

exposure profile: gasoline

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ABSTRACT

This report details the available exposure data for gasoline and gasoline products. It provides information on estimated release rates; measured human exposure data for occupationally exposed groups, consumers and the general public; and environmental exposure data for air, water, soil and sediments. The potential for indirect exposure to gasoline hydrocarbons via the food chain is also addressed. As gasoline is a complex substance, the exposure data is presented in terms of total hydrocarbons and the main hazardous constituents, namely 1,3-butadiene, n-hexane, benzene, toluene, ethylbenzene and xylenes.

The report also gives a summary of the composition, hazards and occupational exposure limits for gasoline and lists supply and consumption figures.

KEYWORDS

gasoline, composition, occupational exposure limits, human exposure, environmental exposure.

CONTENTS		Page
PREFACE		IV
1.	INTRODUCTION	1
	1.1 DESCRIPTION	1
	1.2 USE	1
	1.3 PRODUCTION AND CONSUMPTION	1
	1.4 COMPOSITION	2
	1.4.1 Blending components	2
	1.4.2 Hazardous constituents	2
	1.4.3 Composition of gasoline vapours	2
	1.5 HAZARD IDENTIFICATION	2
	1.5.1 Physico-chemical hazards	2
	1.5.2 Health hazards	2
	1.5.3 Environmental hazards	3
	1.6 OCCUPATIONAL EXPOSURE LIMITS	3
2.	HUMAN EXPOSURE	4
	2.1 EXPOSURE ROUTES	4
	2.2 OCCUPATIONAL EXPOSURE	4
	2.2.1 Air measurements	5
	2.2.2 Biological monitoring	5
	2.2.3 Occupational exposure modelling	5
	2.3 CONSUMER EXPOSURE	5
	2.4 INDIRECT EXPOSURE OF THE GENERAL PUBLIC VIA THE ENVIRONMENT	6
	2.4.1 Routes of exposure	6
	2.4.2 Indirect exposure via inhalation of air	6
	2.4.3 Indirect exposure via the food chain	6
	2.4.4 Environmental modelling	7
3.	ENVIRONMENTAL EXPOSURE	8
	3.1 EXPOSURE ROUTES	8
	3.2 ATMOSPHERIC EXPOSURE	9
	3.3 AQUATIC EXPOSURE	10
	3.4 SOIL AND GROUND WATER EXPOSURE	10
	3.5 MAJOR SPILLAGES	11
4.	REFERENCES	13
	TABLES	18
	APPENDIX	39

PREFACE

The risk assessment of chemical substances is based on a comparison of the potential adverse effects of a substance with the known or foreseeable exposure for man and the environment. Identification of the intrinsic hazards of a substance together with data on the extent to which man and the environment are exposed are therefore two key sets of information in the risk assessment process.

Hazard assessment procedures are well developed and are based on the principles laid down in the Dangerous Substances Directive. For petroleum substances, comprehensive information on the human and environmental toxicological characteristics has been extensively reviewed and is published in CONCAWE Report 95/59 and the CONCAWE Product Dossiers.

However, the collection of the corresponding exposure data for petroleum substances is less well advanced and, in consequence, a CONCAWE Task Force has been established to collate and review the available information. The objective of the work has been to identify exposed populations for each of the main petroleum substance groups and to quantify the level of exposure to which they are subjected. This has been done by assessing available data from member companies and from the published literature, and documenting it in the form of Exposure Profiles for the main petroleum substance groups. These Profiles will eventually form companion documents to the Product Dossiers and will be available for use by member companies and by the risk assessors.

Generally, there are three groups of persons that potentially may be exposed to petroleum substances, namely, workers through exposure in the work place (occupational exposure), consumers during the normal use of the substance, and the general population through exposure to contaminated air, soil, water and via the food chain. For environmental risk assessment, the potential exposure of aquatic systems, sediments, soil and air are considered.

Exposure data can be obtained by field measurements and may include sampling of air concentrations in the breathing zone for workers and consumers, biological monitoring where such techniques are available, and the measuring of concentrations in soil, air and water. However, for complex hydrocarbon mixtures such as petroleum substances, difficulties arise because on release into the environment, the individual components of the mixture have different fate and distribution patterns. Although monitoring techniques can measure total hydrocarbons and specific individual hydrocarbons, attributing measured concentrations to a particular petroleum substance is rarely possible.

To overcome some of these monitoring difficulties and to compensate for the lack of measured data generally, the Risk Assessment Regulation (1488/94) allows the use of computer modelling techniques for the estimation of exposure. Such models have been referenced in the text as appropriate. Nevertheless, some measured values are needed to validate the model predictions and to assess the relevance of the predicted output to actual situations. The collection of meaningful exposure data is therefore an essential prerequisite for the risk assessment of petroleum substances.

Each Exposure Profile report is being structured along the following lines:

- Substance description: use, production and consumption figures, composition, summary of hazard characteristics, applicable occupational exposure limits.
- Human exposure
 - Exposure routes
 - Occupational exposure
 - Consumer exposure
 - Indirect exposure of the General Public via the environment.
- Environmental exposure
 - Exposure routes
 - Atmospheric exposure
 - Aquatic exposure, including sediments
 - Soil and ground water exposure
 - Major spillages.

1. INTRODUCTION

This Exposure Profile is a review of the available published data on exposures to gasoline, a product that is widely used as a fuel for automotive and aviation purposes. The profile considers human exposure data in respect of workers and the consumer, plus indirect exposure to the general public via the food chain and through inhalation of air. Environmental exposure covers releases to air, water, soil and ground water. Major accidental spills are also noted.

1.1. DESCRIPTION

Gasolines are complex mixtures of volatile hydrocarbons distilling between approximately 30°C and 220°C and consisting of compounds predominantly in the C4 to C12 range. They are produced by blending appropriate refinery streams to meet the required performance and legally imposed specifications. Composition may vary widely depending on refining facilities available, crude source and total petroleum product demand.¹

In addition, marketed gasolines may also contain blending components of non-petroleum origin, including oxygenates (mainly ethers and alcohols) used as high octane blending components and additives to enhance performance features. Lead alkyls are also used to meet octane requirements, but an increasing proportion of gasoline is now unleaded. This exposure profile does not cover specifically the effects of these additional non-petroleum components, although some of the exposure data quoted will relate to gasolines containing such constituents.

1.2. USE

The sole use of gasoline is as a fuel for spark-ignition, internal combustion engines, mainly for domestic and industrial automotive applications. A small quantity is also used for aviation purposes.

Known misuses of gasoline include use as a solvent, a cleaning agent and gasoline sniffing (solvent abuse). Exposures from misuse are not addressed in this report.

1.3. PRODUCTION AND CONSUMPTION

Figures for the production and consumption of motor gasoline and aviation gasoline in the fifteen Member States of the European Union are given in **Tables 1.1 and 1.2** respectively.²

In these tables, refinery output excludes refinery losses; imports and exports relate to the quantities of the product crossing the European Union boundaries; and total consumption is the net observed inland consumption. Stock levels refer to the quantity of the product held in storage at the end of the relevant year. (Due to statistical differences in reporting and internal transfers between countries, the theoretical and reported total consumption figures are not identical).

1.4. COMPOSITION

1.4.1. Blending components

The major component streams used in the blending of automotive and aviation gasoline are shown in **Table 1.3**. A listing of the relevant EINECS entries for gasoline and gasoline components is given in CONCAWE Report 95/59.³

1.4.2. Hazardous constituents

Gasoline contains a number of chemical compounds which are classified as hazardous under the EU Dangerous Substances Directive.⁴ These include 1,3-butadiene, n-hexane, benzene, toluene, xylene and ethylbenzene. **Table 1.4** shows concentrations of these components in 48 automotive German gasolines as reported in a recent study by DGMK.⁵

1.4.3. Composition of gasoline vapours

The composition of gasoline vapours is significantly different from that of the bulk liquid on account of the differing vapour pressures of the individual components. For example, aromatic hydrocarbons make up a significant proportion of the gasoline liquid, but their presence in the vapour phase is far less due to the relatively low vapour pressure of aromatics compared with lower molecular weight components. In a study reported by CONCAWE, the vapours from several European gasolines were found to contain on average 90% by volume of hydrocarbons C₅ and below, compared with 32% by volume in the liquid phase: for the C₆ - C₈ aromatics the corresponding figures were about 2% by volume in the vapour and 27% by volume in the liquid.⁶

1.5. HAZARD IDENTIFICATION

The principal hazards associated with gasoline are flammability, chemical pneumonitis following aspiration, carcinogenicity, skin irritation, and effects on the central nervous system caused by inhalation of vapour. Gasoline is also considered Dangerous for the Environment.³

1.5.1. Physico-chemical hazards

Gasoline is classified as extremely flammable and the vapours form explosive mixtures with air in the range of approximately 1 to 6% (V/V). The vapours are heavier than air and may travel substantial distances. Hazardous concentrations can build up in confined spaces, drains and other poorly ventilated areas.¹

1.5.2. Health hazards

The European Commission has classified gasoline as a Category 2 carcinogen, unless the benzene content is less than 0.1% (m/m).⁷ This may be the case for some products, notably aviation gasolines, but typically, benzene concentrations for motor gasolines are in the range 1 to 3% (m/m). The legal maximum for the benzene content of gasoline in the European Union is 5% (V/V). Gasoline may also contain 1,3-butadiene, but concentrations are generally below 0.1% (m/m).

The International Agency for Research on Cancer (IARC) has placed gasoline in Group 2B, possibly carcinogenic to humans, based on limited animal evidence and the presence of benzene and 1,3-butadiene. IARC considered that evidence for carcinogenicity in humans was limited.⁸

If gasoline is accidentally ingested, small quantities may be aspirated into the lungs either directly or during any subsequent vomiting. This can lead to intense irritation of lung tissues and chemically induced pneumonitis which can be fatal.¹

In contact with the skin, gasoline is an irritant and repeated and/or long-term exposure may cause defatting of the skin that can ultimately lead to dermatitis. It is not considered an eye irritant, nor skin sensitiser. In addition, gasoline is not acutely toxic by single dose applications by any route of exposure.¹

Gasoline is a highly volatile material and may produce significant concentrations of vapour at ambient temperature that are hazardous from both the human health and safety points of view. Gasoline vapours may be irritant to the eyes and the upper respiratory tract, and inhalation of high concentrations may give rise to narcotic effects such as headache, dizziness, nausea, impairment of judgement and, in severe cases, loss of consciousness. Short term exposures by consumers such as experienced during refuelling and tank filling are unlikely to give rise to any adverse effects.¹

1.5.3. Environmental hazards

Acute aquatic toxicity values for gasolines are in the range 1-100 mg/l and the data indicate that gasoline should be classified Dangerous for the Environment. However, the components of gasoline that cause aquatic toxicity are highly volatile, and hence rapidly lost from the aquatic environment. Furthermore, although gasolines may not meet the EU criteria for ready biodegradability, there is evidence that many of the individual components of gasoline are readily biodegraded.

Also, gasoline has a potential to bioaccumulate based on consideration of the octanol/water partition coefficients (K_{ow}) for gasoline components; typically the components of gasoline have log K_{ow} values in the range of 3 to greater than 6. However, these components are generally both volatile (and, therefore, rapidly lost from the aquatic environment) and well metabolised in a wide range of organisms. In practice, there is little evidence of bioaccumulation of gasoline components in environmental species.

1.6. OCCUPATIONAL EXPOSURE LIMITS

Occupational exposure limits for gasoline have been set by the American Conference of Governmental Industrial Hygienists (ACGIH),⁹ and by the Dutch¹⁰ and Swedish¹¹ authorities. These limits are listed in **Table 1.5**.

In addition, exposure limits have been set for a number of hazardous gasoline components including 1,3-butadiene, n-hexane, benzene, toluene, xylene and ethylbenzene. Values set by the ACGIH and a number of European authorities are listed in **Table 1.6**.

2. HUMAN EXPOSURE

2.1. EXPOSURE ROUTES

By far the most significant route of exposure for gasolines is via inhalation, because of its high vapour pressure. Although exposure via ingestion is possible in theory, it is usually the result of misuse e.g. storage in inappropriate containers leading to accidental ingestion, or siphoning gasoline by mouth.

There are no data indicating that systemic effects result from dermal exposure to gasoline. However, it is known that gasoline will cause local effects by degreasing the skin, leading to dermatitis after repeated or prolonged exposure. These effects can be minimised by the use of appropriate skin protection and good hygiene practices.¹

Regarding exposure to gasoline vapours, analysis of the atmospheres inhaled by refinery and distribution workers shows clearly that exposures are predominantly to the lower carbon number, non-aromatic components.⁶

A number of factors can be expected to cause variations in the composition of vapours to which humans are exposed, such as the variability of gasoline composition, the proximity of the exposed person to the source of the vapour, the degree of ventilation, the time periods over which vaporisation and exposures occur, ambient weather conditions and simultaneous exposures to other petroleum products, process streams or solvents.

2.2. OCCUPATIONAL EXPOSURE

The manufacture and distribution of gasoline involves a variety of work activities and types of job ranging from production and ancillary operations within the refinery and distribution depots, e.g. tank dipping, pump repairs, filter cleaning, to loading of ships, railcars and road tankers, delivery to service stations and, finally, attendant or self-service filling of customers' vehicles.

A broad description of job groups and associated tasks involving potential exposure for workers is given in **Table 2.1a**. The information is divided by type of location/activity and covers refinery, distribution, service station and airport workplace situations. As well as providing an overview of the type of tasks carried out, this table also provides an indication of the control measures that are usually employed. Additionally, further information on task details is given in **Appendix 1** to clarify the nature of the exposure, where this is considered appropriate.

Because of the high volatility of some components, gasoline is manufactured and distributed as far as is practicable in enclosed systems in order to minimise evaporation which could lead to safety hazards, environmental contamination and product losses. Such systems reduce the possibilities of exposures to gasoline vapour.

2.2.1. Air measurements

Measured exposure data for the job groups identified in **Table 2.1a** have been collated and presented as follows:

Table 2.1b Summary of personal arithmetic mean, 8-hour time-weighted average exposures,

Table 2.1c Summary of personal arithmetic mean short-term exposures.

The exposure data are presented in terms of total hydrocarbons and the following hydrocarbon components where such data are available: 1,3-butadiene, n-hexane, benzene, toluene, ethyl benzene and xylenes. In addition to the arithmetic mean, the minimum and maximum exposure levels, number of samples and sampling time (if other than 8 hours) are provided, where available.

Job types for which the highest exposures were measured include: top loading of road and rail cars and barrel filling. In these cases, exposures are being significantly reduced by the introduction of engineering control measures such as vapour recovery and local exhaust ventilation respectively.

2.2.2. Biological monitoring

Biological monitoring techniques are available for evaluating exposure to certain components of gasoline, including xylenes, toluene and benzene.

The analytical techniques for the measurement of benzene exposure comprise of the determination of benzene in blood,¹² phenol in urine and, more recently, S-phenylmercapturic acid (S-PMA) and trans-muconic acid (*tt*-MA) in urine. A comparison between phenol, S-PMA and *tt*-MA methods and further relevant references are given by Boogaard and van Sittert.¹³

In respect of the determination of phenol in urine, this has proved an unsuitable parameter for estimating benzene exposure at levels lower than 32 mg/m³. This conclusion was reported in DGMK Report 477¹⁴ which reviewed phenol in urine and benzene in blood levels for workers in a variety of jobs involving exposure to gasoline. Recently, the measurement of phenol in urine has been replaced by the more sensitive S-PMA and *tt*-MA techniques, with S-PMA the more reliable biological marker for benzene exposures down to 1 mg/m³ (8h time-weighted average). It should be noted that ACGIH has announced its intention to support the S-PMA technique as the recommended Biological Exposure Index for benzene.⁹

2.2.3. Occupational exposure modelling

No data derived by modelling has been included in this review.

2.3. CONSUMER EXPOSURE

Consumer exposure to gasoline occurs during the dispensing of gasoline into vehicles, small storage containers or gasoline-powered equipment such as lawn mowers and chain saws. In addition, gasoline is known to be used as a degreasant in workshops and at home by DIY enthusiasts. However, within the oil industry, this use of gasoline is considered to be a misuse and is not condoned.

Exposure to ambient levels of gasoline vapour may also occur whilst travelling in gasoline-engined vehicles or using gasoline-powered equipment. The exposure in these cases results from vapour emissions from the storage tanks or from spillages.

A summary of consumer activities involving potential exposure to gasoline and comments on control measures are given in **Table 2.2.a**. Exposure data for consumers during the filling of motor vehicle tanks and for drivers and passengers in vehicles are given in **Table 2.2.b**. In general, activities involving consumer exposure are usually infrequent and of short duration.

Exposures experienced by service station attendants working an 8-hour shift refuelling vehicles are given **Table 2.1c**, (item 3.1).

2.4. INDIRECT EXPOSURE OF THE GENERAL PUBLIC VIA THE ENVIRONMENT

2.4.1. Routes of exposure

Indirect exposure of the general public to gasoline and gasoline components via the environment may occur through inhalation of vapours in air, contamination of water, and through accumulation in the food chain. Gasoline vapours enter the environment from refining, distribution and from vehicles, particularly automobiles. Contamination of water and possible accumulation in the food chain may arise from spills and leaking storage tanks. An overview of all indirect exposure routes is given in **Table 2.3a**.

2.4.2. Indirect exposure via inhalation of air

Atmospheric exposure is the main route whereby the general public encounters gasoline components. Typical measured environmental concentrations of common hydrocarbon constituents of gasoline are reviewed in **Section 3.2**. The data covers rural and urban locations and the boundaries of service stations and distribution terminals.

2.4.3. Indirect exposure via the food chain

The indirect exposure of man to gasoline and gasoline components due to bioaccumulation in the food-chain is theoretically possible based on consideration of the octanol/water partition coefficients (K_{ow}) for gasoline components. Nearly all of the hydrocarbons found in gasoline have $\log K_{ow}$ values of above 3 and this suggests a potential to bioaccumulate and consequently biomagnify in food-chains.

In practice, most of the hydrocarbons found in gasoline are known to be metabolised by both bacteria and by higher organisms. This metabolism, together with the volatility of these compounds, makes it unlikely that they will bioaccumulate to any significant extent. There is no evidence of some of the higher K_{ow} components of gasoline, such as octane ($\log K_{ow} = 5.0$), accumulating in foodstuffs such as fish or plants including vegetables. Based on the contribution of foodstuffs to human exposure to benzene, it may be concluded that such routes represent a very minor pathway for human exposure to gasoline components.¹⁵

2.4.4. Environmental modelling

Computer modelling is an alternative approach that can be used to establish the concentration of gasoline components in the environment and consequent indirect exposure of the general population. A suitable method for modelling complex substances based on the Hydrocarbon Block Method is described in **Section 3**.

3. ENVIRONMENTAL EXPOSURE

Existing data on measured gasoline hydrocarbons in air, water and soil are reviewed in **Sections 3.2, 3.3 and 3.4**. However, these data should be used with caution for a number of reasons. In the main, the data are not derived from comprehensive monitoring programmes and, as a result, they may not be typical. Furthermore, the relationship of the sampling point to local or regional emission sources is often not reported. When the raw data are examined, there are frequently many samples with specific hydrocarbons present at concentrations below their detection limit. Such values are not always taken into account when mean concentrations are calculated, resulting in erroneously high figures. In other cases, insufficient information is included in publications to allow evaluation of the significance of results: often only the range or mean values are reported and information on the frequency, duration and number of samples collected are not included.

When a complex substance such as gasoline is released into the environment, the hydrocarbon constituents separate and distribute in varying amounts to the different environmental compartments according to their individual physico-chemical properties. Thus, the measurement of individual hydrocarbon components in the environment cannot be used directly to predict the environmental concentration of gasoline itself. Neither can this be predicted from measurement of total hydrocarbons, since in each environmental compartment, there are many sources of hydrocarbons, both man-made and natural.

However, predicted environmental concentrations (PEC) for complex hydrocarbon mixtures like gasoline in each environmental compartment (air, surface water, sediment, soil and ground water) can be estimated by computer based, multi-media fate modelling and such techniques have been proposed for use in risk assessment. The Hydrocarbon Block Method developed by the CONCAWE Ecology Group¹⁶ has been adopted by the European Commission and details of its use are included in Appendix IX of the Technical Guidance Document on risk assessment¹⁷ and Version 2.0 of the USES model.¹⁸ The process requires extensive data input including compositional data to allow identification of 'blocks' of hydrocarbons with similar physico-chemical properties, environmental fate and effects. Information on the release rates of individual blocks is also required.

3.1. EXPOSURE ROUTES

The wide use of gasoline as an automotive fuel results in numerous releases to the environment in the form of non-point source emissions from vehicles during re-fuelling and from within the distribution network. Gasoline is a volatile material and emissions are almost exclusively to air through evaporation. However, evaporative emissions from automobiles are decreasing due to the continuing introduction by manufacturers of fuel systems which contain vapours more tightly. Evaporative losses throughout the distribution system are also being reduced.¹⁹

Significant concentrations of gasoline hydrocarbons are also found in vehicle exhaust emissions. Some of the hydrocarbons pass unchanged through the engine, but others are synthesised in the combustion zone. Where catalytic converters are fitted to vehicles, hydrocarbon concentrations in exhaust emissions are reduced.

Regarding the emission of gasoline to surface waters, the volatility of gasoline and the need to store it in closed tanks limits the amount emitted by this route. Run-off of

liquid gasoline from roadways into streams as a result of spillages and leaks is not a major issue since the high vapour pressure of gasoline will result in rapid evaporation. However, ground water contamination may result from large terrestrial gasoline spills and from leaking underground storage tanks. This subject is dealt with in **Section 3.4**.

Spills from ships, barges, pipelines and storage tanks used in the transport and distribution system for gasoline may also result in the contamination of surface waters. A number of such incidents have been reported and examples are included in **Section 3.5**. However, such accidental releases are rare occurrences and give rise to infrequent high, but localised exposures. As such, they are outside the intent of the risk assessment process.¹⁷

Another source of release of gasoline components to water comes from oil refineries during the manufacture, storage and loading of gasoline. This topic is covered in **Section 3.3** and is the only scenario where a point source of gasoline emissions to water is likely. However, refineries produce a variety of petroleum products so that it is not possible to attribute total hydrocarbons in refinery effluents to a specific product such as gasoline.

As discussed in **Section 2.4** on indirect human exposure, the physical and biological properties of the hydrocarbons found in gasoline make it unlikely that they will accumulate through the food-chain.

The disposal of gasoline is not generally an issue of environmental concern.

3.2. ATMOSPHERIC EXPOSURE

A summary of the volatile organic compound (VOC) emissions for Western Europe in 1983 has been reported by CONCAWE.^{20, 21} The major emissions of gasoline vapours to the environment were estimated to be evaporation directly from vehicles and during refuelling (983 kt) and from evaporation during the bulk distribution (510 kt). The hydrocarbons contained in these evaporative emissions had the composition of gasoline vapour in equilibrium with the liquid, that is, the vapour was enriched by the more volatile components such as butanes and pentanes relative to their percentages in the liquid phase.

Total hydrocarbon vapour emissions from refineries were estimated to be 220 kt, but these VOCs are somewhat different in composition from gasoline vapour and also represent the volatile components of crude oil, gaseous by-products and other petroleum distillates products. Nevertheless, a worst case estimate of air emissions would be attained by ascribing all these refinery emissions to gasoline. In this case, the total of all the emissions directly to air in 1983 from vehicles, refineries and distribution was 1713 kt. The emissions from all these sources are expected to decrease due to improvements in control technology.¹⁹

An additional 2407 kt/year of VOC were estimated to arise in 1983 from vehicle exhausts.²⁰ These exhaust gases from the combustion of gasoline do contain some gasoline components, both as unburned hydrocarbon and as combustion products.

The tonnage emitted to air per year and the composition of the vapour may be used in multi-media models to predict subsequent concentrations of these components in air, water and soil. The direct emissions to water and soil must also be considered

in this calculation. This modelling is beyond the scope of this profile, but the results of modelling using single substance "blocks", such as benzene, may be compared with measured environmental concentrations for these single substances. Since these single substances may come from a variety of sources, the predicted concentrations should not exceed the measured values reviewed in **Table 3.1**. Generalised background concentrations equivalent to a regional scenario are somewhere between the rural and urban range.

3.3. AQUATIC EXPOSURE

As stated earlier, the only identifiable and continuous emission of gasoline components to surface water occurs during the refining process. Aqueous effluent from refineries contains both suspended hydrocarbons (grease and oil) and dissolved individual chemical species measured variously as total organic carbon, (TOC). The concentration of oil in refinery effluents has decreased over time to the average value reported for 1993 of 0.75 mg/l.^{22, 23}

The principal components of gasoline are aliphatic and aromatic hydrocarbons in the range C₄ to C₁₂. These components are quite volatile and somewhat more soluble than the substance measured as 'insoluble oil'. They are expected to be contained in the total organic carbon portion of the effluent analysis described above. Furthermore, simulation models predict that a major portion of these chemicals will be removed in waste water through air stripping and biodegradation.

A large-scale monitoring study of refinery effluents was conducted by the US EPA in conjunction with the American Petroleum Institute.²⁴ It was reported that concentrations of selected hydrocarbons such as benzene, toluene, ethylbenzene and naphthalene were, on average, less than the detection limits of 6, 2, 1 and 1 mg/l, respectively. Mean total dissolved organic carbon was 35 mg/l in untreated effluents in this study.

As a worst case estimate, if one assumes that the entire reported total organic carbon in refinery effluent is due to gasoline, the 700 million tonnes of waste water reported for all European refineries^{22, 23} containing 35 mg/l gives rise to a total emission to surface water of 24.5 kt expressed as organic carbon.

Measured concentrations quoted in the literature for 1,3-butadiene, n-hexane, benzene, toluene, ethylbenzene and xylenes in various water sources, including refinery effluents, are summarised in **Table 3.2**.

3.4. SOIL AND GROUND WATER EXPOSURE

Soil and ground water contamination may result from terrestrial gasoline spills and leaking underground storage tanks. The fate of a leak or spill is determined by the properties of the spilled product and soil and ground water conditions, e.g. geology and hydrology. For spills and leaks near the soil surface, gasoline will undergo a fractionation process and some hydrocarbons, for example, the alkanes, will primarily be transported upwards by vapour diffusion and partition into air. However, this process will be slower than in an aquatic environment due to the slower diffusion characteristics of gasoline through soil. Many of the individual components of gasoline, both aliphatic and aromatic, are known to be rapidly biodegraded and a major fate of gasoline as a whole in soil is through biodegradation.^{25, 26}

A further aspect of the degradation process is through the leaching of components by the downward percolation of rainwater. The more hydrophobic alkanes sorb tightly to soil and have little mobility, but the lower molecular weight aromatics such as benzene, toluene and xylene will be leached out and eventually collect in ground water. Biodegradation of gasoline components will continue in the ground water, but if the availability of oxygen is restricted, the biodegradation of benzene, toluene, xylene and other pollutants will be much reduced. Nevertheless, anaerobic biodegradation of toluene is known to occur through micro-organisms which utilise nitrate in place of oxygen.^{27, 28} The anaerobic biodegradation of benzene is less certain. Being the gasoline component with the highest soil mobility, benzene is the component most likely to be detected in ground water.

The environmental exposure resulting from an accidental spill or leakage is very site specific and equivalent levels of contamination can result in very different environmental impacts at different locations. However, as a specific example, an incident which involved the accidental release of 4.5 t of gasoline from a service station underground storage tank gave rise to concentrations of gasoline hydrocarbons from 0.1 mg/l up to 6000 mg/l close to the release point (radius less than 10 m) over the following three months. At the same time, no hydrocarbons were detected outside the boundaries of the service station (radius less than 50 metres); a detection limit of 1 µg/l applied. Hydrocarbon concentrations at the closest point to the spill were less than 2 mg/l after one year and hydrocarbons were not detectable outside the boundaries. Ground water pumping, treatment and soil venting were used as the remediation techniques.²⁹

Naturally occurring background concentrations of benzene, toluene and xylenes have been predicted in soils by several modelling studies,²⁵ but the predicted levels are considerably lower than routine analytical detection limits. The non-spill related sources of these aromatics in soils are from atmospheric partitioning of emissions from motor vehicles, industrial plant, forest fires, the burning of wood and other biomass, and seepages from natural petroleum deposits.

A summary of direct measurements of benzene, toluene and xylene levels in ground water and soil is given in **Tables 3.2 and 3.3** respectively.

3.5. MAJOR SPILLAGES

A number of accidental releases of gasoline have occurred and some of those which have been well documented are noted below:

- In 1968, a leakage of 280-700 tonnes occurred from a tank in Los Angeles.³⁰
- In 1971, a pipeline break resulted in the loss of 225 tonnes into an underground formation at Ambler, Pennsylvania.³¹
- In 1973, there was a spillage of 19 tonnes of aviation gasoline into a stream known as Grace Coolidge Creek, South Dakota.³²
- In 1976, a pipeline break resulted in 150 tonnes entering a freshwater lake in Alaska.³³
- In 1977, there was a spillage of 225 tonnes into the Ohio river.³⁴
- In 1978, the grounding of the barge "Ocean 250" in Block Island Sound, Rhode Island, resulted in the loss of 1900 tonnes.³⁵

- In 1985, a ruptured pipeline resulted in the release of 100 tonnes into a stream in Idaho.³⁶
- The ship "Dona Marika" spilt 2000 to 3000 tonnes into enclosed bays in Milford Haven.³⁷

4. REFERENCES

1. CONCAWE (1992) Gasolines. Product Dossier No. 92/103. Brussels: CONCAWE
2. IEA/OECD (1996) Oil and gas information 1995. Paris: International Energy Agency
3. CONCAWE (1995) The classification and labelling of petroleum substances according to the EU dangerous substances directive. Report No. 95/59. Brussels: CONCAWE
4. EU (1967) Council Directive of 27 June 1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances (67/548/EEC). Official Journal of the European Communities No. L196, 16.08.1967
5. Dietzel, B. (1994) Zusammensetzung von Ottokraftstoffen aus deutschen Raffinerien. DGMK Projekt 502. Hamburg: DGMK
6. CONCAWE (1987) A survey of exposures to gasoline vapour. Report No. 4/87. Brussels: CONCAWE
7. EU (1994) Commission Directive 94/69/EC of 19 December 1994 adapting to technical progress for the 21st time Council Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances. Official Journal of the European Communities No. L381, 31.12.1994
8. IARC (1989) IARC Monographs on the evaluation of carcinogenic risks to humans, Volume 45: Occupational exposures in petroleum refining; crude oil and major petroleum fuels. Lyon: International Agency for Research on Cancer
9. ACGIH (1996) Threshold limit values (TLVs) for chemical substances and physical agents and biological exposure indices (BEIs) - 1996. Cincinnati: American Conference of Governmental Industrial Hygienists
10. Ministerie van Sociale Zaken en Werkgelegenheid (1996) De nationale MAC-lijst 1996. Publication No. P 145. The Hague: Sdu Uitgevers
11. Arbetskyddsstyrelsens Författningssamling (1993) Hygieniska gränsvärden (Occupational exposure limit values). AFS 1993:9. Solna: Swedish National Board of Occupational Safety and Health
12. Angerer, J. et al (1991) The determination of benzene in human blood as an indicator of environmental exposure to volatile aromatic compounds. *Fresenius J Anal Chem* **339**, 740-742
13. Boogaard, P.J. and van Sittert, N.J. (1995) Biological monitoring of exposure to benzene: a comparison between S-phenylmercapturic acid, *trans,trans*-muconic acid, and phenol. *Occup and Environ Med* **52**, 9, 611-620
14. Jungen, H. et al (1994) Exposure to hydrocarbon vapours during production and handling of motor gasolines. Forschungsbericht 477. Hamburg: DGMK

-
15. CONCAWE (1994) Exposure and health risks associated with non-occupational sources of benzene. Report No. 1/94. Brussels: CONCAWE
 16. CONCAWE (1996) Environmental risk assessment of petroleum substances: the hydrocarbon block method. Report No. 96/52. Brussels: CONCAWE
 17. EC (1996) Technical Guidance Documents in support of the Commission Directive 93/67/EEC on risk assessment for new notified substances and the Commission Regulation (EC) No. 1488/94 on risk assessment for existing substances. Ispra: Joint Research Centre
 18. Jager, D.T. and Visser, C.J.M. (1994) Uniform system for the evaluation of substances (USES), computer program. The Hague: Ministry of Housing, Spatial Planning and the Environment (VROM)
 19. CONCAWE (1990) Closing the gasoline system - control of gasoline emissions from the distribution system and vehicles. Report No. 3/90. Brussels: CONCAWE
 20. CONCAWE (1986) Volatile organic compound emissions: an inventory for Western Europe. Report No. 2/86. Brussels: CONCAWE
 21. CONCAWE (1987) Volatile organic compound emissions in Western Europe: control options and their cost-effectiveness for gasoline vehicles, distribution and refining. Report No. 6/87. Brussels: CONCAWE
 22. CONCAWE (1994) Trends in oil discharged with aqueous effluents from oil refineries in Western Europe - 1993 survey. Report No. 3/94. Brussels: CONCAWE
 23. CONCAWE (1995) Oil refinery waste disposal methods, quantities and costs - 1993 survey. Report No. 1/95. Brussels: CONCAWE
 24. API (1981) Refinery wastewater priority pollutant study - sample analysis and evaluation of data. API Report No. 4346. Washington DC: American Petroleum Institute
 25. API (1991) Naturally occurring benzene, toluene and xylenes in soils. API Report No. DR195. Washington DC: American Petroleum Institute
(N.B. Above information takes much data from: Golder Associates (1987) Testing of specific compounds in soils in background urban areas Port Credit and Oakville/Burlington, Ontario. Working paper 2 to Shell Canada Limited and Texaco Canada Limited)
 26. API (1994) Transport and fate of non-BTEX petroleum chemicals in soil and groundwater. API Report No. 4593. Washington DC: American Petroleum Institute
 27. Hutchins, S.R. (1991) Optimizing BTEX biodegradation under denitrifying conditions. *Environ Toxicol and Chem*, 10, 1437-1448
 28. Hutchins, S.R. et al (1991) Effect of nitrate addition on bioremediation of fuel-contaminated aquifer: field demonstration. *Ground Water* 29, 4, 571-580
 29. Kesoil, H. (1995) Monitoring of an accidental gasoline spillage (in Finnish). Report No. 9774. Hollola, Finland: Paavo Ristola Oy

-
30. McKee, J.E. et al (1972) Gasoline in groundwater. *J Water Pollut Control Fed* 44, 2, 293-302
 31. Jamison, V.W. et al (1976) Biodegradation of high-octane gasoline in groundwater. *Dev Ind Microbiol* 16, 305-312
 32. Bugbee, S.L., and Walter, C.M. (1973) The response of macroinvertebrates to gasoline pollution in a mountain stream. API Publication No. 4172, p. 725-731. Washington DC: American Petroleum Institute
 33. Horowitz, A. and Atlas, R.M. (1977) Response of microorganisms to an accidental gasoline spillage in an Arctic freshwater ecosystem. *Appl and Environ Microbiol* 33, 6, 1252-1258
 34. Roubal, G.E. et al (1979) Disappearance of hydrocarbons following a major gasoline spill in the Ohio River. *Dev Ind Microbiol* 20, 503-507
 35. Dimock, C.W. et al (1980) Field and laboratory methods for investigating a marine gasoline spill. *Environ Sci Technol* 14, 12, 1472-1475
 36. Graves, N.A. (1985) A Northern Idaho gasoline spill and cleanup using stream bed agitation. In: Proc. 1985 Oil Spill Conference (Prevention, Behavior, Control, Cleanup), p. 189-191. API Publ. No. 4385. Washington DC: American Petroleum Institute
 37. Baker, J.M. (1976) Ecological changes in Milford Haven during its history as an oil port. In: Baker, J.M. (Ed). *Marine Ecology and Oil Pollution*, p. 55-66. New York: John Wiley & Sons
 38. CONCAWE (1985) Health aspects of petroleum fuels - potential hazards and precautions for individual classes of fuels. Report No. 85/51. Brussels: CONCAWE
 39. CONCAWE (1995) Motor vehicle emission regulations and fuel specifications in Europe and the United States - 1995 update. Report No. 5/95. Brussels: CONCAWE
 40. INRS (1995) Valeurs limites d'exposition professionnelle aux agents chimiques en France. ND 1945-153-93. Paris: Institut National de Recherche et de Sécurité
 41. Deutsche Forschungsgemeinschaft (1995) List of MAK and BAT values 1995. Report No 31. Weinheim: VCH Verlagsgesellschaft
 42. UK HSE (1996) Occupational exposure limits 1996. UK Health and Safety Executive Guidance Note EH40/96
 43. CONCAWE (1994) Review of European oil industry benzene exposure data (1986 - 1992) Report No. 7/94. Brussels: CONCAWE
 44. Rappaport, S. et al (1985) Gasoline exposures in the petroleum industry, January 24, 1985. Prepared on behalf of the American Petroleum Institute
 45. Halder, C.A. et al (1986) Gasoline vapor exposures. Part I. Characterization of workplace exposures. *Am Ind Hyg Assoc J* 47, 3, 164-172

-
46. Verma, D.K. et al (1992) Hydrocarbon exposures at petroleum bulk terminals and agencies. *Am Ind Hyg Assoc J* 53, 10, 645-656
 47. In-house oil company data (1990) A short survey of exposure to hydrocarbon vapour during the off-loading of unleaded gasoline from a coastal vessel to a road distribution terminal. June 1990
 48. Nicastro, L. and Sperduto, B. (1993) Evaluation of benzene exposure of employees and customers in filling stations of the AgipPetroli sector. Prepared on behalf of AgipPetroli by Universita Cattolica del Sacro Cuore
 49. Castellino, N. et al (1996) Service stations personnel exposure to benzene. *Unione Petrolifera*, 31.01.1996
 50. McDermott, H.J. and Vos, G.A. (1979) Service station attendants' exposure to benzene and gasoline vapors. *Am Ind Hyg Assoc J* 40, 4, 315-321
 51. Kearney, C.A. and Dunham, D.B. (1986) Gasoline vapor exposures at a high volume service station. *Am Ind Hyg Assoc J* 47, 8, 535-539
 52. In-house oil company data (1988) Avgas exposure data of light aircraft refuelling Aug./Sept. 1988 at Bremen Airport, Germany.
 53. In-house oil company data (1992-1995) Avgas and Jet A1 exposure data from aircraft refuelling at French airports.
 54. Arbete och Hälsa (1982) Scientific basis for Swedish occupational standards II. Consensus report for benzene (1981-03-04).
 55. Irving, W.S. and Grumbles, T.G. (1979) Benzene exposures during gasoline loading at bulk marketing terminals. *Am Ind Hyg Assoc J* 40, 6, 468-473
 56. In-house oil company data (1995) Exposure to benzene from gasoline during specific tasks.
 57. Sherwood, R.J. (1972) Evaluation of exposure to benzene vapour during the loading of petrol. *Brit J Ind Med* 29, 65-69
 58. API (1991) Gasoline vapor exposure assessment at service stations. API Med. Res. Publ. 40-31151. Washington DC: American Petroleum Institute
 59. Lawryk, N.J. et al (1995) Exposure to volatile organic compounds in the passenger compartment of automobiles during periods of normal and malfunctioning operation. *J Expos Anal Environ Epidemiol* 5, 4, 511-531
 60. Bertorelli, V. and Derwent, R. (1995) Air quality A to Z: a directory of air quality data for the United Kingdom in the 1990s. Bracknell: Atmospheric Processes Research Branch, Meteorological Office
 61. Akland, G.G. (1993) Exposure of the general population to gasoline. *Environ Health Perspect* 101, Suppl 6, 27-32
 62. CONCAWE (1995) A year long study of ambient air concentrations of benzene around a service station. Report No. 95/63. Brussels: CONCAWE

63. YTV (1993) Report on air quality in Helsinki Metropolitan area, Pääkaupunkiseudun julkaisusarja (Helsinki Metropolitan Area Council) C 1993. Report No. 8 (in Finnish)
64. Ewing, B.B. et al (1977) Monitoring to detect previously unrecognised pollutants in surface waters. Appendix: organic analysis data. US EPA Report EPA-560/6-77-015A. Washington DC: US Environmental Protection Agency
65. IPCS (1991) Environmental health criteria 122: n-Hexane. Geneva: World Health Organisation
66. IPCS (1993) Environmental health criteria 150: Benzene. Geneva: World Health Organisation
67. Fraunhofer Institute (1995) Application of a selection scheme for the identification of hazardous substances relevant for the aquatic environment. Schmallenberg: Fraunhofer-Institut
68. IPCS (1985) Environmental health criteria 52: Toluene. Geneva: World Health Organisation
69. ECETOC (1986) Ethylbenzene. JACC Report No. 7. Brussels: European Chemical Industry Ecology and Toxicology Centre
70. ECETOC (1986) Xylenes. JACC Report No. 6. Brussels: European Chemical Industry Ecology and Toxicology Centre

Table 1.1 Motor gasoline supply and consumption in the European Union.*000 metric tonnes*

	1991	1992	1993	1994	1995
Refinery output	131324	137072	139101	139515	139998
Imports	28422	26427	26550	24777	24760
Exports	35550	36488	38415	41353	38859
Total consumption	119567	122176	121463	119676	118250
Stock level at year end	18375	18610	20187	20073	20068

Source: OECD (1996) ²**Table 1.2** Aviation gasoline supply and consumption in the European Union*000 metric tonnes*

	1991	1992	1993	1994	1995
Refinery output	184	163	180	182	122
Imports	104	108	133	76	79
Exports	170	161	155	157	112
Total consumption	137	134	129	118	105
Stock level at year end	55	47	54	44	35

Source: OECD (1996) ²

Table 1.3 Main component streams used for blending automotive and aviation gasolines

Refinery stream	Generic short name ⁷	Automotive gasoline (% V/V)	Aviation gasoline (% V/V)
Butanes	Petroleum gas	0 - 10	0 - 2
Light straight run gasoline	Low boiling point naphtha	0 - 30	0
C5/C6 Isomerate	Low boiling point modified naphtha	0 - 30	0 - 15
Alkylate	Low boiling point modified naphtha	0 - 5	50 - 70
Catalytically cracked gasoline	Low boiling point cat-cracked naphtha	0 - 60	0
Catalytic reformat	Low boiling point cat-reformed naphtha	30 - 80	0 - 40
Thermally cracked gasoline	Low boiling point thermally cracked naphtha	0 - 5	0
Steam cracked (pyrolysis) gasoline	Low boiling point naphtha - unspecified	0 - 50	0
Methanol	-	0 - 3	0
MTBE (Methyl tertiary butyl ether)	-	0 - 15	0

Source: CONCAWE ^{38, 39}

Table 1.4 Concentration of selected hazardous components in automotive gasolines.

Component	Mean (% m/m)	Range (% m/m)
1,3-butadiene	< 0.1	< 0.1
n-hexane	2.5	0.8 to 5.0
benzene	2.5	0.2 to 4.7
toluene	11.4	2.7 to 21.0
ethylbenzene	2.6	1.0 to 5.4
xylene (o,m,p)	10.6	5.8 to 15.8

Source: DGMK ⁵

Table 1.5 Occupational Exposure Limits for gasoline

units: mg/m³

COMPONENT	ACGIH ⁹		Netherlands ¹⁰		Sweden ¹¹	
	TWA	STEL	TWA	STEL	TWA	STEL
Gasoline	890	1480	240	480	200	300

Notes:

- (1) Swedish NGVs are a function of the aromatics content of the gasoline. Figures quoted are for a typical Swedish gasoline with an aromatics content of 50% (m/m)
- (2) Dutch OEL for gasoline agreed but not yet published.

Table 1.6 Occupational Exposure Limits for selected gasoline components

units: mg/m³

	LIMIT	ACGIH ⁹	France ⁴⁰	Germany ⁴¹	NL ¹⁰	Sweden ¹¹	UK ⁴²
1,3-butadiene	TWA STEL	4.4 NA	NA NA	Note (1)	46 NA	1 10	22 NA
n-Hexane	TWA STEL	176 NA	170 NA	180 360 (30 min)	90 NA	90 180	70 NA
Benzene	TWA STEL	32 NA (Under review)	16 80 (Ceiling)	Note (2)	7.5 (Sk) NA	1.5 9.0	16 NA
Toluene	TWA STEL	188 (Sk) NA	375 550	190 950 (30 min)	150 NA	200 400	188 560 (Sk)
Xylene (isomers)	TWA STEL	434 651	435 650	440 (Sk) 880 (30 min)	210 (Sk) NA	200 450	435 650 (Sk)
Ethylbenzene	TWA STEL	434 543	435 NA	440 (Sk) 880 (5 min)	215 (Sk) NA	200 450	435 545

Notes:

(1): 1,3-butadiene:

TWA 34 mg/m³, STEL 170 mg/m³ for reconditioning after polymerisation, loading,
TWA 11 mg/m³, STEL 55 mg/m³ for other operations.

(2): Benzene:

TWA 8 mg/m³ (Sk), STEL 40 mg/m³ for repair and maintenance of equipment containing benzene and gasoline.
TWA 3.2 mg/m³ (Sk), STEL 16 mg/m³ Other operations.

TWA:

Time Weighted Average for 8-hour day and 40 hour week

STEL:

Short Term Exposure Limit (measured over a 15 -min period, unless noted otherwise).

Sk

Can be absorbed through the skin.

NA

Not assigned. No figure quoted by the authority.

See original references for details of the individual exposure limits.

Table 2.1.a Tasks involving potential for exposure and usual control measures for Workers.
(See also Appendix 1 for fuller description of tasks and nature of exposure)

	Job Group	Tasks	Pattern of control
1.	REFINERY		
1.1.	On-site operator	Operators carry out tasks involved in controlling plants which process hydrocarbon streams to produce gasoline, e.g. valve operation, sample collection, blowing down gauges.	Full containment; Natural ventilation; PPE (skin)
1.2.	Off-site operator	Ancillary operations carried out by refinery workers, e.g. laboratory technicians (quality control/research tests), tank farm activities (dipping/sampling), water effluent treatment.	Full containment; Local exhaust ventilation (laboratory); Natural ventilation; Procedure; PPE (skin)
1.3.	Maintenance worker	Carry out a variety of tasks some of which may involve exposure to gasoline vapour when draining, cleaning, opening up and working on enclosed equipment.	Natural ventilation; Procedure: PPE (skin)
1.4.	Drum/barrel filler	Filling drums with 200 l of gasoline.	Local exhaust ventilation (not in all cases); Dilution ventilation; PPE (skin)
1.5.	Tank cleaning	A specialist activity involving cleaning out sludge from bulk storage tanks.	Mechanically induced dilution ventilation; Procedure (Permit to Work); PPE (skin and breathing)
2.	DISTRIBUTION		
2.1.	Road Tanker tasks		
2.1.a.	Road Tanker Driver: Top loading	Drivers fill their own vehicles using the top loading procedure.	Natural ventilation; Procedure; PPE (skin)
2.1.b.	Road Tanker Driver: Bottom loading	Drivers fill their own vehicles using the bottom loading procedure.	<i>Stage I vapour recovery</i> . Full containment; Natural ventilation; PPE (skin)
2.1.c.	Road Tanker Driver: Other measurements	Delivery only, driving and delivery, loading/driving/delivery where it is not known if loading was top or bottom.	<i>Stage I vapour recovery</i> . Natural ventilation; Procedure; PPE (skin)
2.1.d.	Rack operators and supervisors	Duty to load road tanker vehicles for drivers.	Natural ventilation; Procedure; PPE (skin)
2.2.	Rail car tasks		
2.2.a.	Rail car operator: top loading	Operators involved in top loading of rail cars.	Full containment (bottom loading with vapour recovery). Natural ventilation; Procedure; PPE (skin)
2.2.b.	Rail car operator: off-loading to storage	Operators involved in hose connection/ disconnection and sampling.	Full containment; Natural ventilation; Procedure; PPE (skin)

Table 2.1.a Tasks involving potential for exposure and usual control measures for Workers. *Continued.*

	Job Group	Tasks	Pattern of control
2.3.	Marine tasks		
2.3.a.	Jetty staff	Supervision of ship loading operations, sampling, tank dipping, handling of hoses.	Natural ventilation; Procedure; PPE (skin)
2.3.b.	Deck crew: Ships - open loading	Loading of ships with the cargo hatches open. Tasks include connection/disconnection of cargo lines, checking tank fill levels, tank dipping.	Natural ventilation; Procedure; PPE (skin)
2.3.c.	Deck crew: Ships - closed loading	Loading of ships with displaced vapours discharged remotely and ullage measurements are read automatically.	Full containment; Natural ventilation; Procedure; PPE (skin)
2.3.d.	Deck crew: Barges closed loading	This is similar to ships - closed loading, however, decks of barges are generally flatter than for ships and vapour vents may be at lower level.	Full containment; Natural ventilation; Procedure; PPE (skin)
2.4.	Product storage tasks		
2.4.a.	Terminal operators	Carry out tasks as per 1.2. 'off site operators' within the Distribution depot. May also carry out drum filling operations (see 1.4).	Natural ventilation; Procedure; PPE (skin)
3.	SERVICE STATIONS		
3.1.	Service station attendants	Exposure may occur from filling customers vehicles and ambient air concentrations in and around the service station.	Natural ventilation; Procedure
3.2.	Cashiers	Exposure to ambient concentrations of vapour in the service station shop.	Dilution ventilation
3.3.	Service station mechanic	Exposures may occur from residual fuel in the vehicle's fuel tank and background levels from the refuelling pumps on the forecourt.	Dilution ventilation.
4.	AIRPORTS (aviation gasoline)		
4.1.	Operators	Bottom loading of road tankers and over-wing loading of light aircraft.	Full containment (loading); Natural ventilation; Procedure; PPE (skin).
4.2.	Yard staff	Fuel testing for water, meter proving and meter servicing.	Natural ventilation; Procedure; PPE (skin)

Notes:

(1) PPE: Personal protection equipment.

Table 2.1.b Summary of personal arithmetic mean, 8-hour time-weighted average exposures.

Job Group	Region	Concentration in mg/m ³ : Arithmetic Mean [no. of samples] (range)							Ref (date)	
		1,3-butadiene	n-Hexane	Benzene	Toluene	Ethylbenzene	Xylenes	Total hydrocarbons		
1. REFINERY										
1.1. On-site operator	Europe	0.3 [62] (0 - 11.4)	3 [62] (0- 154.3)	0.9 [62] (0 - 23.8)	2 [62] (0 - 67.1)	0.2 [62] (0 - 7.2)	0.1 [62] (0 - 4.9)	52.8 [62] (0.7 - 1819)	6 (1987)	
	Europe (1986-94)			0.6 [449] (0.2 - 25.3)					43 (1994)	
	USA		0.47 [56] (0 - 3.18)	0.17 [56] (0 - 1.17)	0.55 [56] (0 - 8.16)	0.08 [56] (0 - 1.2)	0.5 [56] (0 - 8.0)	18.9 [56] (0.1 - 191.6)	44 (1985)	
	- Reforming plants	Germany (1983/1985)			0.62 [183] (0.01 - 39.7)	1.53 [146] (0.01 - 52.4)	included with the xylenes	1.34 [130] (0.02 - 46.5)		14 (1994)
	- Cracking plants	Germany (1983/1985)			0.96 [46] (0.01 - 14.4)	1.93 [51] (0.02 - 35.3)	included with the xylenes	2.45 [48] (0.01 - 60.1)		14 (1994)
	- Ethylene plants	Germany (1983/1985)			0.91 [51] (0.02 - 8.6)	0.18 [51] (0.01 - 2.13)	included with the xylenes	0.19 [37] (0.02 - 1.11)		14 (1994)
1.2. Off-site operator	Europe	0.1 [27] (0 - 1.6)	2.8 [27] (0 - 13.5)	1.0 [27] (0 - 14.1)	2.2 [27] (0 - 19.6)	0.6 [27] (0 - 4.7)	0.07 [27] (0 - 0.8)	66.0 [27] (3.8 - 922.8)	6 (1987)	
	Europe (1986-94)			1.8 [426] (0.2 - 42.2)					43 (1994)	
	Germany (1983/1985)			2.11 [54] (0.03 - 21.1)	5.36 [46] (0.15 - 34.1)	included with the xylenes	3.24 [42] (0.01 - 22.1)		14 (1994)	
	- Laboratory Technician	Europe (1986-94)			1.2 [218] (0.2 - 35.5)					43 (1994)
		USA		1.56 [19] (0.3 - 6.0)	0.34 [19] (0.08 - 0.8)	2.0 [19] (0 - 9.2)	0.07 [19] (0 - 0.3)	0.4 [19] (0 - 1.6)	22.0 [19] (2.33 - 51.46)	44 (1985)
	- Bottle washer	Europe (a) (1986-94)			5.2 [75] (0.2 - 42.6)					43 (1994)

Table 2.1.b Summary of personal arithmetic mean, 8-hour time-weighted average exposures. *Continued*

Job Group	Region	Concentration in mg/m ³ : Arithmetic Mean [no. of samples] (range)							Ref (date)
		1,3-butadiene	n-Hexane	Benzene	Toluene	Ethylbenzene	Xylenes	Total hydrocarbons	
1.3. Maintenance worker	Europe (b) (1986-94)			2.5 [55] (0.2 - 61.8)					43 (1994)
	Germany (1983/1985)			0.8 [43] (0.01 - 25.6)	3.82 [53] (0.05 - 81.8)	included with the xylenes	4.43 [52] (0.01 - 150)		14 (1994)
1.4. Drum/Barrel filler	Europe (c)	not detected	51.8 [9] (2.4 - 297.3)	27.2 [9] (0 - 116.3)	41.3 [9] (3.1 - 194.8)	5.2 [9] (0 - 28.5)	not detected	858.4 [9] (61.1 - 1748)	6 (1987)
2. DISTRIBUTION									
2.1. Road Tanker tasks									
2.1.a. Road tanker driver: top loading	Europe (d)	0.4 [63] (0 - 4.7)	2.9 [63] (0 - 58.6)	1.7 [63] (0 - 30.7)	3.9 [63] (0 - 66.3)	0.4 [63] (0 - 6.8)	0.2 [63] (0 - 2.8)	117.6 [63] (4.1 - 1229.4)	6 (1987)
	Europe (1986-94) (d)			0.8 [186] (0.2 - 6.6)					43 (1994)
	Germany (1983/1985) (d)			1.89 [54] (0.31 - 6.18)	3.43 [57] (0.27 - 18.57)	included with the xylenes	2.38 [57] (0.32 - 10.05)		14 (1994)
	USA (d)			0.9 [43] (0.1 - 2.3)				46.4 [10] (9.9 - 109.0)	45 (1986)
2.1.b. Road tanker drivers: bottom loading	Europe (d)	0.4 [34] (0 - 14.1)	1.3 [34] (0 - 19.8)	1.2 [34] (0 - 12.0)	1.5 [34] (0 - 13.0)	0.3 [34] (0 - 3.2)	0.1 [34] (0 - 2.5)	65.6 [34] (0.5 - 728.3)	6 (1987)
	USA (d)			1.1 [38] (0.2 - 5.9)				89.8 [7] (21.9 - 184.0)	45 (1986)
	USA (e)			1.0 [56] (0.2 - 8.9)				39.6 [8] (9.4 - 195.0)	45 (1986)

Table 2.1.b Summary of personal arithmetic mean, 8-hour time-weighted average exposures. *Continued*

Job Group	Region	Concentration in mg/m ³ : Arithmetic Mean [no. of samples] (range)							Ref (date)
		1,3-butadiene	n-Hexane	Benzene	Toluene	Ethylbenzene	Xylenes	Total hydrocarbons	
2.1.c. Road Tanker Drivers - other measurements Large storage facility As previous but agency facility	Delivery & driving Europe (f)	not detected	3.1 [29] (0 - 37.7)	5.1 [29] (0 - 101.9)	10.3 [29] (0.5 - 189.2)	1.6 [29] (0 - 35.9)	0.02 [29] (0 - 0.7)	218.9 [29] (3.2 - 3615)	6 (1987)
	Loading, delivery & driving. USA		1.0 [49] (0.01 - 13.35)	0.45 [49] (0 - 4.6)	1.53 [49] (0 - 46.1)	0.1 [49] (0 - 0.49)	0.84 [49] (0 - 23.5)	45.8 [49] (0.5 - 655.1)	44 (1985)
	- loading, driving, unloading, return to storage. Canada			0.5 [38] (no data)				37.9 [38] (no data)	46 (1992)
	ditto plus tank dipping, drum filling, bulk product deliveries			0.7 [21] (no data)				81.3 [21] (no data)	46 (1992)
2.1.d. Rack operators and supervisors	Europe (d) (1986-94)			1.9 [40] (0.16 - 60.5)					43 (1994)
	Germany (d) (1983/1985)			1.13 [50] (0.17 - 7.11)	3.2 [60] (0.03 - 38.2)	included with the xylenes	3.0 [57] (0.03 - 50)		14 (1994)
2.2. Rail car tasks									
2.2.a. Rail car operator: top loading	Europe (g)	0.6 [32] (0 - 6.2)	1.2 [32] (0 - 4.9)	1.5 [32] (0 - 9.5)	2.9 [32] (0.1 - 27.9)	0.2 [32] (0 - 1.3)	0.6 [32] (0 - 17.6)	84.7 [32] (2 - 535.4)	6 (1987)
	Europe (g) (1986-94)			5 [183] (0.2 - 133.1)					43 (1994)
2.3. Marine tasks									
2.3.a. Jetty staff	Europe	2.6 [21] (0 - 15.9)	1.6 [21] (0 - 7.0)	1.5 [21] (0 - 5.9)	2.4 [21] (0.05 - 8.9)	0.2 [21] (0 - 1.3)	0.5 [21] (0 - 4.5)	120.1 [21] (3.3 - 658.2)	6 (1987)
	Europe (h) (1986-94)			6.3 [92] (0.2 - 265.9)					43 (1994)

Table 2.1.b Summary of personal arithmetic mean, 8-hour time-weighted average exposures. *Continued*

Job Group	Region	Concentration in mg/m ³ : Arithmetic Mean [no. of samples] (range)							Ref (date)
		1,3-butadiene	n-Hexane	Benzene	Toluene	Ethylbenzene	Xylenes	Total hydrocarbons	
2.3.b. Deck crew	Ships open loading Europe	1.1 [8] (0 - 4.2)	1.8 [8] (0 - 4.7)	1.5 [8] (0.1 - 4.6)	3.1 [8] (0.1 - 12.9)	0.6 [8] (0.05 - 2.7)	0.9 [8] (0 - 1.9)	118 [8] (2.4 - 322)	6 (1987)
	Ships closed loading Europe (i) (g)	6.4 [9] (0 - 21.0)	4.2 [9] (0 - 10.1)	4.6 [9] (0 - 21.9)	4.2 [9] (0.1 - 17.9)	0.05 [9] (0 - 0.5)	0.2 [9] (0 - 1.6)	339.7 [9] (2.4 - 1089)	6 (1987)
	Barges closed loading - Europe (i) (g)	2.6 [11] (0 - 15.2)	6.3 [11] (0 - 46.1)	4.7 [11] (0 - 31.5)	5.8 [11] (0.1 - 24.4)	0.5 [11] (0 - 2.7)	0.3 [11] (0 - 2.1)	262.9 [11] (1.5 - 1750.4)	45 (1986)
	loading open/closed unknown - Europe (1986-94)			2.3 [19] (0.2 - 11.4)					43 (1994)
2.3.c. Bridge crew	Barges closed loading - Germany (1983/1985)			0.22 [7] (0.08 - 0.41)	0.3 [16] (0.05 - 1.13)	included with the xylenes	0.41 [13] (0.01 - 2.74)		14 (1994)
2.3.d. Marine loading other measurements	USA (j)			2.3 [11] (0.1 - 19.5)				246.0 [11] (9.1 - 1580)	45 (1986)
2.4. Product storage tasks									
2.4.a. Terminal operators - as per 1.2. Off-site operator above Bulk terminal plant man: sample collection; maintaining loading racks; general maintenance e.g. grass cutting, painting; paperwork 8 hour exposure involving following tasks: Ship off-loading; sample collection; sample testing; cleaning fuel filters.	Europe	0.1 [27] (0 - 1.6)	2.8 [27] (0 - 13.5)	1 [27] (0 - 14.1)	2.2 [27] (0 - 19.6)	0.6 [27] (0 - 4.7)	0.07 [27] (0 - 0.8)	66 [27] (3.8 - 922.8)	6 (1987)
	Canada			0.4 [23] (no data)				20.1 [23] (no data)	46 (1992)
	UK		7.8 [3] (1.6 - 16.3)	0.16 [3] (0.14 - 0.2)	0.9 [3] (0.7 - 1.1)		0.9 [3] (0.5 - 1.1)	18.3 [3] (15.0 - 22.0)	47 (1990)

Table 2.1.b Summary of personal arithmetic mean, 8-hour time-weighted average exposures. *Continued*

Job Group	Region	Concentration in mg/m ³ : Arithmetic Mean [no. of samples] (range)							Ref (date)
		1,3-butadiene	n-Hexane	Benzene	Toluene	Ethylbenzene	Xylenes	Total hydrocarbons	
3. SERVICE STATIONS									
3.1. Service station attendants	Europe	0.3 [13] (0 - 1.1)	0.4 [13] (0 - 3.0)	0.4 [13] (0 - 1.3)	0.6 [13] (0.2 - 1.9)	not detected	0.04 [13] (0 - 0.4)	29.3 [13] (7.9 - 101.0)	6 (1987)
	Europe (1986-94)			0.61 [82] (<0.2 - 10.7)					43 (1994)
	Germany (1983/1985)			0.52 [351] (0.01 - 3.98)	1.06 [342] (0.02 - 10.8)	included with the xylenes	1.91 [332] (0.02 - 32.5)		14 (1994)
	Italy			0.48 [639] (no data)					48 (1992)
	Italy - Motorway (k)			0.3 [108] (no data)					49 (1996)
	Italy - Extra-urban (k)			0.2 [36] (no data)					49 (1996)
	Italy - Urban (k)			0.28 [36] (no data)					49 (1996)
	Italy - all (k)		0.3 [180] (no data)	0.25 [180] (no data)	0.47 [180] (no data)	0.56 [180] (no data)	0.2 [180] (no data)	21.13 [180] (no data)	49 (1996)
	USA			1 [21] (0 - 4.2)				17.9 [21] (1.1 - 130.3)	45 (1986)
	USA		1.2 [49]	0.65 [49] (0.48 - 0.81)	0.75 [49]	0.06 [49]	0.42 [49] (0 - 1.14)	70 [49] (53.0 - 86.8)	44 (1985)
	USA			0.32 [84] (<0.03 - 6.8)				28.8 [84] (1.3 - 343)	50 (1979)
USA (l)							no data [8] (1.9 - 14.3)	51 (1986)	
3.2. Cashiers	Europe (m) (1986-94)			<0.2 [24]					43 (1994)
3.3. Service station mechanic	USA (n)						no data [4] (1.1 - 22.3)	51 (1986)	

Table 2.1.b Summary of personal arithmetic mean, 8-hour time-weighted average exposures. *Continued*

Job Group	Region	Concentration in mg/m ³ : Arithmetic Mean [no. of samples] (range)							Ref (date)
		1,3-butadiene	n-Hexane	Benzene	Toluene	Ethylbenzene	Xylenes	Total hydrocarbons	
4. AIRPORTS									
4.1. Airport operators: Light aircraft loading with Aviation gasoline.	Germany (o)							15.10 [2] (9.62 - 20.56)	52 (1988)
4.2. Airport yard staff	No published exposure data								
4.1. Airport operators: N.B. Operators loading both Avgas (aviation gasoline) and Jet A1 (kerosine).	France (p) Details on the number of refuelling operations and type of fuel being loaded not known.			0.1 [7] (0.005 - 0.6)	1.12 [7] (0.005 - 4.2)		0.14 [7] (0.005 - 0.5)	5.73 [7] (0.05 - 31)	53

Notes

- (a) The highest benzene results for Refinery off-site workers is associated with bottle-washing.
- (b) For maintenance workers daily exposures to benzene may normally be below 3.2 mg/m³, but there is potential for high breathing zone concentrations when containment is broken. Short term exposure measurements have been carried out and are reported in Table 2.1.c. under item 1.3.
- (c) Measurements were collected at installations without proper vapour control systems to remove vapour at source from drum opening. Thus measurements indicate worst case exposures.
- (d) Without vapour recovery
- (e) With vapour recovery
- (f) The Arithmetic Mean exposure for delivery and driving is unexpectedly higher than for road tanker top and bottom loading and appears to be due to one extremely high exposure measurement for one delivery of 3,615 mg/m³ total hydrocarbons. This suggests an unusual event, such as a spillage.
- (g) Exposures vary depending on the nature of the installation, e.g. the degree of enclosure and automation, the throughput, ambient weather conditions and product temperature, the location of other vapour sources in the vicinity, and possibly by occasional spillages.
- (h) Higher exposure measurement results took place when the weather was warm and still and/or when spillages had occurred. Lower results are to be expected with closed loading operations.
- (i) Results for closed loading are unexpectedly higher than for ships open loading. However, the number of measurements collected is small and the anomaly may be due to untypically high results for closed loading and/or unusually low results for open loading or continued use of manual ullaging even where automatic gauging has been installed.
- (j) Nine samples were collected from a tanker loading facility and two from a barge loading facility. Details of Job Type and tasks covered not provided in the report.
- (k) 4-hour sampling period.
- (l) No Arithmetic Mean given but the Geometric Mean is 4.6. mg/m³
- (m) 12 hour fixed position monitoring considered to be indicative of the occupational exposure of the service station cashiers
- (n) No Arithmetic Mean given but the Geometric Mean is 2.9 mg/m³
- (o) Converted from ppm using n-hexane as the reference standard (Molecular Weight 86.17)
- (p) Reported results contain 'less than' figures. In calculating the Arithmetic Mean values half the 'less than' figure has been used.

Table 2.1.c Summary of personal arithmetic mean short term exposures.

Worker: Job Group	Region & Sample duration	Concentration in mg/m ³ : Arithmetic Mean [no. of samples] (range)							Ref (Date)	
		1,3-butadiene	n-Hexane	Benzene	Toluene	Ethyl benzene	Xylene	Total hydrocarbons		
1. REFINERY										
1.3. Maintenance worker	Europe: 30 - 265 min (1986-94)			44.08 [15] (0.15 - 202.0)						43 (1994)
1.5. Tank cleaners	Europe (Sweden): 4 - 8 min (q)			no data [10] (64 - 1680)						54 (1982)
2. DISTRIBUTION										
2.1. Road Tanker tasks										
2.1.a. Road tanker driver: top loading - exposure during loading task	Europe < 1 hour (r)	1.4 [142] (0 - 32.3)	8.3 [142] (0 - 47.4)	6.1 [142] (0 - 60.5)	11.3 [142] (0 - 63.1)	1 [142] (0 - 12.3)	0.5 [142] (0 - 13.3)	450.8 [142] (6.4 - 3029.8)		6 (1987)
	Europe < 1 hour (r) (1986-94)			6.1 [137] (0.2 - 31.0)						43 (1994)
	Canada: 10 - 20 min Bulk terminal							169.8 [24] (no data)		46 (1992)
	Canada: 10 - 20 min Agency							277.0 [32] (no data)		46 (1992)
	USA: 20 min			7.4 [no data] (no data)						55 (1979)
2.1.b. Road tanker driver: bottom loading - exposure during loading task	Europe < 1 hour (r)	0.2 [59] (0 - 3.0)	1.3 [59] (0 - 6.5)	1.4 [59] (0 - 5.5)	6.5 [59] (0 - 43.7)	1.0 [59] (0 - 6.0)	0.4 [59] (0 - 4.2)	76.1 [59] (8.2 - 236.0)		6 (1987)
	Europe < 1 hour (r) (1986-94)			2.5 [56] (0.2 - 10.9)						43 (1994)
	Canada: 10 - 20 min Bulk terminal							80.3 [31]		46 (1992)
	USA: 18 min (r)			3.3 [no data] (no data)						55 (1979)
	USA: 15 min (s)			1.9 [no data] (no data)						55 (1979)
2.1.c. Road Tanker Driver: Other measurements	Delivery only. Europe. 12-58 min (1986-94)			no data [28] (0.2 - 10.7)						43 (1994)

Table 2.1.c Summary of personal arithmetic mean short term exposures. *Continued*

Worker: Job Group	Region & Sample duration	Concentration in mg/m ³ : Arithmetic Mean [no. of samples] (range)							Ref (Date)
		1,3-butadiene	N-hexane	Benzene	Toluene	Ethyl benzene	Xylene	Total hydrocarbons	
2.1.c. Road Tanker Driver: Other measurements, continued	Delivery and unloading. Europe. 81 - 271 min			0.26 [7] (0.06 - 0.7)					56 (1995)
	Road tank compartment dipping. Europe. 10 - 20 min			3.63 [10] (0.06 - 13.28)					56 (1995)
2.2. Rail car tasks									
2.2.a. Rail car operator: top loading	Europe. 4 hours and 5 hours			5.1 [22] (no data) 8.0 [17] (no data)					57 (1972)
	Germany (1983/1985): loading duration			2.53 [102] (0.03 - 40.4)	4.23 [100] (0.01 - 44.4)	included with the xylenes	6.4 [92] (0.01 - 125)		14 (1994)
2.3. Marine tasks									
2.3.b. Deck crew	Ship loading: open/closed unknown Europe: 15 - 70 min (1986-94)			2.8 [6] (0.2 - 11.0)					43 (1994)
	Ship: open loading Germany: 2 - 5 hours (1983/1985)			15 [22] (0.5 - 63.6)					14 (1994)
	Ship: closed loading Germany: 2 - 5 hours (1983/1985)			1.72 [8] (0.27 - 2.91)	3.6 [8] (0.9 - 6.5)	included with the xylenes	1.86 [4] (1.2 - 2.71)		14 (1994)
2.3.c. Bridge crew	Barges: open and closed loading Germany: 2 - 5 hours (1983/1985)			1.67 [44] (0.07 - 10.06)	3.07 [34] (0.03 - 68.8)	included with the xylenes	1.34 [30] (0.04 - 10.4)		14 (1994)
2.4. Product storage tasks									
2.4.a. Terminal operators	Draining storage tank water bottoms. Europe 13 - 60 min			1.6 [5] (0.1 - 6.8)					56 (1995)
	Filter cleaning. Europe 15 - 42 min			1.0 [8] (0.1 - 1.9)					56 (1995)

Table 2.1.c Summary of personal arithmetic mean short term exposures. *Continued.*

Worker: Job Group	Region & Sample duration	Concentration in mg/m ³ : Arithmetic Mean [no. of samples] (range)							Ref (Date)
		1,3-butadiene	N-hexane	Benzene	Toluene	Ethyl benzene	Xylene	Total hydrocarbons	
2.4.a. Terminal operators continued	Fuel testing. Europe. 26 min			1.3 [2] (3.4 - 1.8)					56 (1995)
	Fuel sampling. Europe 9 - 29 min			1.37 [4] (0.54 - 2)					56 (1995)
	Sampling & testing. Europe. 15 - 45 min			1.1 [4] (0.35 - 2.1)					56 (1995)
	Storage tank dipping. Europe. 9 - 31 min			1.33 [7] (0.06 - 7.4)					56 (1995)
3. SERVICE STATIONS									
3.1. Service Station attendant	USA: 10 min Vehicle tank refuelling							no data [12] (3.9 - 63.5)	51 (1986)
	USA: 10 min Vehicle tank refuelling plus vehicle service							no data [14] (0 - 116.3)	51 (1986)
4. AIRPORTS									
4.1. Airport operator	Germany (t) 2.5 - 19.5 min							190 [5] (4.42 - 682)	52 (1988)
4.2. Yard operator: No published data identified									

Notes:

- (q) No mean value given in view of highly varying concentration
- (r) Without vapour recovery
- (s) With vapour recovery
- (t) Converted from ppm using n-hexane as the reference standard (Molecular Weight 86.17). The wide range of exposure measurements is explained by the position of the operator relative to the wind direction.

Table 2.2.a Tasks involving potential for exposure and usual control measures for consumers

	Task	Task description	Pattern of control
1.	Filling motor vehicle tanks	Exposures vary depending on, e.g. ambient/product temperature, wind conditions, layout of the station, spillages.	Natural ventilation; infrequent and short term exposures
2.	Filling other storage containers at a service station	As above	As above
3.	Filling equipment, e.g. lawn mowers, from storage containers	As above	As above

Table 2.2.b Summary of exposure data for consumers

Task	Region	Concentration in mg/m ³ : Arithmetic Mean [no. of samples] (range)							Ref (date)
		1,3-butadiene	n-Hexane	Benzene	Toluene	Ethylbenzene	Xylenes	Total hydrocarbons	
Filling motor vehicle tanks Average Sampling time: 1 min 38 sec	USA	-	2.25 [120] (0.16 - 7.3)	1.31 [120] (0.1 - 8.4)	1.50 [120] (0.13 - 6.3)	-	0.63 [120] (0.1 - 2.2)	151.3 [120] (11-660)	58 (1991)
Driving: in-vehicle concentrations	USA, Boston (1989) Urban	-	-	0.02 [no data] (no data)	0.03 [no data] (no data)	0.01 [no data] (no data)	0.03 [no data] (no data)	-	59
	USA, Raleigh (1988) Urban			0.01 [no data] (no data)	0.05 [no data] (no data)	0.01 [no data] (no data)	0.05 [no data] (no data)	-	59
	USA, Raleigh (1988) Highway			0.01 [no data] (no data)	0.03 [no data] (no data)	0.01 [no data] (no data)	0.03 [no data] (no data)	-	59
	USA, Los Angeles (1987) Urban			0.03 [no data] (no data)	0.11 [no data] (no data)	-	0.13 [no data] (no data) (m+p xylene only)	-	59
	USA, Los Angeles (1988) Urban			0.05 [no data] (no data)	0.16 [no data] (no data)	-	0.15 [no data] (no data) (m+p xylene only)	-	59
	USA, New Jersey/ New York (1991-92) Suburban		0.01 [30] (no data)	0.01 [95] (no data)	0.05 [95] (no data)	0.01 [95] (no data)	0.04 [95] (no data)	-	59
	USA, New Jersey/ New York (1991-92) Urban		0.01 [39] (no data)	0.02 [64] (no data)	0.08 [64] (no data)	0.01 [64] (no data)	0.06 [64] (no data)	-	59
	Sweden, high traffic + queues. (1987)			no data [no data] (0.20 - 0.40)					15
	Sweden, high traffic (1987)			no data [no data] (0.10 - 0.20)					15
	Sweden, rural (1987)			no data [no data] (0.005 - 0.01)					15
	-before starting (1992)			no data [no data] (0.06 - 0.18)					15
-during driving. (1992)			no data [no data] (0.03 - 0.06)					15	

Table 2.3.a Overview of indirect exposure routes

	Environmental compartment	Source of emission	Exposure
1.	Air (inhalation)	Ambient air concentrations dependent on location (rural, urban, close to refineries, depots, service stations, roads, other industries):- - fugitive emissions from refineries, oil depots, other industries; - evaporative losses from the distribution of gasoline - evaporation from vehicle tanks - evaporation due to spills, contaminated soil	Will occur, particularly in urban environments
2.	Water (ingestion/skin contact)	Drinking water; rain fall	Negligible in drinking water
3.	Soil (ingestion/skin contact)	Contaminated soil	Negligible, except at contaminated sites
4.	Food (ingestion)	Contamination, indirect	Negligible

Table 3.1 Measured concentrations of gasoline hydrocarbons in air.

Hydrocarbon	Location	Concentration ($\mu\text{g}/\text{m}^3$)	Reference
1,3-butadiene	Remote rural	not detected - 1.2	60
	Urban	0.09 - 2.47 (mean 1.10)	60
n-hexane	Remote rural	not detected - 4.9	60
	Rural	0 - 14.0	60
	Urban	0.28 - 1.40 (mean 0.94)	60
	Boundaries of six service stations (USA)	3 - 30 (mean 14, 88 samples)	58
Benzene	Remote rural	not detected - 13.0	60
	Rural	0.6 - 6.5	60
	Rural	<1 - 10.0	61
	Urban	0.91 - 5.23 (mean 3.35)	60
	Boundaries of six service stations (USA)	2 - 30 (mean 16, 88 samples)	58
	Boundaries of a single service station (UK)	<1 - 10.6 (mean 3.8, 104 samples)	62
	Boundaries of 12 service stations (Europe)	1.8 - 119 (mean 16.2, 76 samples)	61
	Boundaries of four distribution terminals (Europe)	1.3 - 79.1 (mean, 14.8, 30 samples)	61
Toluene	Remote rural	not detected - 34.5	60
	Rural	0.8 - 15.3	60
	Urban	1.80 - 12.52 (mean 8.43)	60
	Boundaries of six service stations (USA)	7 - 90 (mean 31, 88 samples)	58
Xylenes	Remote rural	not detected - 22.0	60
	Rural	0.4 - 11.0	60
	Urban	0.53 - 34.0 (mean 6.75)	60
	Boundaries of six service stations (USA)	10 - 70 (mean 30, 88 samples)	58
Total hydrocarbons (as butane equivalent)	Urban	100 - 500	63
	Boundaries of six service stations (USA)	50 - 2800 (mean 570, 88 samples)	58

Table 3.2 Measured concentrations of gasoline hydrocarbons in water.

Hydrocarbon	Water Source/location	Concentration (µg/l)	Reference
1,3-butadiene	Sea water/USA (San Francisco Bay)	<1-2 (204 samples)	64
n-Hexane	Drinking water/USA	detected only	65
Benzene	Rainwater/UK	87.2	66
	Rainwater/Germany	0.1-0.5	66
	River water/USA (Bravos, Texas)	0.004-0.9	66
	River water/USA (Potomac)	<2	66
	River water/Netherlands (Rhine)	<0.1	66
	River water/Germany (Rhine & Elbe)	5 (15 samples)	67
	Surface water/Germany	<0.1-1	66
	Surface water/UK (80 water bodies)	<0.1-98.4 (154 samples)	66
	Lake Zürich/Switzerland	0.03	66
	Chemical plant effluent/USA	1-13	66
	Treated refinery effluent/USA	<6	24
	Sea water/USA (Gulf of Mexico)	0.005-0.015	66
	Sea water/USA (Bravos River estuary)	0.004-0.2	66
	Sea water/Atlantic Ocean	0.00006	66
	Sea water/Baltic Sea	0.00001-0.000046	66
	Drinking water/USA	0.1-0.3	66
	Drinking water/Canada	<0.1-0.2	66
	Drinking water/Germany	<0.1-1	66
	Groundwater/USA (Nebraska)	1.6 (63 samples)	66
	Groundwater/Germany	0.02-0.05	66
Groundwater/USA (NY, NJ and Connecticut)	30-300 (contaminated wells)	66	
Groundwater/Netherlands	0.005-0.03	66	
Toluene	Rainwater/Germany	0.00013-0.0007	68
	Rainwater/Germany (Elbe & Rhine)	5 (10 samples)	67
	Drinking water/Canada	2-27	68
	Drinking water/USA (17 cities)	8-11	68
	Well water/USA	5-100	68
	Industrial waste water/USA	10-10,000	68
	Treated refinery effluent/USA	<1	24

Table 3.2 Measured concentrations of gasoline hydrocarbons in water. *Continued.*

Hydrocarbon	Water Source/location	Concentration (µg/l)	Reference
Ethylbenzene	Rainwater/USA (Los Angeles)	0.009	69
	River water/Germany (Elbe & Rhine)	5 (6 samples)	67
	Drinking water/Canada	<1-7 (30 samples)	69
	Surface water/Europe	<1	69
	Sea water/USA (Gulf of Mexico)	0.0006-0.0044	69
	Treated refinery effluent/USA	<1	24
Xylenes	Rainwater/USA (Los Angeles)	0.002-0.009	70
	Rainwater/Germany (Elbe & Rhine)	2.5 (4 samples)	67
	Sea water/USA (Gulf of Mexico)	0.0003-0.0024	70
	Groundwater/USA	<0.025 (uncontaminated site)	70
	Groundwater/USA	max. 830 (contaminated site)	70
	Refinery effluent/USA	6	70
	Refinery effluent/Netherlands	1 000	70

Table 3.3 Measured concentrations of gasoline hydrocarbons in soil and sediment

Hydrocarbon	Source/location	Concentration (µg/kg)	Reference
Benzene	soil/USA (5 industrial sites)	<2-191	66
	soil/Netherlands	<0.005-0.03	66
	soil/USA (7 uncontaminated sites in Florida)	<0.04 (7 samples)	25
	soil/Canada (urban areas near refineries)	<20-160 (found in 10/30 samples)	25
	soil/Canada (from refineries)	1-100 (found in 7/13 samples)	25
	sediment/Japan	0.5-30	66
	sediment/USA (Lake Pontchartrain)	8-21 (found in 37/98 samples)	66
	sediment/USA (335 sites)	<5	66
Toluene	soil/USA (7 uncontaminated sites in Florida)	<0.04 (7 samples)	25
	soil/Canada (urban areas near refineries)	<10-370 (found in 10/30 samples)	25
	soil/Canada (from refineries)	0.9-40 (found in 11/13 samples)	25
Xylenes	soil/USA (7 uncontaminated sites in Florida)	<0.04 (7 samples)	25
	soil/Canada (urban areas near refineries)	<10-70 (found in 1/30 samples)	25
	soil/Canada (from refineries)	<0.1-10 (found in 5/13 samples)	25

APPENDIX 1 Description of tasks.
(Additional information to that given in Table 2.1.a to clarify nature of exposure for workers)

	Job Group	Description of tasks/nature of exposure
1.	REFINERY	
1.1.	On-site operator	<p>Operators carry out tasks involved in controlling plants which process hydrocarbon streams to produce gasoline components, e.g. distillation units, crackers and reformers.</p> <p>Part of the shift is spent in a pressurised control room thereby minimising ingress of hydrocarbon vapours from the plant. Tasks on the plant involving potential exposure to gasoline vapour are e.g. valve operation, sample collection, blowing down gauges, etc.</p> <p>Division of operator's time between control room and units varies between plants and specific job responsibilities. In general tasks involving potential exposure are infrequent and of short duration.</p>
1.2.	Off-site operator	<p>Ancillary operations carried out by refinery workers e.g. laboratory technicians (quality control/research tests), tank farm activities (dipping/sampling), water effluent treatment.</p> <p>These activities are carried out by Terminal Operators within Distribution. In general tasks involving potential exposure are infrequent and of short duration.</p>
1.3.	Maintenance worker	<p>Carry out a variety of tasks some of which may involve exposure to gasoline vapour when draining, cleaning, opening up and working on enclosed equipment. In general irregular exposures are likely with the potential for high breathing zone concentrations when containment is broken.</p>
1.4.	Drum/barrel filler	<p>Filling drums with 200 l of gasoline. In the absence of good local exhaust ventilation the operator is exposed to vapours displaced from the drum. This task is also carried out within Distribution.</p>
1.5.	Tank cleaner	<p>This is a specialist activity usually involving specialist contractors. It is carried out under strict permitry procedures to ensure safe entry into a confined, potentially contaminated space. This task is also carried out within Distribution.</p>

APPENDIX 1 Description of tasks. *Continued*

	Job Group	Description of tasks/nature of exposure
2.	DISTRIBUTION	
2.1.	Road Tanker tasks	
2.1.a	Road Tanker Driver: Top loading	<p>In this task road tanker drivers fill their own vehicles by using the top loading procedure. The tanker compartments are filled through open hatches on top of the vehicle by the driver introducing the fill pipe and lowering it to the bottom of the compartment for 'submerged filling'. This method has generally replaced 'splash loading' in which a short fill pipe was used and liquid gasoline entered the vapour space of the compartment. The submerged filling technique results in less vaporisation of the liquid gasoline. As each compartment is filled, the driver must remove the fill pipe, drain it and insert it into the next compartment.</p> <p>Potential exposure results from displaced vapours through the open hatch as liquid fills the compartment, from spillage, from evaporation of liquid from the surface of the fill pipe as it is removed from one compartment and inserted into the next, tank dipping and closing hatch covers. Drivers stand up wind of the filling operation where possible.</p> <p>Actual exposure is subject to variables, e.g. weather conditions, loading of other tankers in adjacent bays, occasional spillages.</p>
2.1.b	Road Tanker Driver: Bottom loading	<p>In this task road tanker drivers fill their own vehicles by using the bottom loading procedure. The tanker compartments are filled through hose connections to manifolds on the vehicle near ground level. Potential exposure occurs during hose coupling and uncoupling procedures, and from vapour which may drift towards ground level from high level vents. As with top loading, actual exposure is subject to variables, e.g. weather conditions, loading of other tankers in adjacent bays, occasional spillages. Vapour recovery is becoming the norm (<i>Stage I vapour recovery</i>).</p>
2.1.c	Road Tanker Driver: other measurements	<p>This covers measurements made not falling into the categories of 2.1.a and 2.1.b, viz. delivery only, driving and delivery, full shift exposures where it is not known if loading was top or bottom. <i>During transfer of gasoline to storage at service stations vapour recovery is becoming the norm (Stage I vapour recovery)</i>.</p> <p>During driving there may be exposures if overalls/shoes/gloves are contaminated by spillages. During product transfer at delivery, hose handling, spillages, tank vents are possible sources of potential exposure.</p>
2.1.d	Rack operators and supervisors	<p>Duty to load road tanker vehicles for drivers. Potential exposure period greater than for driver loading. These operators are not common in Europe.</p>
2.2.	Rail car tasks	
2.2.a	Rail car operator: top loading	<p>Operators involved in top loading of rail cars. Exposures can occur during opening/closing hatches, checking fill levels and during ancillary activities, e.g. controlling car movements whilst at track level. Exposures vary depending on the design of the installation, e.g. degree of enclosure and automation, throughput, weather, product temperature, location of other vapour sources, spillages. Schedules for loading will vary, but generally last for several hr/day.</p> <p>Bottom loading (with vapour recovery) is replacing top loading. Exposure data given is for top loading operations. Bottom loading exposures are expected to be lower.</p>

APPENDIX 1 Description of tasks. *Continued*

	Job Group	Description of tasks/nature of exposure
2.2.b.	Rail car operator: off-loading to storage	This activity may be carried out by Terminal Operators as part of their overall duties or by dedicated staff. Exposure may occur from spillage during disconnection of hoses, leaks from connections, sampling.
2.3.	Marine tasks	
2.3.a	Jetty staff	Involved in supervision of ship loading operations. There is a potential for exposure from displaced vapours and whilst carrying out tasks such as sampling, tank dipping and handling of hoses. The position of vents, wind speed/direction, ambient/product temperatures are important variables likely to affect the level of exposure.
2.3.b	Deck crew	Ships - open loading: This involves open loading of ships in which tank tops, ullage ports or dip hatches are left open and displaced vapours may be vented close to deck level leading to personnel exposure. In addition, the following tasks carried out by deck crew may involve exposure, connection/disconnection of cargo lines, leaning over open hatches to check fill levels, and during tank dipping.
		Ships - closed loading: Closed loading limits release of vapour. Ullage measurements are read automatically and ullage ports and hatches are closed and displaced vapours are vented remotely. Exposures will vary depending on wind conditions, ambient/product temperature, vent locations in relation to personnel, and reliability of automatic ullage measurements. Exposures may also occur during connection/disconnection of cargo lines.
		Barges - closed loading: This covers similar operations to ships closed loading. Decks of barges are generally flatter than for ships and vapour vents may be at a lower level
2.3.c.	Bridge crew	Personnel who are located on the Ship/Barge bridge during loading.
2.4.	Product storage tasks	
2.4.	Terminal operators	These staff carry out a variety of tasks as per Off-site Operators under Refinery above. Some may also undertake some drum filling, see item 1.4. above.
3.	SERVICE STATIONS	
3.1.	Service station attendants	Exposure may occur during filling of customers' vehicles and from ambient air concentrations whilst handling payments or conducting other general duties, e.g. cleaning. Exposures will vary depending on, e.g. throughput of vehicles, ambient/product temperature, wind conditions, the degree to which the station may be enclosed and the extent of any spillages which occur. <i>(Future: vapour recovery will be included at the vehicle pump, Stage II vapour recovery.)</i>
3.2.	Cashiers	Exposure to ambient concentrations of vapour in the service station shop.
3.3.	Service Station Mechanic	Exposures may occur from residual fuel in the vehicle's fuel tank, background levels from the refuelling pumps on the forecourt (dependent on the location of the workshop in relation to refuelling pumps and climatic conditions). Gasoline is known to be used as a degreasant, although this usage is not condoned by the oil industry.

APPENDIX 1 Description of tasks. *Continued*

	Job Group	Description of tasks/nature of exposure
4.	AIRPORTS (aviation gasoline)	
4.1.	Operators	<p>Road tanker drivers fill their own vehicles. The tanker compartments are filled through hose connections to manifolds on the vehicle near ground level. Potential exposure during hose coupling and uncoupling procedures and from displaced vapour which may accumulate at ground level from the vehicle vent point. Actual exposures are subject to variables, e.g. spillages, weather conditions.</p> <p>During over-wing loading of light aircraft using an injection nozzle, exposure may occur from displaced vapour. This refuelling operation often requires the operator to visually check the fuel level in the tank to prevent over filling.</p>
4.2.	Yard staff	Tasks involving potential short term exposures are water testing (a litmus paper is dipped in the fuel), meter proving and meter servicing.