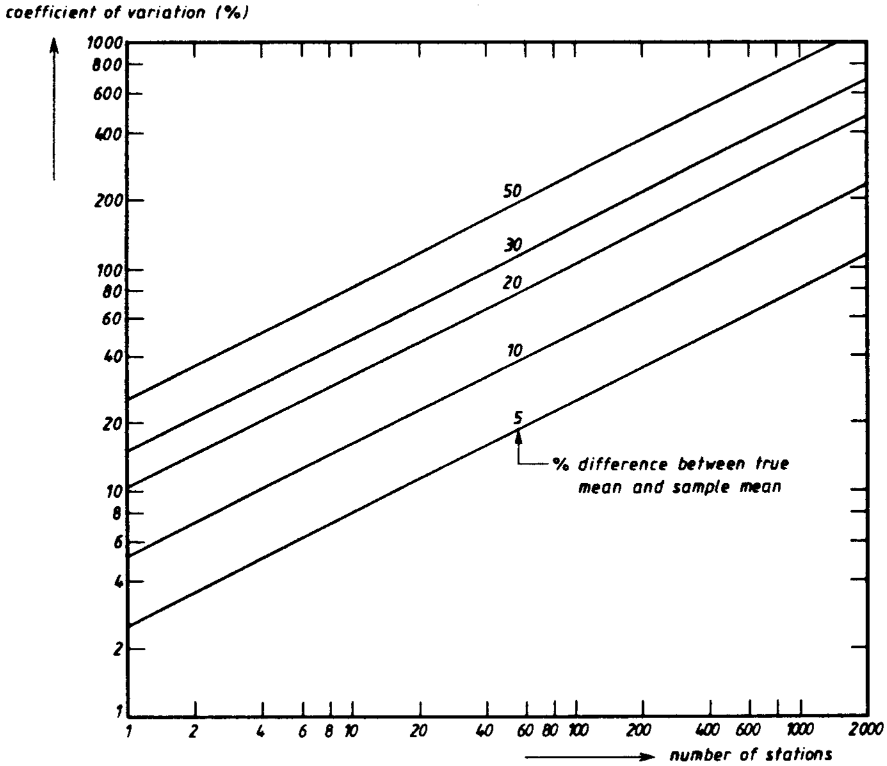

Fig. C.1. Nomogram for the estimation of the number of samples required for the determination of a monthly average within the indicated limits (Stalker and Dickerson, 1962).

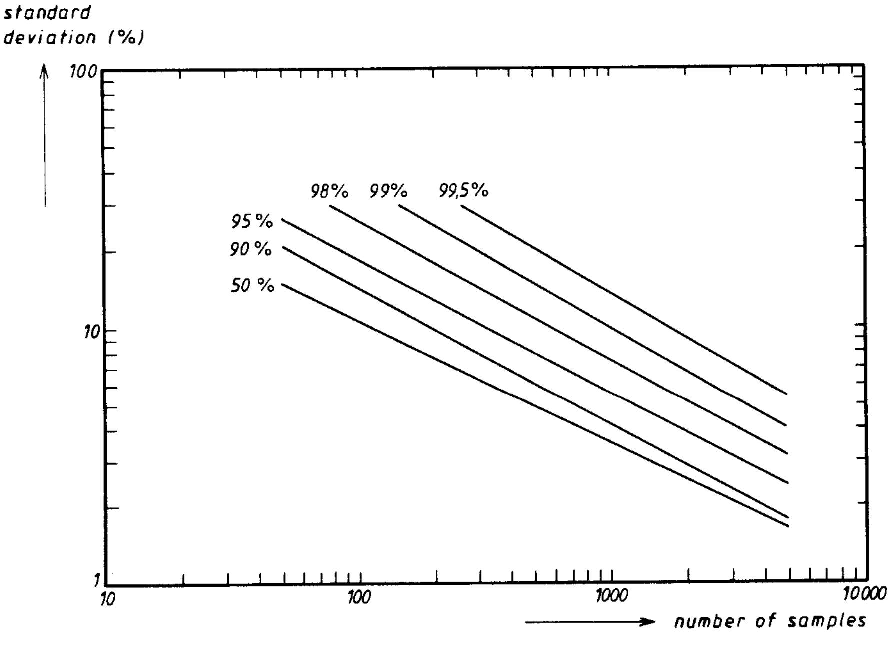

Fig. C.2. Random sampling from a log-normal distribution with a standard deviation of logarithms of 0.9. The standard deviation of the determined percentiles (vertical axis) is about half of the 96%-confidence interval.

Random sampling is not very efficient. Even with simple models a factor 2 is soon gained. The model points out the conditions (strata) in which measuring is interesting. A simple example: leeward sampling is more interesting than to windward. Such a manner of working is called stratification of the sample. A general scheme for stratified measurement has been given by the ISO (1982). This scheme contains also some directions for the (retrospective) determination of the actually achieved accuracy. Recipes for certain situations (point sources, traffic, etc.) are not given however. Such a recipe has been drawn up for point sources by Fett and Lahmann (1971).

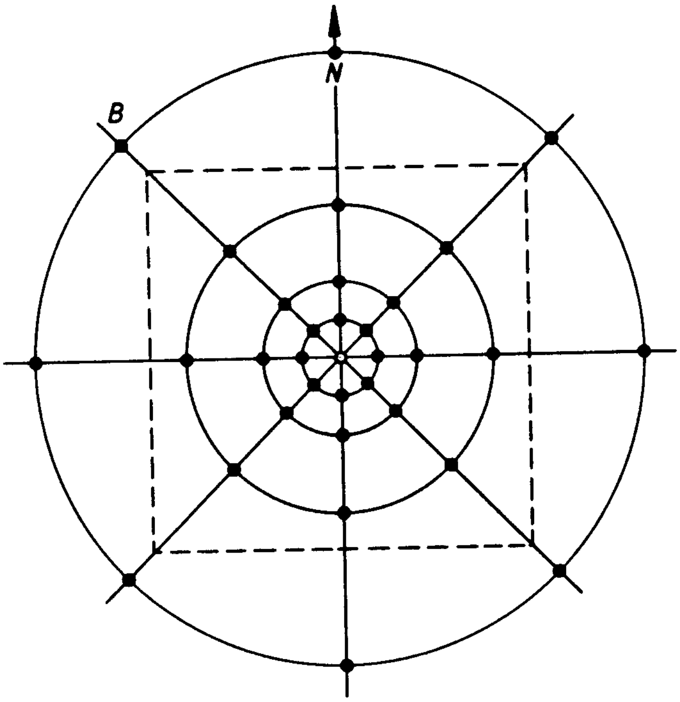

Fig C.3. Fett Lahmann network

Samples were taken at 32 locations lying on 4 concentric circles around the source. The total number of samples ranges from a hundred to a few hundreds. Their method does not include a procedure to determine the precision of the final results. However, experience shows that it works reasonable well (Dreiszigäcker et al., 1971; Fett, 1975), at least for near ground level sources.

The examples of figure C.4a and b are valid for a strongly loaded point in the vicinity of a constant source. At a non-constant source the scale has to be larger. In the variant (b) a larger accuracy of the determination of the 99- and 99.5-percentile has been achieved at the cost of the accuracy of the average and the 90-percentile.

In spite of a reasonably extensive literature (Munn, 1981) hardly any satisfactory methods which are simple in application as well are available. An important aid is simulation, with the help of measured concentrations or those calculated with a model.

Figures C.2. and C.4. have been obtained by simulation. In the latter case the National Model (COL-TNO, 1974 and 1984) and the recommendation (COL-TNO, 1982) have been used. Also the estimates given in chapter 2 are partly based on such simulations.

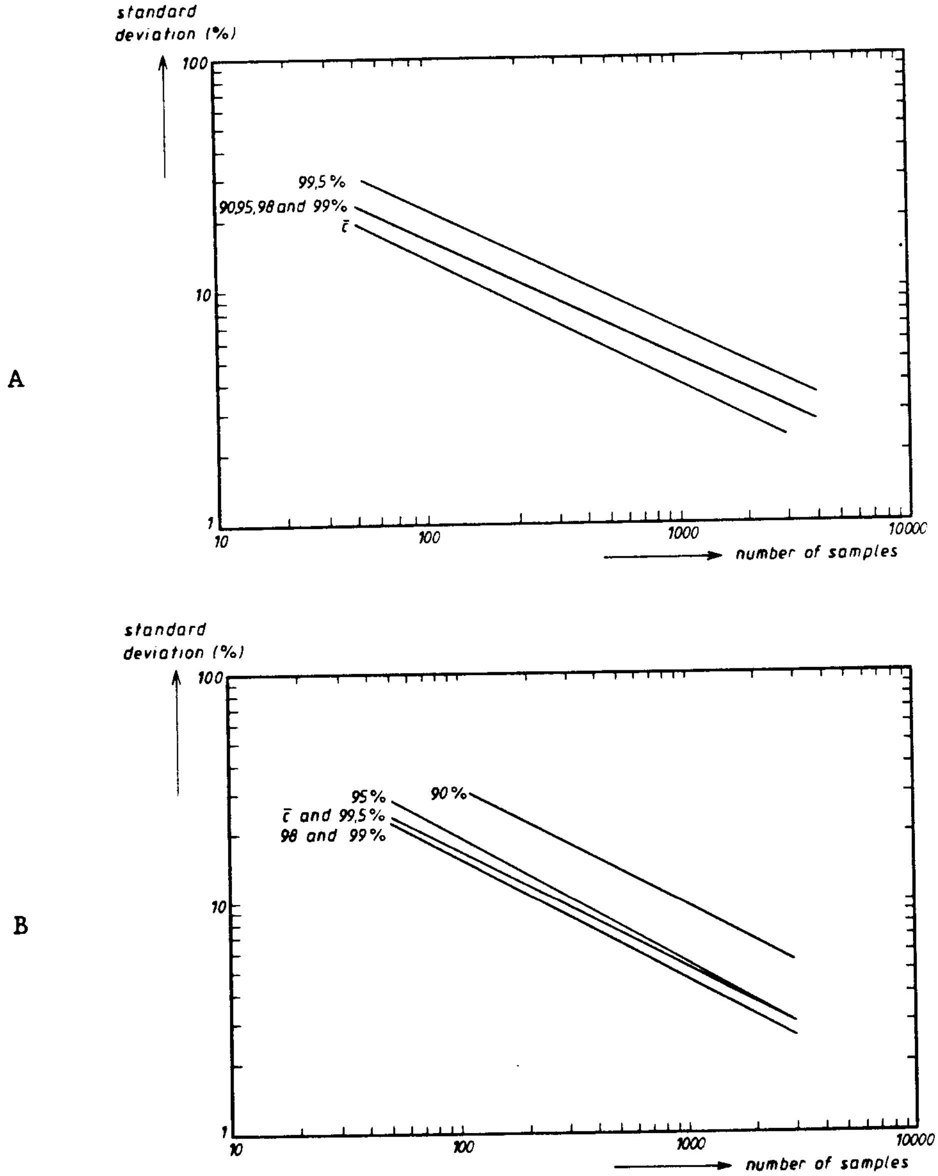

Fig. C.4. Relation between the number of samples taken according to the method of Fett-Lahmann and a variant of this and the accuracy of a number of percentiles and the average ($\bar{c}$) to be expected.

ADDENDUM INDUSTRIE*

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1. INTRODUCTION

In this addendum essential discussion items will be presented with respect to the health risk evaluation of benzene as presented in the RIVM Basisdocument Benzene (Chapter 5-Effects and Chapter 8-Evaluatie, adapted final draft of May 1986). Only essential points will be dealt with, which does not necessarily imply further agreement with the document, on items not referred to in this addendum. We also refer to domments on the RIVM "Rapport van Esch" (Ten Berge et al., 1984).

2. CONCLUSIONS

The RIVM approach to the risk evaluation for benzene is debatable on account of the following points:

2.1. Most published human studies are inadequate for quantitative risk assessment (IARC 1982, p 397).

2.2. The RIVM risk calculation is based on one study (Rinsky et al., 1981) which uses exposure data that are demonstrably incorrect.

2.3. Leukamia cases used for the estimation of risk dated from periods when recommended occupational exposure limits were high and on many occasions the actual benzene exposure was greatly in excess of these limits.

2.4. No cases of leukaemia have been related to atmospheric benzene concentrations below 100 ppm (300 mg/m^3) (OECD, 1982).

2.5. Questionable data have been applied to a mathematical model (linear extrapolation) which does not consider biochemical and biological mechanisms, defence and repair systems, or pharmacokinetics (A.I.H.C., 1985).

2.6. One-hit linear extrapolation methods are based on theoretical considerations alone, and are particularly not appropriate in the case of benzene, which is a non-mutagenic carcinogen.

2.7. The recent update of the "Rinsky Study" (Rinsky et al. 1985) concludes that the risk of benzene induced leukaemia decreases exponentially at low exposure levels and therefore the dose response relationship is not linear.

2.8. Health benefits for the population from reducing the concentration of benzene in ambient air are not measurable or otherwise demonstrable.

These arguments 2.1. - 2.8. are elucidated in sections 3 - 5.

It follows, that the RIVM risk calculation of one excess case of leukaemia among 10^6 of the general population at 0.05-0.6 $\mu g/m^3$ when exposed for a lifetime (page 62 of this basisdocument, ed.) should be considered as inadequately supported and therefore not valid.

The RIVM document Benzene does not comprise new scientific information not already covered by the Dutch Healthe Council in their "Advice with regard to hydrocarbon vapours. Recommended levels for ambient air quality" (1984).

The VNO Working Group, therefore, concurs with the conslusion and advice from the Dutch Health Council:

- that scientific data available are inadequate to recommend a maximum allowable concentration for benzene in ambient air,
- that the present level is regarded acceptable for life-time exposure of the population at large, and
- that it should be recommended not to exceed the present level.

3. EXPOSURE AND HUMAN DATA

The RIVM risk estimate of 0.05-0.6 $\mu g.m^{-3}$ stem from data reported on by OECD for the lower limit of 0.05 $\mu g.m^{-3}$ and on data used by IARC for the upper limit of 0.6 $\mu g.m^{-3}$. In essence, the risk estimate for benzene is based on limited data from the same epidemiological studies.

Several epidemiological studies provide data on occupational exposure. IARC based their relative risk estimates essentially on the retrospective study of Rinsky et al. (1981), which completes the follow-up by Infante et al. (1977). IARC used the other studies available (Ott et al., 1978; Vigliani, 1976; Aksoy 1977) to confirm that estimates based on these data are fairly consistent with that derived from the Rinsky data.

Rinsky et al. (1981) used two groups of rubber hydrochloride workers at different pliofilm plants. Group 1 consisted of 748 persons who had worked at least one day between January 1, 1940, and December 31, 1949. Group 2 consisted of 258 persons who first worked between January 1, 1950 and December 31, 1959. Vital status follow-up was conducted up to June 1975, and eight cases were found whose cause of death indicated leukaemia. Seven of these eight cases occurred in group 1 and one in group 2.

Although no measurements of benzene in air had been carried out before 1946 and only scant analytical data are available since 1946, Rinsky et al. still concluded that for the most part benzene levels generally were within the recommended standard in effect at the time.

Year	Recommended standard (Rinsky et al., 1981, p. 238)
1941	100 ppm
1947	50 ppm 8-hour time weighted average (TWA)
1948	35 ppm 8-hour TWA
1957	25 ppm 8-hour TWA

There is good reason to believe however that exposures of the Rinsky cohort often exceeded the recommended limits. In 50 Fed. Reg. 50519, col. 2 it has been reported that workers at one of the two Pliofilm plants (group 2) entered areas where benzene exposures ranged from 19 - 680 ppm, at a time when the recommended exposure limit was 35 ppm. Although respirator usage allegedly was required in such high exposure areas, it is known that, even as late as 1973-1974, workers at the same facility often did not wear respirators when they entered areas of high benzene concentrations (well above the recommended exposure standard).

Exposure information was severely limited for the Pliofilm plant at which most of the leukemia cases were found (group 1). At that facility, benzene levels ranging up to 100 ppm were measured in 1957, when the recommended exposure limit was 25 ppm (50 Fed. Reg. 50519, col. 3). At the plant for which more exposure information is available, 73 percent of the 15 measurements taken from 1946-1950 were above the permissible exposure limit in effect at the time.

In sum, average benzene exposures of the Pliofilm cohort studied by Rinsky et al., were far in excess of the exposure levels that are used in the RIVM risk calculation. Furthermore, all of the leukemia cases were found in workers first exposed to benzene prior to 1951, when a Threshold Limit

Value of 35 ppm was proposed by ACGIH (50 Fed. Reg. 50514, col. 3). No leukemia deaths have been found among cohort members first exposed after 1951.

In addition, the numerically low incidence of leukemia in the study and "the marked heterogeneity of benzene exposure in the work force studied" further complicate the effort to attribute the increased leukemia incidence to particular exposure levels (Goldstein, B.D., 1983), (CMA, 1986).

The most recent update on the "Rinsky Study" cohort (Rinsky et al., 1985) shows that the Standardized Mortality Ratio (SMR) for leukemia has declined from the earlier reported 560 to 328. It also demonstrates a marked, progressive-non-linear increase with increased exposure dose (expressed in ppm-years). From the update one can estimate that the relative risk of leukemia deaths in the first 16 years of the follow-up period (1950 - 1965) is about 12 (8 versus 0.67 expected) and in the second 16 years (1966 - 1981) about 0.5 (1 versus 2.07 expected). The factor causing leukemia death thus appears to be absent in the second period, and therefore absent in the lower exposed group of workers.

In summary

- the RIVM risk calculation is based on one study (Rinsky et al., 1981) which uses exposure data that are demonstrably incorrect.
- All of the leukemia cases in the Rinsky cohort were found in workers first exposed to benzene prior to 1951. No leukemia deaths have been found among Rinsky cohort members first exposed after 1951.
- Levels below 100 ppm, which are significantly higher than the present MAC-TGG of 10 ppm (Dutch Labour Inspectorate, 1985), could not be associated with leukaemia.

4. MODEL FOR RISK ESTIMATION

RIVM have applied a linear extrapolation model without a threshold, using data (3) from occupational exposures. Like other linear extrapolation methods, this one-hit (no threshold) model is not very plausible (NAS,1983; Claus et al., 1974), as it does not concur with biological principles. Particularly for benzene and other non-mutagens, this model is not applicable, as illustrated below.

4.1. Linear extrapolation models were developed to reflect the apparent dose-response relationship observed in radiation carcinogenesis. Chemical carcinogenesis, however, differs from radiation carcinogenesis in several significant respects, including the following:

- Chemical agents are inhibited by physical transport barriers, while radiation reaches cell nuclear material without such inhibitions.
- Many chemical agents, such as benzene, require metabolic activation; radiation does not.
- In contrast to radiation, the body has various detoxification, excretion and repair processes that operate on chemical agents. A linear model "cannot take into account repair, detoxification reactions and metabolic activation" (50 Fed. Reg. 50512, 50530, col. 3).
- The high level of energy ion radiation can break chemical bonds; by contrast, chemical reactions are modulated by the limited molecular energies available from the reactants to overcome activation energy.

Thus, radiation derived extrapolation models reflecting linearity may not be appropriate for chemical carcinogenesis even if they accurately reflect the effects of radiation. However, questions have been raised as to wheter linear models are appropriate even in the case of radiation when low doses are involved. Thus it has recently been reported that at radiation doses below 10 rad., the carcinogenic effect per rad. diminishes markedly, thus throwing into question assumptions of low dose linearity even in the case of radiation (Kohn and Fry, 1984).

4.2. In the case of benzene, there are some special reasons to suspect that a carcinogenic threshold may exist. Benzene may exert its carcinogenic effect via non-genotoxic mechanisms (EPA, 1984, XI-16). Further evidence for non-linearity in the dose-response curve for benzene-related leukemia is provided by Rinsky et al., 1985. They concluded that "the association between cumulative benzene exposure and leukemia" was explained best by a log-linear model, under which the incidence of benzene-induced leukemia decreases exposnentially between exposures of 400 and 40 ppm. years.

4.3. Also for potent mutagens there is now evidence that the one-hit linear extrapolation model is not appropriate. Russell et al., (1982 a and b) studied the dose response curve for ethyl nitroso urea-induced specific locus mutation in mouse spermatogonia, and concluded that spermatogonia have an efficient repair system, even against a potent mutagen.

4.4. Benzene did not induce mutations, both with and without metabolic activation. Whatever its mechanism of leukemogenic action, mutagenic metabolites are unlikely to be instrumental.

4.5. Benzene has been reported to cause cytogenetic effects, including aberations and other chromosomal damage in humans, and increased production of Sister Chromatid Exchanges and micronuclei in experimental animal test systems. There is as yet no direct link between these cytogenetic effects and the carcinogenic effects of Benzene (Soderman, 1982; Federal Register, 1985).

It is therefore included that:
- the one-hit linear extrapolation model is inappropriate to evaluate the risk of cancer due to exposure to chemicals;
- the one-hit linear extrapolation is particularly inappropriate to estimate the risk associated with exposure to non-mutagenic carcinogens such as benzene.
- in the case of benzene it has been demonstrated that the risk of leukemia decreases exponentially at low exposure levels and therefore the dose-response relationship is nonlinear.

5. RELEVANCE OF EXPOSURE TO BENZENE IN AMBIENT AIR FOR THE HEALTH OF THE POPULATION AT LARGE

The total leukemia mortality rate in The Netherlands is about 980 per year. Following the RIVM calculation (the basis of which we questionned in the preceeding chapters), 4 - 40 of these leukemia cases would be caused by Benzene at current concentrations in ambient air and 43 - 84 cases would be caused by uptake from food and smoking (chapter 4 and 8). The relative risk from exposure to current ambient air can then be calculated as 1.013. To detect if such a risk actually exists a follow up of 530 x 10^6 person per year is needed, or a cohort of 26 x 10^6 people would have to be observed over a period of 20 years. It is not feasible to perform such a cohort study.

This demonstrates the difficulty to observe health benefits for the general population from a reduction of the benzene concentration in ambient air. Health benefits for the population from measures to reduce current benzene concentrations in ambient in air cannot be measured or observed.

The Van Raalte paper, although perhaps not powerful enough to prove that there is no effect at all from exposure to benzene at ambient air concentrations, at least illustrates that the effect of increasing benzene concentrations in ambient air from doubling gasoline consumption had no significant effect on the number of leukemia cases in the population of a number of European countries (Van Raalte, 1982). The paper also suggest that the higher end of the RIVM risk estimate (40 cases/year) must be an over estimate. The lower end of the RIVM risk estimate (4 cases/year in the total Dutch population or a risk of 0.3 x 10^{-6}) is within the acceptable level as described in the IMP Milieubeheer 1986 - 1990. Moreover RIVM qualifies their overall risk estimation as conservative and susceptible to critique.

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