European Chemicals Bureau

CAS: 100-42-5
EC: 202-851-5

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Institute for Health and
Consumer Protection

**European
Chemicals
Bureau**

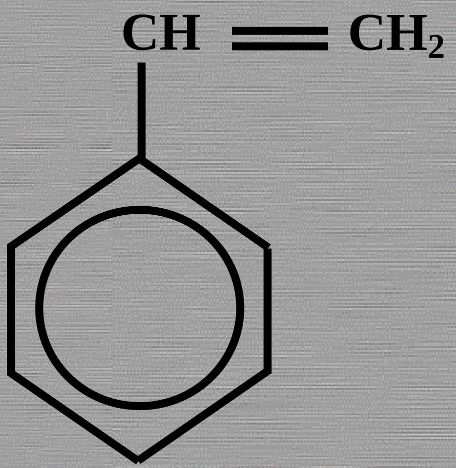
Existing Substances

European Union
Risk Assessment Report

CAS No: 100-42-5

EINECS No: 202-851-5

styrene
Part I - environment



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European Union Risk Assessment Report

STYRENE

Part I - Environment

CAS No: 100-42-5

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RISK ASSESSMENT

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STYRENE

Part I – Environment

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RISK ASSESSMENT

Final Report, 2002

United Kingdom

This document has been prepared by the UK rapporteur on behalf of the European Union. The scientific work on the environmental part was prepared by the Building Research Establishment (BRE), under contract to the rapporteur.

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Final report: 2002

(The last full literature survey for the environmental part was carried out in 1995 - targeted searches for plant toxicity information were carried out subsequently in December 2001).

Foreword

We are pleased to present this Risk Assessment Report which is the result of in-depth work carried out by experts in one Member State, working in co-operation with their counterparts in the other Member States, the Commission Services, Industry and public interest groups.

The Risk Assessment was carried out in accordance with Council Regulation (EEC) 793/93[1] on the evaluation and control of the risks of "existing" substances. "Existing" substances are chemical substances in use within the European Community before September 1981 and listed in the European Inventory of Existing Commercial Chemical Substances. Regulation 793/93 provides a systematic framework for the evaluation of the risks to human health and the environment of these substances if they are produced or imported into the Community in volumes above 10 tonnes per year.

There are four overall stages in the Regulation for reducing the risks: data collection, priority setting, risk assessment and risk reduction. Data provided by Industry are used by Member States and the Commission services to determine the priority of the substances which need to be assessed. For each substance on a priority list, a Member State volunteers to act as "Rapporteur", undertaking the in-depth Risk Assessment and recommending a strategy to limit the risks of exposure to the substance, if necessary.

The methods for carrying out an in-depth Risk Assessment at Community level are laid down in Commission Regulation (EC) 1488/94[2], which is supported by a technical guidance document[3]. Normally, the "Rapporteur" and individual companies producing, importing and/or using the chemicals work closely together to develop a draft Risk Assessment Report, which is then presented at a Meeting of Member State technical experts for endorsement. The Risk Assessment Report is then peer-reviewed by the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) which gives its opinion to the European Commission on the quality of the risk assessment.

If a Risk Assessment Report concludes that measures to reduce the risks of exposure to the substances are needed, beyond any measures which may already be in place, the next step in the process is for the "Rapporteur" to develop a proposal for a strategy to limit those risks.

The Risk Assessment Report is also presented to the Organisation for Economic Co-operation and Development as a contribution to the Chapter 19, Agenda 21 goals for evaluating chemicals, agreed at the United Nations Conference on Environment and Development, held in Rio de Janeiro in 1992.

This Risk Assessment improves our knowledge about the risks to human health and the environment from exposure to chemicals. We hope you will agree that the results of this in-depth study and intensive co-operation will make a worthwhile contribution to the Community objective of reducing the overall risks from exposure to chemicals.

Barry Mc Sweeney
Director-General
DG Joint Research Centre

Catherine Day
Director-General
DG Environment

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[1] O.J. No L 084, 05/04/199 p.0001 – 0075

[2] O.J. No L 161, 29/06/1994 p. 0003 – 0011

[3] Technical Guidance Document, Part I – V, ISBN 92-827-801 [1234]

0 OVERALL RESULTS OF THE RISK ASSESSMENT

CAS-No.:	100-42-5
EINECS-No.:	202-851-5
IUPAC name:	Styrene

Environment

Conclusion (ii) There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

This conclusion applies to all steps in the production and use of styrene and the use of styrene-containing products, for the aquatic compartment (including sediment), to microorganisms in wastewater treatment plants, to the terrestrial compartment and to the air compartment. No assessment of secondary poisoning for predators via the food chain has been carried out.

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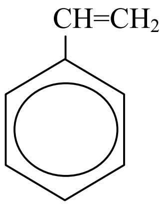
Euses Calculations can be viewed as part of the report at the website of the European Chemicals Bureau: http://ecb.jrc.it

TABLES

1 GENERAL SUBSTANCE INFORMATION

1.1 IDENTIFICATION OF THE SUBSTANCE

CAS-No.:	100-42-5
EINECS-No.:	202-851-5
IUPAC name:	Styrene
Molecular formula:	C_8H_8
Molecular weight	104.15
Structure:	



Styrene is a liquid at room temperature. The most common synonyms are cinnamene, ethenyl benzene, phenylethene, phenylethylene and vinylbenzene, together with the equivalent names in other languages. Styrene polymerises at room temperature in the presence of oxygen and oxidises in the presence of light and air. It is slightly soluble in water, but soluble in most organic solvents.

1.2 PURITY/IMPURITIES, ADDITIVES

1.2.1 Purity

The suppliers state that the purity varies from 99.7% to greater than 99.9% w/w.

The impurities (where stated in IUCLID) as % w/w comprise some or all of the following:

Ethylbenzene	<0.1
Isopropylbenzene (cumene)	<0.1
2-Phenylpropene	<0.1
Water	<0.025
Phenyl acetate	<0.02
p-Xylene	<0.06
m-Xylene	<0.001

The impurities vary with the plant and production method.

1.2.2 Additives

The only stated additive was 4-tert-butylpyrocatechol (4-tert-butylbenzene-1,2-diol) which is added as a polymerisation inhibitor at <0.006 – 0.01% w/w.

1.3 PHYSICO-CHEMICAL PROPERTIES

Data on the physico-chemical properties of styrene have been obtained from the IUCLID entries, from handbooks and from a number of other sources including a monograph on styrene. Neither the IUCLID data (which frequently quote handbooks) nor the handbooks give the conditions under which the tests were carried out, particularly the purity of the styrene used. Furthermore, while the literature may imply that there are a large number of measurements within a narrow range, suggesting a degree of consistency between independent measurements, the lack of reference to original papers means that it is possible that all of these are derived from one source value. Consequently it is hard to assess the quality of some of the data available and some of the data presented should be treated with caution.

The styrene monograph (Boundy and Boyer, 1952) does provide data on highly purified material (99.94 - 99.95% pure) which is of a similar order of purity to that sold commercially (99.7 - >99.9%). The monograph also provides details of test conditions used, and references to other original papers.

1.3.1 Physical state (at ntp)

Commercially-produced styrene is a colourless to slightly yellow volatile liquid with a sweet and pungent odour. The odour threshold is reported to be 0.15 ppm (BASF, 1989).

On exposure to light and air styrene polymerises but it can also oxidise to form certain aldehydes and ketones giving a sharp, penetrating, disagreeable odour (Boundy and Boyer, 1952).

1.3.2 Melting point

The melting point of styrene has been measured at -30.6, -30.7 and -31°C. The first value was presented in the consolidated IUCLID data set (BASF, 1990) and is the value quoted in the Merck Index (1989), by Mackay et al. (1993), and by Kirk-Othmer (1997). The latter two figures were presented in a second IUCLID entry and the CRC Handbook (1994), respectively.

Boundy and Boyer (1952) give a value of -30.63°C for high purity (99.4 - 99.5%) styrene, together with original literature references and experimental details.

1.3.3 Boiling point

The boiling point of styrene has been placed between 145 and 146°C. A value of 145.2°C is presented in the consolidated IUCLID data set (BASF, 1990). A range of 145 - 146°C is presented in the Merck Index (1989) and the CRC Handbook (1994), and by Mackay et al. (1993).

The value of 145.2°C is also presented in Boundy and Boyer (1952) as the boiling point for high purity (99.4 - 99.5%) material.

1.3.4 Relative density

The relative density of styrene has been measured at 0.901 - 0.906 at 20°C. The latter value is presented in the consolidated IUCLID data set (BASF, 1990), in the Merck Index (1989), the

CRC Handbook (1994) and Mackay et al. (1993). A value of 0.907 at 19.9°C is presented in Beilstein, while a value of 0.9014 at 25°C is presented by Chaiyavech et al. (1959).

A figure of 0.906 at 20°C is represented in Boundy and Boyer (1952) for high purity material (99.4-99.5%). The original literature references describe the experimental methods used.

1.3.5 Vapour pressure

A number of individual values for the vapour pressure of styrene have been presented both in IUCLID and from other sources: 3.4 hPa (0.34 kPa) at 10°C (Shell, unpublished); 6 - 10 hPa (0.6 - 1.0 kPa) at 20°C (BASF, 1990); 10 hPa (1 kPa) at 20°C (Elf Safety Data Sheet, quoted in IUCLID); 6.67 hPa (0.667 kPa) at 20°C, 12.66 hPa (1.266 kPa) at 30°C (Verschueren, 1983); 33 hPa (3.3 kPa) at 50°C (BASF, 1990); 53 hPa (5.3 kPa) at 60°C (unreferenced); 360 hPa (36 kPa) at 110°C (Shell, unpublished).

In addition to these, two sets of original data have been obtained and these are presented in **Table 1.1** (Dreyer et al., 1954; Chaiyavech et al., 1959).

Table 1.1 Vapour pressure data

Dreyer et al. (1954)		Chaiyavech et al. (1959)	
Temperature (°C)	Vapour pressure (kPa)	Temperature (°C)	Vapour pressure (kPa)
29.92	1.093	32.4	1.333
39.21	1.827	45.6	2.666
60.04	5.106	53.86	4.001
63.23	5.906	60.05	5.333
74.42	9.639	65.45	6.666
80.17	12.066	76.6	10.666
85.53	14.999	82.19	13.31
99.51	25.105		
110.06	35.877		
113.1	39.383		
123.81	50.329		
125.39	57.662		
125.41	57.915		
134.83	76.207		
137.23	81.326		
144.77	100.511		

The two sets of data are consistent with each other but unfortunately do not cover the range of greatest interest for the environmental assessment, between 10 and 30°C. However it is possible to extrapolate into this range to predict vapour pressure and to compare the predicted values with those quoted above to check their consistency.

The plot suggests that the critical vapour pressures are approximately 0.6 kPa at 20°C, 1 kPa at 25°C and 1.6 kPa at 30°C, suggesting that the "other information" including IUCLID data is consistent with the two sets of series information.

The value quoted by Verschueren for 20°C, 6.67 hPa (0.667 kPa), has been used for environmental modelling purposes later in this report.

1.3.6 Solubility

Styrene is slightly soluble in water (300 mg/l at 20°C). This value was presented in the consolidated IUCLID data set (BASF, 1990) and in Verschueren (1983) and Mackay et al. (1993). Kirk-Othmer (1997) presents an additional value of 0.032 % wt (320 mg/l) at 25°C.

Values of 0.029 g/100 g of water (290 mg/l) at 20°C and 0.034 g/100 g of water (340 mg/l) at 30°C are presented in Boundy and Boyer (1952), referenced to the original literature (Lane, 1946).

The solubilities presented for styrene are consistent with variations in purity, a degree of experimental variability and a certain amount of rounding of values. Apparently, experiments carried out "recently" indicate a solubility of 40 mg/l and 20 mg/l in fresh and seawater respectively (CSTEE personal communication, 2001). The source of these data was not given and so they have not been reviewed for this assessment. These values would not affect interpretation of the aquatic toxicity tests, as the effect levels are five to ten times lower, but the estimates of partitioning behaviour may be affected. Nevertheless, it should be noted that there is an existing measured Henry's law constant value that fits the existing solubility and vapour pressure values, but which would be an order of magnitude different using the new value for solubility. In addition, although the solubility values are from old studies, they appear to be consistent (around ten times higher than those mentioned by the CSTEE), and so a value of 300 mg/l is used for environmental modelling purposes in this report.

Styrene is miscible in all proportions with organic solvents such as ether, methanol, ethanol, acetone, benzene, toluene and carbon tetrachloride.

1.3.7 Partition coefficient

Three measured values for the octanol-water partition coefficient (as log Kow) are included in the IUCLID data set. These are 2.95 (Hansch and Leo, 1979), 2.96 (BASF, 1987) and 3.16 (Banerjee et al., 1980). In addition there are two calculated values presented, 2.82 (BASF, 1989) and 3.05 (Sangster, 1989). A value of 2.89 has been calculated using the SRC program KOWWIN.

The BASF measured value used OECD method 107, described in IUCLID as the shake-flask method. The styrene used was of high purity (99.7%); the concentration in the water phase was measured, and the concentration in the octanol phase was estimated by difference. The value from Hansch and Leo comes from an unpublished analysis, most likely using the shake-flask method. Banerjee et al. employed a version of the shake flask method using stainless steel centrifuge tubes and precautions to minimise volatility. They measured the concentration in both phases. The exact purity of the material used in these last two determinations is not known. The variability observed is in line with that expected from the method used. The value proposed by Sangster, 3.05, appears to be the mean of the two values available in the open literature (Hansch and Leo and Banerjee et al.). This value was recommended by Mackay et al. (1993) in their review of the data for styrene. Mackay et al. (1993) also quoted two determinations by HPLC, giving values of 2.76 (Fujisawa and Masuhara, 1981) and 2.90 (Wang et al., 1986).

In view of the agreement between the shake flask results, the mean log value from these studies has been used in the environmental modelling in this risk assessment (this is equivalent to taking the geometric mean of the actual measurements). This gives a value of 3.02.

1.3.8 Flash point

Values for the flash point, measured by the closed cup method, are presented as 31.0°C (BASF, 1990) and 34.4°C (NIOSH, 1983, quoted in a second IUCLID entry). Values measured by the open cup method are presented as 31.1 and 34.4°C (Kirk-Othmer, 1997).

A flash point of 31°C (open cup to ASTM standard) is presented in the styrene monograph (Boundy and Boyer, 1952). This figure is also quoted by the NFPA (1994). The latter quotes the fire point (the temperature at which the substance continues to burn once the source of ignition is removed) as 34°C.

The values presented can be considered as valid, noting that variation may occur depending on the purity of the styrene, the precise definition of “flash point” and the observation characteristics of the particular test method. The flash point of styrene will be considered to be 31°C.

1.3.9 Autoflammability

The autoflammability (autoignition) point of styrene has been quoted as 490°C in the consolidated IUCLID data set (BASF, 1990). The same value is quoted in the Merck Index (1989) and Kirk-Othmer (1997), the National Fire Protection Association (NFPA, 1994) and Boundy and Boyer (1952), the latter referring to a test method according to ASTM guidelines.

The autoignition point will be considered to be 490°C.

1.3.10 Explosivity

Styrene is not explosive as defined by Directive 67/548/EEC, on the basis of structure and oxygen balance calculations (Annex V to 79/831/EEC). However, the heavy vapour may burn explosively if ignited in an enclosed area (McLellan, 1994).

Flammability limits are quoted as 0.9 (lower) and 6.8 (higher) (NFPA, 1994) and 1.1 to 6.1 (quoted as a percentage in air, McLennan, 1994). The latter set of figures is also quoted by Boundy and Boyer (1952). The NFPA data are considered to be the best estimate since the values quoted by Boundy and Boyer have been calculated from vapour pressure studies, rather than measured test data.

Styrene can polymerise explosively in the absence of a stabiliser (McLellan, 1994). Styrene oxidises slowly in the presence of light and air to form peroxides.

1.3.11 Other physico-chemical properties

The vapour density of styrene is quoted as 3.6 (air = 1) (WHO, 1983).

1.3.12 Summary

Where several values for the physico-chemical properties of styrene are available, these are generally within a narrow range, consistent with experimental variability.

There is no value for the surface tension but this is not considered critical for the risk assessment.

Table 1.2 presents the values for the physico-chemical properties of styrene as used in this assessment report.

Table 1.2 Physico-chemical properties of styrene

Property	Value
Physical state	liquid
Boiling point (at 1 atmosphere)	145 - 146°C
Melting point	-30.6°C
Vapour pressure	5 mmHg (667 Pa) at 20°C
Water solubility	300 mg/l at 20°C
Octanol-water partition coefficient	3.02 (log value)
Density	0.906 g/cm^3 at 20°C
Vapour density (air = 1)	3.6
Flash point (closed cup)	31°C
Autoflammability	490°C
Conversion factors	1 mg/m^3 = 0.23 ppm:1 ppm = 4.33 mg/m^3

1.4 CLASSIFICATION

Styrene is classified as a dangerous substance within the meaning of Directive 67/548/EEC and is listed in Annex 1 of this directive, being assigned risk and safety phrases:

R10: Flammable
R20: Harmful by inhalation
R36/38: Irritating to eyes and skin
S2: Keep out of reach of children
S23: Do not breathe gas/fumes/vapour/spray.

There is currently no classification for the environment.

The acute toxicity values for fish, daphnia and algae all lie between 1 and 10 mg/l, which is the range for R51. Styrene is readily biodegradable and so is not expected to persist in the environment. However styrene has a log Kow value of ~3 so it may accumulate in organisms. An experimental study which indicated that styrene did not bioconcentrate to the levels expected from its Kow value is not considered valid. The available data therefore leave styrene on the borderline for classification. No further testing is required for the risk assessment as the available data are sufficient for this purpose. Rather than propose any testing solely for the purpose of classification, a search of IUCLID for information on related substances has been carried out (for toluene the draft ESR RAR was consulted). The results of this search are presented in **Table 1.3**.

Table 1.3 Aquatic bioconcentration data for related substances

Substance	Organism	Duration	BCF	Ref
Toluene [a)]	*Anguila japonica* (eel)	10 d	13.2	Ogata & Miyake (1978) *
	Leuciscus idus melanotus	3d	90	Freitag et al. (1985)
	Carrasius auratus		8.3	Ogata et al. (1984)
	Tapes semidecussata	8 d	1.9	Nunes & Benville (1979)
	Mytilus edulis	8 h	4.2	Geyer et al. (1982)
Ethylbenzene	*Carrasius auratus*		15	Ogata et al. (1984)
	Carassius auratus		79.43	Chiou et al. (1983) - not a BCF [b)]
	Tapes semidecussata	8 d	4.6	Nunes & Benville (1979)
o-Xylene	*Anguila japonica* (eel)	10 d	21.4	Ogata & Miyake (1975) *
	Tapes semidecussata	8 d	7.3	Nunes & Benville (1979)
	Carrasius auratus		14	Ogata et al. (1984)
m-Xylene	*Anguila japonica* (eel)	10 d	1.37	Ogata & Miyake (1975) *
	Carrasius auratus		15	Ogata et al. (1984)
	Tapes semidecussata	8 d	6.0	Nunes & Benville (1979)
p-Xylene	*Anguila japonica* (eel)	10 d	1.37	Ogata & Miyake (1975) *
	Carrasius auratus		15	Ogata et al. (1984)
	Carrasius auratus		2.2	Ogata & Miyake (1975) *

* reference not seen

[a)] taken from draft RAR except for Ogata et al. 1984

[b)] this paper deals with adsorption to soil organic matter, and does not appear to contain any BCF data

There are not many values available. The Ogata et al. (1984) study is the one in which styrene was tested and is not considered valid. The Freitag et al. (1985) study used radiolabelled substance, which may overestimate bioconcentration by including metabolites.

In the Nunes & Benville (1979) study the test organisms *Tapes semidecussata*, the Manila clam, were exposed to the water soluble fration from a crude oil. The exposure apparatus was designed to minimise volatilisation. Over the eight-day exposure the concentration of individual substances was monitored three times per day. The BCF values in the table are based on the concentrations in the water and in the organisms after eight days.

In addition to the studies reported above, Roubal et al. (1978) carried out exposures of coho salmon (*Oncorhyncus kisutch*) and starry flounder (*Platichthys stellatus*) to the water soluble fraction from a crude oil. Individual component substances were monitored in the water (including toluene, ethylbenzene, xylene isomers). In the fish the concentrations were measured as C_2 substituted, C_3 substituted etc. The bioconcentation factors for the C_2 group (the most relevant for styrene) were: in salmon muscle 1.1, 2.4, 2.0, and 1.0 after 2, 3, 5, and 6 weeks of exposure respectively; in starry flounder muscle 5.5 and 1.0 after 1 and 2 weeks, respectively .

There are no very high bioconcentration factors among the results for these substances. However there are no clear, well-reported determinations available. The highest value reported is 90 for toluene, which would be expected to give the lowest bioconcentration on the basis of the Kow values. All the other experimental results show much lower levels of accumulation. This includes in shellfish, where in general bioconcentration factors tend to be higher than for fish. On the basis of this comparison, styrene would not be expected to accumulate significantly. In the risk assessment a bioconcentration factor of 74 is used, as predicted from the partition coefficient. On the basis of the balance of the information available it is concluded that styrene will not accumulate in aquatic organisms and that R53 is therefore not appropriate. The Commission working group on the Classification and Labelling of Dangerous Substances at their meeting on 15-17 September 1999, agreed not to classify styrene for environmental effects.

2 GENERAL INFORMATION ON EXPOSURE

2.1 PRODUCTION METHODS

Styrene is produced commercially from crude oil by a sequence of processes.

Steam cracking of naphtha, obtained from the refining of crude oil, produces ethylene, propylene and a mixture of monocyclic hydrocarbons including benzene. Ethylene and benzene, fractionated from this mixture, are then reacted together in the presence of a catalyst to produce ethylbenzene.

Styrene is manufactured from ethylbenzene by one of two routes (Reinders, 1984; WHO, 1983). Firstly, it can be manufactured by dehydrogenation:

$$PhC_2H_5 \xrightarrow{\text{catalyst}} PhCH{=}CH_2 + H_2$$

Iron oxide is used as a catalyst, together with zinc and magnesium oxides. Steam is added as a dilution agent and to improve the heat transfer. The reaction is carried out at approximately 700°C and 0.8 bar. The purification of the reaction product is done by vacuum distillation. To prevent the polymerisation of the styrene, the conversion is carried out to only 60%, and there is always a reasonable dilution. The by-product gases formed in this reaction are either used as a fuel or flared.

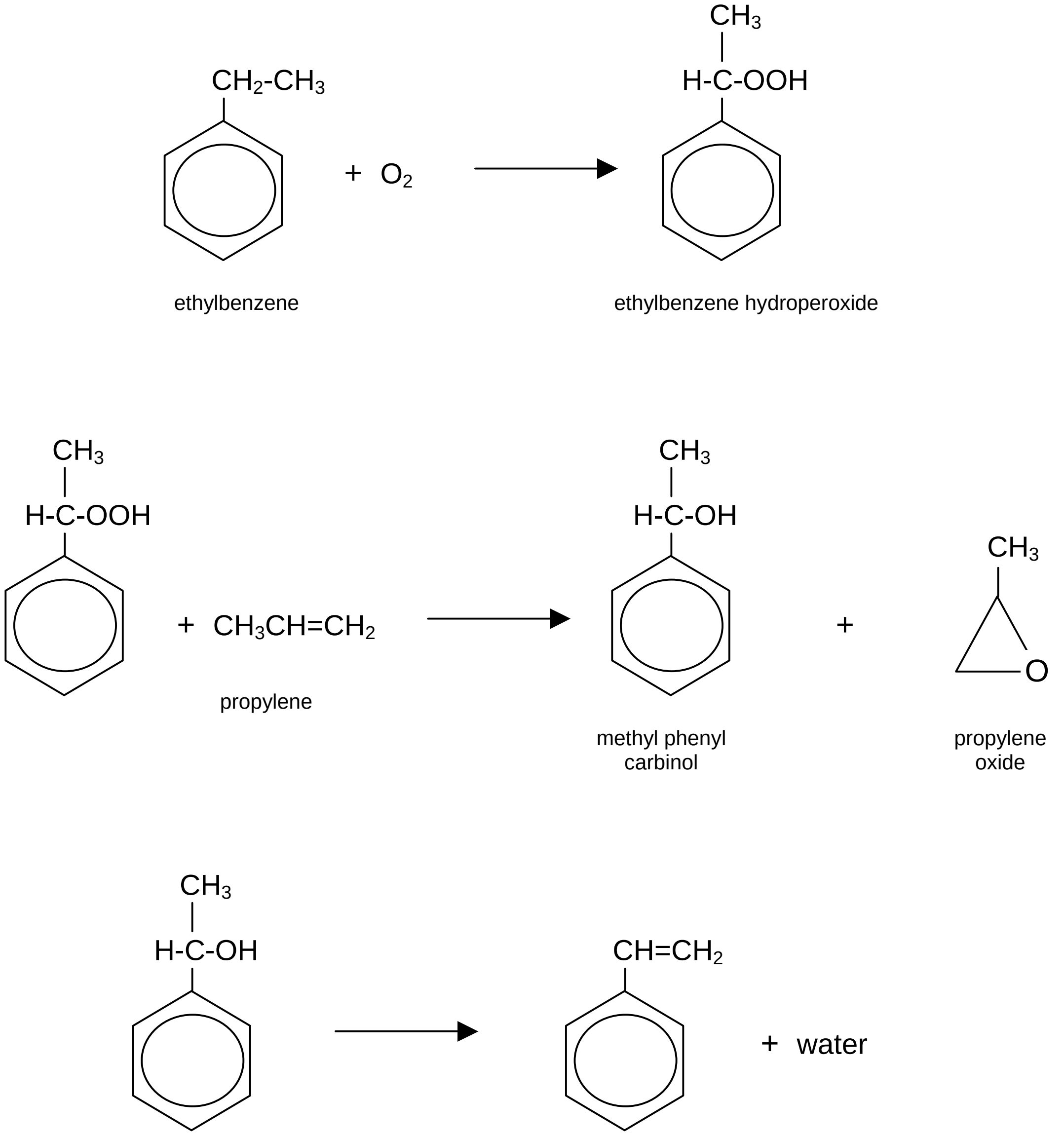
Alternatively, styrene may be manufactured by oxidation of ethylbenzene to the hydroperoxide by bubbling air through the liquid reaction mixture. The hydroperoxide is then reacted with propylene to yield propylene oxide and a co-product, methyl phenyl carbinol, again in the liquid phase. The carbinol is dehydrated to styrene over an acid catalyst at about 225°C. This reaction is shown in **Figure 2.1**.

2.2 PRODUCTION VOLUMES

Approximate world production of styrene in 1995 is given as 16.5 million tonnes (Kirk-Othmer, 1997). From information in IUCLID the range of production in EU countries is 2.22 to 4.91 million tonnes per year and the range of import tonnages is 30,000 to 150,000 tonnes, with nine companies producing or importing styrene in quantities of over 1,000 tonnes per annum.

A CEFIC report gives a figure for the production and use of styrene in Western Europe (including some countries not within the EC) as 3,743,000 tonnes in 1993. This is a more accurate estimate than simply adding the maximum capacities and so will be used throughout the report.

Figure 2.1 Reaction scheme for styrene production



2.3 USES

Styrene is processed in closed systems as an intermediate in the chemical industry. It is the monomer for polystyrene (general purpose, GP-PS; high impact, HI-PS; and expanded, EPS) and copolymer systems (acrylonitrile-butadiene-styrene, ABS; styrene-acrylonitrile, SAN; methyl methacrylate-butadiene-styrene, MBS; and others) and in the production of styrene-butadiene rubber (SBR) and related latices (SB latex for example). It is also used as a component of unsaturated polyester (UPE) resins. More details of the uses of styrene are given in the sections below (information taken from: Ashford (1994), Buchanan (1989), Heaton (1986), Kirk-Othmer (1997) and Reigel (1974)). **Table 2.1** presents a brief summary of the main uses of styrene polymers and copolymers, world-wide.

Table 2.1 Uses of styrene polymers and copolymers world-wide

Styrene products	Industrial and consumer applications
Polystyrene, GP-, HI-	General packaging, furniture, electrical equipment (e.g. audio-visual cassettes), industrial mouldings (e.g. dental, medical)
Polystyrene, EPS	Packaging, thermal insulation of refrigeration equipment and buildings
ABS	Interior and exterior automobile parts, drains, ventilation pipes, air conditioning, hobby equipment, casings etc.
SBR	Tyres, radiators and heater hoses, belts and seals, wire insulation
SB latex	Paper coatings, carpet backings, floor tile adhesives
UPE resins – glass reinforced	Building panels, marine products, household consumer goods, trucks
UPE resins – non-reinforced	Casting resins used for producing liners and seals, in putty and adhesives

The distribution of styrene usage in production of polymers and copolymers in Europe (1986 and 1993) and world-wide is presented in **Table 2.2**.

Table 2.2 Usage of styrene monomer

Use	World 1993 a)		Europe 1993 b)		Europe 1986 c)	
	tonnes	%	tonnes	%	tonnes	%
GP-, HI-PS	8,063,000	56.7	1,879,000	50.2	2,000,000	64
EPS	1,519,000	10.7	696,000	18.6		
ABS	1,559,000	11	397,000	10.6	360,000	11
SAN	271,000	1.9				
SB latex	1,027,000	7.2	389,000	10.6	410,000	13
SB rubber	1,011,000	7.1	209,000	5.6		
UPE resin	289,000	2	172,000	4.6	145,000	5
MBS	26,000	0.2				
SB resins	26,000	0.2				
Miscellaneous	418,000	2.9			210,000	7

Sources: a) Miller et al. (1994)
b) BP personal communication, derived from 1993 CEFIC figures
c) BUA (1990)

Detailed breakdowns of usage are not available, but in the UK there is some indication from the industry that SBR may be more widely produced than ABS, and the quantity of styrene monomer used in the production of UPE resins may be higher as a percentage of total styrene use than for Europe as a whole. Within the UK a small number of companies produce polystyrene, SBR and UPE resin. However there are hundreds of small and medium sized companies using these products: some 700 companies, for example, use UPE resins in the manufacture of glass-reinforced plastic and this number is expected to rise.

As an example of breakdown of use, the quantity of styrene polymers used in the UK have been estimated by industrial sector as shown in **Table 2.3** (Jolly et al., 1994).

Table 2.3 Consumption of styrene polymers by application in the UK

	Annual consumption	
	in tonnes	%
Polystyrene		
Packaging	59,800	31
Housewares	34,200	18
White goods	31,200	16
Brown goods	25,900	14
Miscellaneous	25,300	13
Building	10,000	5
Transport	3,500	2
Total	190,000	100
Expanded polystyrene		
Packaging	26,000	65
Building	12,400	31
Agriculture	1,600	4
Total	40,000	100
Acrylonitrile-butadiene-styrene copolymer		
Brown goods	27,600	43
White goods	32,100	37
Packaging	13,800	18
Miscellaneous	1,500	2
Total	75,000	100

Notes: “white goods” are domestic appliances such as washing machines fridges etc
“brown goods” are domestic equipment such as TVs videos etc

2.3.1 Polystyrene

General purpose grade polystyrene (GP-PS) is made by either a continuous mass process or by a suspension process. In the continuous process styrene, sometimes mixed with a non-polymerisable volatile diluent, is passed through two or more reactors with several heat exchange zones and agitators. The reaction mixture, now containing ~85% PS together with residual monomer, is then transferred to a low pressure high temperature devolatilisation tower where unreacted monomer and the diluent are removed and recycled. The hot polymer is then fed into an extruder where the polymer strands are cooled and cut into pellets.

In the suspension process, styrene is dispersed in water in the presence of 0.01-0.05% suspending agent and a polymerisation initiator (usually a mix of organic peroxides). The reaction mix is heated until polymerisation is substantially complete. The polymer beads are washed, dried and pelletised. GP-PS is easily processed to stable mouldings which have a variety of uses.

High impact polystyrene (HI) is a less brittle form of PS made by copolymerisation of styrene with up to 10% of polybutadiene or styrene-butadiene rubber. It too can be made by continuous or suspension processes. HI-PS is used mainly in packaging, in household/office equipment, refrigerator fittings and linings etc.

Information from producers indicates that the continuous process dominates the production of GP- and HI-PS, accounting for 90-95% of the production of these materials. The suspension process is only used for specialist products where particular properties are required.

A third form of polystyrene is expandable polystyrene, EPS, which is mainly produced by suspension polymerisation of styrene with the addition of a blowing agent such as *n*-pentane. It is used in insulation and protective packaging where it is blown out to become expanded polystyrene.

2.3.2 Styrene copolymers

A second major use of styrene is in the production of copolymer resins, ABS and SAN. Acrylonitrile/butadiene/styrene (ABS) usually consists of a styrene-acrylonitrile copolymer with a grafted disperse phase of polybutadiene rubber. The polybutadiene (or styrene-butadiene) rubber is first polymerised in water to give aqueous emulsions or latex. Acrylonitrile and styrene monomers are then added to continue polymerization within the latex.

In addition to the emulsion polymerisation described above, ABS can also be made by suspension and continuous mass processes. The suspension process involves dissolving polybutadiene rubber in the styrene and acrylonitrile monomers and adding a free-radical initiator and chain transfer agents. When a monomer conversion of 25-35% is reached the mixture is transferred to a suspension reactor where it is dispersed in water. Once the required degree of conversion has been reached the product is washed, dewatered and then dried.

The continuous mass process also begins with polybutadiene rubber dissolved in styrene and acrylonitrile monomers together with initiators and modifiers. The reaction begins in a pre-polymeriser in which the reaction causes ABS rubber to precipitate. When monomer conversion reaches around 30% the mixture is transferred to the bulk polymeriser and the reaction continues to 50-80% monomer conversion. The unreacted monomers are removed and recycled and the ABS is extruded, cooled in a water bath and pelletised. As this process does not use water as the reaction medium the need for dewatering and drying the product is removed and the amount of wastewater reduced.

The composition of ABS can vary widely depending on the required properties of the product. Additions such as methyl styrene or methyl methacrylate are also possible depending on the intended end use. A typical composition of ABS would be: 15-25% acrylonitrile, 5-30% 1,3-butadiene and 50-75% styrene. ABS is used on its own or with a range of other polymers in blends.

Styrene/acrylonitrile (SAN) resins are made by the controlled addition of styrene monomer to a solution of acrylonitrile. Copolymers with a high acrylonitrile content (70-80%) have low gas permeability and are used for containers and other household items.

Styrene is also used to make a number of other copolymers with butadiene, isoprene, methacrylate and methylstyrene amongst others (styrene butadiene rubbers are dealt with below).

2.3.3 Unsaturated polyester (UPE) resins

Styrene is added to unsaturated polyester resins to act as a cross-linking agent and reactive diluent in the production of glass-reinforced plastic. It also acts as a solvent for the resins. The styrene content of the resins can range from 30-50% depending on the degree of cross-linking required.

2.3.4 Styrene-butadiene rubbers

Styrene-butadiene rubber (SB rubber or SBR) is largely made by the co-polymerization of the two monomers in water although solution polymerisation (in an organic solvent) is also used. Reigel (1974) suggests one part styrene to three parts butadiene in eight parts water (by weight), using an emulsifying agent to disperse the monomers. Catalyst and modifying agent are added and the reaction allowed to proceed to the required extent. The resulting colloidal aqueous emulsion or latex (SB latex) is stripped of unreacted monomer (butadiene removed with a compressor and styrene by vacuum steam distillation) and homogenised after an antioxidant is added. This latex can be used directly for some purposes, or the rubber can be isolated from the latex by coagulation, removal and drying.

SB rubber can also be made by solution polymerisation, with the monomers dissolved in solvent. This allows greater manufacturing flexibility, and random, tapered and block co-polymers can be produced. More recent composition figures suggest a styrene content of 20-35% in latex and 23-25% in rubber, with up to 40% in some grades. SB latex is used in adhesives, paper coatings and foams; SB rubber is used in tyres, insulation and moulded rubber goods amongst others.

Other latices can be produced using styrene and butadiene. High styrene copolymers can have styrene contents of 80-85% and are produced by emulsion polymerisation. They are used as impregnating resins and for shoe soling. The addition of 5% carboxylic acid produces a carboxylated latex XSBR, with a solids content of 50-55%. The styrene content varies from 35-85%. They are used in adhesives and binders, for example in carpet underlay. The use of pyridine gives a latex known as PSBR, with 15% styrene, used in tyre cords and drive belt manufacture. In some statistics, particularly those describing the use of styrene, all these latices appear to be counted in together. Statistics on rubber production, on the other hand, tend to separate out the XSBR latices, but include others such as PSBR in the general SB latices.

2.4 RELEASES FROM PRODUCTION AND USE SITES

The production and usage of styrene monomer within individual EU member states varies, the major producer and user countries being Germany, France, the United Kingdom, Italy and The Netherlands.

In Section 3 estimates of releases from styrene production and use sites will be made. For this purpose it is necessary to obtain or estimate realistic sizes of large sites producing and using styrene. The largest production sites listed in IUCLID have capacities between 500,000 and 1,000,000 tonnes per year. **Table 2.4** lists the capacities of the largest users of styrene identified in Europe. For some areas information was only available for the UK, and in these cases the largest UK site is listed. The European production in each area is also given.

Table 2.4 Largest users of styrene in Europe

Product	Largest capacity (tonnes)	Note	European production (tonnes)	Note
GP-, HI-PS	125,000	a	1,879,000	
EPS	60,000	a	696,000	
ABS	50,000	b	794,000	d
SAN	50,000	e		
UPE	30,000	b	430,000	f
SBR	160,000	c	951,000	g
SB latex	35,000	c	188,000	g
XSBR	55,000	c	685,000	g

Notes:
- a - largest user identified from available information
- b - largest user in UK from Chem-Intell (1991)
- c - largest European user from IISRP (1994)
- d - from styrene usage figure for ABS and SAN assuming average styrene content of 50%
- e - assumed to be same as ABS
- f - from styrene usage figure assuming average styrene content of 40%
- g - European capacities from IISRP (1994)

2.5 CONTROLS

Styrene is an existing substance with a long history of production and use. A number of effective control measures to reduce emissions currently exist, whether simply adopted as part of plant design or added later in response to demands to reduce emissions into the workplace or the environment.

No information has been obtained on current legislative controls of emissions into the environment, or in relation to use in consumer products. Within the workplace, there are existing controls relating to particular industries; these are noted in more detail in the section on occupational exposure.

Occupational exposure limits vary, and should be considered in the context of the measurement and enforcement regimes used to ensure that the limits are met. Looking at the limits in isolation may be misleading in terms of the levels of exposure and consequently of risk that they imply.

3 ENVIRONMENT

3.1 EXPOSURE ASSESSMENT

3.1.1 Environmental releases

In this section information will be presented on the release of styrene to the environment at various points in its lifecycle. Releases can occur from production sites, from the processing of the monomer (with or without other monomers) into polymers, and from the further processing of the polymers to make articles. As the plastics produced can contain residual monomer, releases are possible during the lifetime of the articles. There may also be release on disposal at the end of their useful life. There are also 'indirect' sources of styrene release to the environment such as from cigarettes and from fuel. This section discusses these various possibilities and, as far as is possible, attempts to quantify the releases. These quantities will then be used in the assessment of environmental concentrations. Information relating specifically to styrene will be used where available, with default values from the Technical Guidance Document (TGD) being used to fill gaps in the data. Information on emissions to air and to water has been provided by producers and processors and this is used to estimate release factors in these sections. It is also used to calculate site-specific PECs in later sections.

3.1.1.1 Releases during production of styrene

Releases to air from production

Production and processing of styrene may occur on the same site, but there are also sites where the chemical is brought in for use in the production of polymers. Therefore the most appropriate Main Category for styrene is 1c, i.e. isolated intermediate stored off-site. The default emission factor from the TGD for a chemical with a vapour pressure of 667 Pa is 0.001, i.e. 1 kg/tonne. It is assumed throughout that production is continuous for 300 days per year.

Estimates of styrene emission to air from production have been found from a number of sources. Bouscaren et al. (1986) estimated a release of styrene of 0.2 kg/tonne produced. The BUA (1990) quoted figures from two German manufacturers of 0.001 and 0.007 kg/tonne.

Information on releases from specific plants has been provided by a number of manufacturers. This information has been used to calculate emission factors for these sites. In some cases the emission quantities provided are the result of both production of styrene and subsequent processing, so that they are likely to over-estimate the actual emission factor for styrene production alone. For six sites the emission factors obtained range from 0.001 to 0.13 kg/tonne; the highest factor for a site where only production takes place was 0.05 kg/tonne. For the generic assessment the highest factor, 0.13 kg/tonne, will be used. It should be noted that the release from which this factor was derived also includes some releases from processing.

The site-specific information will be used later in this report to calculate PECs for air at those sites. Applying the largest factor, 0.13 kg/tonne, to the largest size of plant identified in Section 2, with a capacity of 1,000,000 tonnes per annum gives a generic annual release of 130 tonnes of styrene.

The largest plant size, at 1,000,000 tonnes, is more than 10% of the styrene production capacity in the EU. Therefore the regional emission will be taken to be that from such a plant, at 130 tonnes per annum. The continental emissions are calculated by applying the factor above, 0.13 kg/tonne, to the remaining production tonnage, giving a release of 357 tonnes/year.

Releases to water from production

The default emission factor from the TGD for monomer production (category 1c) is 0.003, i.e. 3 kg/tonne.

No general values for releases from styrene production were found in the literature. BUA (1990, with subsequent amendment, J Ahlers, personal communication,1996) presented information on releases from two styrene production sites in Germany. From this information, emission factors of $8.0 \cdot 10^{-3}$ and $2.8 \cdot 10^{-4}$ kg/tonne have been estimated (releases after wastewater treatment).

Environment Canada (1993) estimated a total release of 64 tonnes per year from a production of 718,000 tonnes, giving an overall release factor of 0.089 kg/tonne styrene. The compartment of release was not specified. In the same report measurements on effluents from six industrial sites in the organic chemicals manufacturing sector were described. The highest average concentration measured was 71.7 µg/l, representing a loading of 0.511 kg/day from this source. This corresponds to 153 kg/year for 300 days operation.

Information has been provided by manufacturers of styrene on releases to water. This information is a mixture of released quantities and concentrations, measured at different points in the waste stream. Some of the values also include emissions of styrene from processing to polymers as well as from production. It is therefore difficult to derive a representative emission factor. The estimates of emission factors for releases to wastewater treatment plants range from 0.48 g/tonne to 0.25 kg/tonne (six values), with a mean value of 0.048 kg/tonne. Two values are available for emission factors for release to water following wastewater treatment: $1.0 \cdot 10^{-5}$ and $2.5 \cdot 10^{-4}$ kg/tonne. There are also two values for discharges directly into estuarine or marine waters, without wastewater treatment: 0.24 and 0.5 kg/tonne (one of these two sites ceased production in 1999, but the calculations for this site have been retained in the assessment).

Specific information is available for all production sites, and this will be used later in the report to calculate local PECs.

A worst-case emission factor for a generic release would be 0.25 kg/tonne; for a plant of 1,000,000 tonnes capacity this would give a release to wastewater treatment of 250 tonnes/year. This plant size is more than 10% of the styrene production capacity in the EU. Therefore the regional emission will be taken to be that from such a plant, at 250 tonnes per annum. The continental emissions are calculated by applying the factor above, 0.25 kg/tonne, to the remaining production tonnage, giving a release of 686 tonnes/year. This will be an over-estimate, as some of the releases are to estuarine or marine waters, and most production sites have lower release factors than that used.

3.1.1.2 Production of polymers and resins

Polystyrene

Releases to air during polystyrene production

Table A3.10 in the TGD gives the default emission factor for a monomer with a vapour pressure of 667 Pa in polymer production as 0.01, i.e. 10 kg/tonne.

Reinders (1984) gave an estimate for styrene emission from the production of polystyrene of 0.05-0.1 kg/tonne polystyrene, while Bouscaren et al. (1986) gave a higher figure of 1 kg/tonne polystyrene. BUA (1990) gave a figure of 0.03-0.3 kg/tonne polystyrene.

Information on releases from production of polystyrene at sites in Europe has been provided by Industry. This information has been used to estimate emission factors for this process. The values obtained are: 0.22, 0.3, **0.043**, 1.02, 0.053, 0.14, **0.36** and **0.22** kg/tonne. The values in bold underlined include emissions from styrene production in addition, and so are likely to be over-estimates to some degree.

Losses to air are mainly expected to occur during drying operations. As described in Section 2.3, 95% of GP- and HI-PS is made by the continuous mass process and so does not involve water except for cooling purposes. In contrast EPS is made by the suspension process; hence emissions from EPS production are expected to be greater. Unfortunately it is not possible to distinguish between the types of PS produced at the sites for which information is available. Therefore one value will be used to represent all production processes. As a worst-case realistic figure, 1.02 kg/tonne polystyrene will be used.

The largest site processing styrene to GI- and HI-PS polystyrene identified from the available information has a capacity of 125,000 tonnes/year (Section 2.4). Applying the derived emission factor to this gives a release of 127.5 tonnes/year to air. For EPS a representative site appears to be 60,000 tonnes; this gives a release of 61 tonnes/year to air. For releases on a regional scale, 10% of the EU production of polystyrene (all forms) was given in Section 2.4 as 257,000 tonnes. Applying the above factor to this gives a regional release to air of 263 tonnes/year, and a continental release of 2,364 tonnes/year.

Releases to water during polystyrene production

The default values from the TGD for styrene release during polymer production are 0.001 (i.e. 1 kg/tonne) for a wet process and zero for a dry process (Table A3.10, Type I). There is little published information available on releases to water.

Information has been supplied by Industry on releases from a number of sites producing polystyrene. From this information emission factors for this process have been estimated. It has been possible to identify the specific processes used at some of the sites. As noted above the vast majority of GP- and HI-PS is made by the continuous mass process involving little water, whilst EPS is made by a suspension process in water. For GP- and HI-PS production by the continuous mass process, estimates of $3.0 \cdot 10^{-6}$ and $1.2 \cdot 10^{-4}$ kg/tonne have been made. For non-specific production methods, the following values have been estimated: $1.25 \cdot 10^{-4}$, **$3.6 \cdot 10^{-4}$**, **$4.1 \cdot 10^{-3}$**, **$4.3 \cdot 10^{-3}$**, $5.3 \cdot 10^{-3}$, $6.3 \cdot 10^{-3}$ and **$1.1 \cdot 10^{-2}$** kg/tonne. Again, those values in bold underlined include emissions from styrene production in addition to polystyrene production.

APME (personal communication 1995) commented that the water used to cool the polymer before it is cut into pellets will contain ~1 µg/l, and that most of the residual monomer tends to partition into the polymer rather than remain in the water.

As there is some variation between the values the highest value for a plant making only polystyrene, $6.3 \cdot 10^{-3}$ kg/tonne, will be used for releases from EPS production. For GP- and HI-PS, as 95% is produced by the continuous mass process the higher value of those available for this process will be used, i.e. $1.2 \cdot 10^{-4}$ kg/tonne. It will be assumed that releases from the 5% of GP- and HI-PS made by other processes are similar to that from EPS.

From the information provided a realistic large site for PS production by the continuous mass process has a capacity of 125,000 tonnes. This gives a local release of 15 kg/year to water. For EPS production a realistic size appears to be 60,000 tonnes; hence the local release is 378 kg/year to water.

For the regional and continental scales there are 3 contributions to be calculated: GP- and HI-PS by the continuous mass process (95%); GP- and HI-PS by suspension polymerisation (5%); and EPS production. The regional tonnage of GP- and HI-PS is 188,000 tonnes; 95% of this gives 178,600 tonnes, and applying the factor of $1.2 \cdot 10^{-4}$ kg/tonne to this gives a release of 21 kg/year. For the 5% of GP- and HI-PS made by the suspension process, a factor of $6.3 \cdot 10^{-3}$ kg/tonne is used, giving a release of 59 kg/year. Finally, for EPS production the regional tonnage is 69,600 tonnes/year; applying the factor of $6.3 \cdot 10^{-3}$ kg/tonne gives a release of 438 kg/year. The total regional release from polystyrene production is 518 kg/year.

The equivalent continental tonnages are: continuous mass GI- and HI-PS 193 kg/year; suspension GI- and HI-PS 533 kg/year; EPS 3.95 tonnes/year; total 4.7 tonnes/year.

Styrene copolymers

Releases to air

Emissions to air from the reactors, driers and extruders have been estimated to be 0.1-4.0 kg/tonne ABS produced (Reinders, 1984). BUA (1990) suggested a lower range of 0.03-0.3 kg/tonne for ABS and SAN. As described in Section 2, continuous, suspension and emulsion processes can all be used to manufacture copolymers, depending on the properties required in the product. Industry has commented that in general there has been a move to continuous processing where possible, with resulting lower emissions. The most recent air emission values quoted above are similar to those estimated for polystyrene production.

No specific information on releases from copolymer production has been provided by Industry. In the absence of such information it will be assumed that releases are similar to those from polystyrene production. As a realistic worst-case estimate a value of 1.02 kg styrene/tonne styrene will be used. The release is assumed to relate to the amount of styrene used rather than the quantity of product; for polystyrene these are virtually the same so this distinction was not applied.

From Section 2.4 the largest capacity plant for ABS production in Europe is 50,000 tonnes. Taking a styrene content from the high end of the typical range, at 75%, this corresponds to a styrene usage of 37,500 tonnes/year. Applying the emission factor of 1.02 kg/tonne gives a release of 38.3 tonnes/year.

For SAN polymers the same capacity of plant as for ABS is assumed, at 50,000 tonnes. In this case the styrene content is 30%, giving a styrene usage of 15,000 tonnes. Applying the same emission factor gives a release of 15.3 tonnes/year.

For regional and continental releases the quantities of ABS and SAN are combined, giving a total polymer production of 794,000 tonnes/year. Taking the average styrene content as 50% this corresponds to a styrene usage of 397,000 tonnes. On the regional scale this gives a release of 40.5 tonnes/year; on the continental scale the release is 364 tonnes/year.

Releases to water

No specific information on release to water from ABS or other copolymer production is available. In view of the fact that the processes used are similar to those for polystyrene, it is assumed that similar release factors will apply. As there is no indication of the breakdown between continuous mass production and the other processes, as a worst-case assumption the value of $6.3 \cdot 10^{-3}$ kg/tonne styrene used will be applied. The release is assumed to relate to the amount of styrene used rather than the quantity of product; for polystyrene these are virtually the same so this distinction was not applied.

For ABS production the largest site identified has 50,000 tonnes capacity, using 37,000 tonnes of styrene (see above). An emission factor of $6.3 \cdot 10^{-3}$ kg/tonne results in a release of 233 kg/year.

For SAN production the production site is taken to be the same as for ABS, 50,000 tonnes, in this case using 15,000 tonnes of styrene. Applying the same emission factor gives a release of 95 kg/year.

The combined usage of styrene in ABS/SAN production in Europe is 397,000 tonnes (see above). The regional release is estimated as 250 kg/year, and the continental release as 2.3 tonnes/year.

UPE resins

Releases to air

The production of UPE resins effectively involves dissolving the other components in styrene, and as such is treated as a formulation step. The default emission factor from the TGD (Table A2.1) is 0.05, i.e. 50 kg/tonne of formulated product.

Emissions to air from plants producing UPE resins have been estimated as 0.3-0.6 kg/tonne resin (Reinders, 1984) and 0.03-0.3 kg/tonne resin (BUA, 1990). Information from the industry suggests that further control measures are being put in place in most countries in Europe which reduce these emissions effectively to negligible levels. However, the only specific information provided for this risk assessment leads to an emission factor of 0.8 kg/tonne resin, or 2 kg/tonne styrene. In the absence of a wider range of recent quantitative estimates the above factor will be used. This may lead to over-estimation of releases on the regional and continental scales.

The largest works producing UPE resins identified in the UK has a capacity of 30,000 tonnes resin; this uses 12,000 tonnes/year styrene monomer at ~40% styrene in the resin. Hence using the factor of 2 kg/tonne gives a local release to air of 24 tonnes/year. The EU production of UPE resins was estimated in Section 2.4 to be 430,000 tonnes resin/year, corresponding to a styrene usage of 172,000 tonnes. Applying the same factor leads to emissions of 34 tonnes/year to the region and 310 tonnes/year on the continental scale.

Releases to water

The default release from formulation of UPE resins from the TGD (Table A2.1) is 0.003, i.e. 3 kg/tonne of formulated product.

No literature information on releases to water was found. According to Industry, water is not used in the formulation process; the only losses to water would therefore come from spillages or accidents. Two producers of UPE resins provided information on concentrations in water discharged from their sites, and these give two quite different estimates of emission factors: $7.5 \cdot 10^{-6}$ and 0.049 kg/tonne styrene. The larger value will be used as a worst-case estimate.

For a site of capacity 30,000 tonnes, the water release is estimated as 588 kg/year. On the regional scale releases are 843 kg/year, and on the continental scale 7.6 tonnes/year.

Styrene butadiene rubber (SBR)

Releases to air

Emission factors for release of styrene to air are given by Bouscaren et al. (1986) as 5 kg/tonne for rubber and 1 kg/tonne for latex. The processes involved are again similar to those used for polystyrene and copolymers, involving both emulsion and solution polymerisation processes. A value of 0.23 kg/tonne has been estimated from information supplied by one producer; the site concerned produces both rubber and latex. In the absence of better information it will be assumed that the emissions are similar to those for polystyrene and an emission factor of 1.02 kg/tonne will be used.

A plant with capacity for 160,000 tonnes of SBR was identified in Section 2.4; for a styrene content of 25% this would use 40,000 tonnes of styrene. Using the emission factor of 1.02 kg/tonne gives a release of 41 tonnes/year. For latex production, a plant with a capacity of 55,000 tonnes for XSBR was identified in Section 2.4; at a styrene content of 60% (range 35-85%) this corresponds to 33,000 tonnes of styrene. The resulting emission is 34 tonnes/year.

Styrene use in this area in the EU is given as 598,000 tonnes in **Table 2.2**. Applying the release factor of 1.02 kg/tonne to 10% of this tonnage gives a regional release of 61 tonnes/year. Continental emissions are 549 tonnes/year.

Releases to water

No literature estimates of releases to water from SB rubber or latex production were found. Three producers of SB and SB latex provided information, which was used to derive the following emission factors: $4.4 \cdot 10^{-3}$, 1.0, and $1.4 \cdot 10^{-4}$ kg/tonne styrene used. The site giving a factor of 1.0 kg/tonne has a direct discharge to sea. The information available does not allow distinction to be made between rubber and latex production. As the production methods are similar to those used for some polystyrene production, the larger factor from polystyrene production, $6.3 \cdot 10^{-3}$ kg/tonne styrene, will be used here as well.

As described above, a plant producing 160,000 tonnes of SB rubber would use 40,000 tonnes of styrene. This leads to a local emission of 252 kg/year. For XSBR latex production a 55,000 tonne plant leads to a local emission of 208 kg/year. As above, styrene usage in this area of 598,000 tonnes in the EU leads to a regional release of 377 kg/year and a continental release of 3.4 tonnes.

3.1.1.3 Releases from processing of polymers

The polymers produced according to the processes described in the previous section contain some residual styrene monomer. **Table 3.1** shows historical levels of residual styrene in polymer and copolymer pellets. The trend is towards lower levels of monomer in polymers.

Table 3.1 Historical levels of residual styrene in polymer and copolymer pellets (MAFF, 1983)

Residual styrene (mg/kg) a)										
	Polystyrene		Expanded polystyrene e)		High impact polystyrene		Acrylonitrile-butadiene-styrene		Styrene-acrylonitrile	
Year	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max
1976	870	970			800	1,270	700 b)	1,600 b)		
1977	700; 800	1,020; 1,100			600	990	300 b)	1,060 b)	3,400	5,000
1978	380	580	1,400		420	840	300 b)	800 b)	1,000	1,550
1979	400	790	1,400		380	600	300 b); 600 c); 890 d)	700 b); 790 c); 1,220 d)	950	1,300
1980	410	600	1,000		360	490	300 b); 600 c); 700 d)	600 b); 1000 c); 870 d)	950	1,250

Notes:
a) - results obtained from a number of different converters. Each result refers to a specific converter
b) - Intended for food tubs
c) - Intended for refrigerator applications
d) - Intended for household appliances
e) - Level in expandable polystyrene beads

There can be release of monomer from this material during processing. Such releases are expected to be to air. BUA (1990) quote releases from polystyrene (GP, HI) and styrene copolymers as 0.07 kg/tonne polymer, and from expanded polystyrene as up to 0.9 kg/tonne. This seems a very high figure as the styrene content of modern EPS is only around 0.8 kg/tonne. More recent information from the industry (APME personal communication) suggests that around one third of this residual monomer is lost during processing, i.e. 0.25-0.3 kg/tonne EPS.

Table 3.2 (MAFF, 1983) shows the levels of styrene monomer in some plastics before and after processing (concentrating on food contact materials).

Table 3.2 Effect of processing on residual styrene levels in polymers and copolymers (MAFF, 1983)

				Residual styrene (mg/kg)			
				Granules		Final article	
Polymer/ copolymer	Nature of final article	Method of processing	Number of samples	Range	Mean	Range	Mean
HIPS	Food containers	Injection moulding	12	600-800	708	700-1,000	833
HIPS	Food Containers	Thermoforming	3	390-700	493	320-700	450
HIPS	Cups	Thermoforming	3	430-800	593	350-800	567
HIPS	Cutlery	Injection moulding	1		470		580
HIPS	Refrigerator lining	Thermoforming	1		630		700
PS	Cups	Injection moulding	3	490-610	557	550-700	640
PS	Food container	Injection moulding	1		1300		1,070
PS	Crisper tray	Injection moulding	1		770		810
PS	Cutlery	Injection moulding	1		750		800
EPS	Cups	Steam moulding	2	930-1,020	975	330-650	490
EPS	Trays	Thermoforming	2	340-510	425	360-500	430
ABS	Food containers	Thermoforming	24	150-500	315	120-400	246
ABS	Flour shaker	Injection moulding	1		380		370
SAN	Coffee percolator	Injection moulding	1		820		850

The figures show a general tendency for styrene levels to fall during thermoforming operations. In contrast the levels appear to rise slightly in injection moulding. This latter effect is thought to be due to slight thermal decomposition caused by the higher temperatures involved in injection moulding.

For dispersions containing styrene (e.g. SB latex), BUA (1990) suggests that between 50 and 100% of the residual monomer could be released to the atmosphere depending on the coating and drying processes. The residual level of styrene in most latices is <500 mg/kg, with a lower figure of <200 mg/kg having been agreed by European manufacturers for dispersion for use in the carpet industry. The worst-case release would be 0.25-0.5 kg/tonne.

The polyester resins are a different case in that they contain large quantities of styrene monomer at the processing stage (~40% by weight, as both reactant and solvent). Consequently the losses here can be much higher. In simple terms processing involves mixing the resin with a catalyst and applying it to glass fibre reinforcement. There are various methods by which this is done, including spray application of resin and reinforcement and hand application by brush or roller depending on the scale of the operation. The article is then left to cure at room temperature for a period. Smaller manufactured articles may undergo a post-curing period at 80-85 °C for several hours to reduce the residual levels of styrene. This is especially true for items likely to come into contact with food. BUA (1990) estimated losses from this process as 40 kg/tonne, with a maximum of 120 kg/tonne. Crandall and Hartle (1985) suggest losses of 10-15% of styrene into air; for a styrene content in resin of 40% this is 40-60 kg/tonne. Styrene losses may be reduced by the addition of a skin-forming chemical, which migrates to the surface of the resin after the catalyst is added but before the resin gels. This acts as a barrier to the evaporation of styrene.

Brighton et al. (1979) point out that these agents can only act over a short period of time and so may have a limited effect. However, Laplanche et al. (1985) measured styrene losses from ordinary resins and reduced emission resins; they found 25 and 16% loss for the ordinary resins and 12 and 11.5% loss from the low emission resins. These figures are all at the high end of those measured by other researchers.

In much of Northern Europe styrene emissions from UPE processing have been reduced through the use of improved low emission resins and through the use of closed mould processes. Thus a more recent estimate of releases of styrene from the use of UPE resins is given by GPRMC (European Organisation of Reinforced Plastics/Composite Materials) as 5-8% of the styrene content. The higher figure will be used for the regional and local releases, giving 1,376 tonnes/year to air in the region and 12,384 tonnes/year to air on the continental scale. For the local release as a worst case it will be assumed that such measures are not in place, and so a higher value of 100 kg/tonne resin will be used.

The sites where these processing activities take place are likely to be much smaller than those producing styrene and raw polymers. A study on the UK plastics industry (UCD, 1998) estimated that there were around 4,000 converters (processors) in the UK. This study also estimated the sizes of the plants converting polymers, based on numbers of workers, for use as realistic worst cases. These sizes are included in **Table 3.3** in the column "Use per site". The values for SB rubber and latex have been estimated by similar methods to those in UCD 1998. **Table 3.3** shows the estimated releases from processing.

Table 3.3 Styrene releases from plastics processing (all to air)

Material	European styrene consumption (kt)	Fraction in product (%)	Quantity of product (kt)	Use per site (tonnes)	Release factor (kg/tonne)	Local release (tonnes)	Regional release (tonnes)	Continental release (tonnes)
HI,GP PS	1,879	100	1,879	1,617	0.07	0.11	13.2	118
EPS	696	100	696	2,790	0.3	0.84	20.9	188
ABS/SAN	397	50 [a)]	794	506	0.07	0.04	5.6	50
SB latex [c)]	40	25	160	96	0.5	0.05	8	72
XSBR latex [c)]	347	60	582	359	0.5	0.17	29	262
SB rubber	210	25	840	504	0.5 [b)]	0.25	42	378
UPE	172	40	430	781	100 [d)]	78	1376	12,384

Notes: [a)] - ABS content 60%, SAN content 20-30%
[b)] - in absence of data assumed to be same as SB latex
[c)] - styrene usage in latices (389 kt in total) split in ratio of capacities for styrene use in each area (from IISRP 1994 figures)
[d)] - worst-case estimate assuming no use of low emission resins

3.1.1.4 Releases from articles in use

As discussed above polymers can contain residual monomer. In some cases this is reduced by processing but most finished articles will contain some styrene monomer. Some or all of this may be released during the useful lifetime of the article. Residual levels in processed materials (in 1980) are shown in **Table 3.4**.

Table 3.4 Levels of residual styrene in polymer and copolymer food contact materials and articles in 1980 (MAFF, 1983)

Polymer or copolymer	Residual styrene (mg/kg)	
	Typical	Maximum
Polystyrene	300-1,000	2,500
Expanded polystyrene	300-1,000	2,000
High impact polystyrene	300-1,000	2,500
Acrylonitrile-butadiene-styrene (for food tubs)	200-300	600
Acrylonitrile-butadiene-styrene (for other uses)	300-1,000	2,000
Styrene-acrylonitrile	600-1,200	2,000
Methyl methacrylate-butadiene-styrene	ND-10	30
Styrene-butadiene block copolymer		
Glass reinforced plastic	20-200	1,000
Styrene-acrylic copolymers	60 in latex	
Styrene-butadiene-styrene [a)]		
Styrene-isoprene-styrene [a)]		
Methylstyrene-vinyltoluene resin [a)]		
Styrene-butadiene - raw polymer	10-30	
- cured polymer		

Note: [a)] - not used for direct food contact purposes

Levels have been reduced by improvements in production methods; a more recent estimate is that most polystyrene is made to have a residual content of 300-600 mg/kg styrene, with typical levels being ~400 mg/kg (APME personal communication, 1995). An exception is expandable polystyrene where the typical level is 800 mg/kg. ABS polymers also typically contain ~400 mg/kg.

It is clear from measurements on levels in food (see Section 3.1.6.1) that migration of the monomer from plastic to food can occur. Varner and Breder (1981a) measured leaching rates from foam cups into water, tea and coffee of 0.0077, 0.0078 and 0.0078 $\mu g/cm^3$, respectively. Leaching into ethanol solution was greater.

There is less evidence of losses of styrene to air from finished articles although this might be expected owing to the volatility of the chemical. Varner and Breder (1981b) examined three types of polystyrene at an interval of six months to determine any loss of residual monomer. No change was seen in flexible or rigid polystyrene cold drinks cups, but there appeared to be some loss (from 104 ppm to 71 ppm residual styrene) from foam hot drinks cups. BUA (1990) reported that measurements on the residual monomer content of polystyrene and styrene copolymers (300-500 ppm) did not reveal any loss of monomer over 2 years. From studies on the behaviour of filling materials, BUA (1990) estimated emissions of styrene as ~1 g/tonne plastic, equivalent to an annual release in Germany of <1 tonne. APME (personal communication) suggests that emissions are more likely to be in the range 0-50 g/tonne. An average value of 25 g/tonne will be taken.

The emissions from expanded polystyrene were estimated by BUA (1990) to be higher, at 110 tonnes/year. The consumption of all polystyrene in Germany was 500,000 tonnes; assuming 30% of this was EPS, 115,000 tonnes of EPS emitted 110 tonnes, a release rate of 0.07%. APME (personal communication) comments that the typical level of styrene in an EPS moulding will decrease from an initial value of 500 mg/kg to an equilibrium level of ~200 mg/kg over a period of 2-5 years depending on use. They suggest a more realistic emission factor of 0.03% (0.3 g/kg) which would be more appropriate for long-term use (e.g. insulation in buildings) and would over-estimate losses for short lifetime applications such as packaging.

No data were found on emissions from polyester resin articles. As noted above, such articles may undergo post curing to remove most of the monomer, but residual levels may still be as high as 20-200 mg/kg (MAFF, 1983). This may reduce as further cross-linking occurs. There is also no information on releases from styrene-containing dispersions, although BUA (1990) suggests that most of the release occurs when they are processed as coating materials, as discussed above. Hence, later releases from these materials are expected to be low.

In the absence of detailed information it will be assumed that the release factor of 25 g/tonne applies to all materials except EPS, for which the higher factor of 0.3 g/kg will be used. It will also be assumed that the materials produced in one year replace those disposed of in the same period, i.e. that there is a 'steady state' in the amount of styrene-containing materials in use. The releases will be disperse and so will be calculated for the regional and continental scales only. For the region, 69,600 tonnes EPS gives a release of 21 tonnes/year, and 468,500 tonnes of other materials gives 12 tonnes. The continental figures are nine times greater than these, at 189 and 105 tonnes, respectively.

3.1.1.5 Release on disposal

There are two main routes for the disposal of articles made from styrene-containing polymers - incineration and waste burial. Releases to the environment may arise from each of these routes. WHO (1983) states that styrene may be released through the incineration of many types of styrene polymer. Plastics are valued for incineration because although emissions can be a problem they have a high calorific value and are ideal as fuel for heat recovery. There is little information on release from incineration, but it has been suggested that removal rates of better than 99.98% can be achieved (personal communication, Dow Chemicals). If it is assumed that 30% of styrene-containing waste goes for incineration then this accounts for 1,122,900 tonnes of styrene. If the maximum release is 0.02% then this gives a maximum amount from incineration of 225 tonnes/year in Europe; the regional release is 22.5 tonnes and the continental release is 202.5 tonnes.

BUA (1990) comments that styrene waste from production and processing is incinerated when recycling is no longer possible.

The other likely disposal route is burial. As styrene-containing polymers decay they may release any residual monomer, to the atmosphere or into leachate. However, polystyrene and styrene copolymers are considered resistant to biodegradation so decomposition to the monomer is unlikely (Hamilton et al., 1995). Little information is available on the extent of such releases. Studies on degradation (see Section 3.1.2.1.2) suggest that styrene may degrade in ground water, but high levels of styrene have been measured in ground water near sites where styrene waste was buried. BUA (1990) estimated a release of 160 tonnes/year of styrene in Germany on the assumption that all the residual monomer from polymers and copolymers was released. This comes from a consumption of 1,000,000 tonnes of styrene in polymers and other products. Assuming that 70% of this goes to landfill then 700,000 tonnes of styrene gives rise to 160 tonnes released, or an emission rate of 0.023%. Consumption of styrene in Europe is 3,743,000 tonnes, assuming negligible net import or export. Assuming 70% to landfill, the total release is thus 600 tonnes/year; the regional release is 10% of this at 60 tonnes and the continental release is 540 tonnes. These releases are arbitrarily divided 50:50 between air and water. It is recognised that this is likely to be a large over-estimate.

3.1.1.6 Other sources

Other disperse releases of styrene have been found in a number of different areas, including cigarette smoke and vehicle exhausts.

Various estimates of emission of styrene from cigarettes have been reported. Environment Canada (1993) suggests 10 µg/cigarette, whilst WHO (1983) reports levels from 18 to 48 µg/cigarette. Higgins et al. (1983) analysed gas phase styrene in mainstream smoke of cigarettes with tar levels 45 to <0.01 mg/cigarette and found styrene quantities at 13 to 0.002 µg/cigarette. In general styrene levels reduced with tar level; the authors note that styrene distributes more into the particulate phase than the gas phase.

In the UK there were approximately 85,000 million cigarettes sold in 1992 (CSU, 1994). Assuming an average release of 20 µg styrene per cigarette, this constitutes a release of 1.7 tonnes per year in the UK. The regional model contains 20 million inhabitants, so scaling this figure down (from the 55 million inhabitants in the UK) the disperse release from cigarettes is 0.62 tonnes. Clearly there are a number of approximations in this analysis, but the release is so small that further refinements do not seem necessary.

Styrene is not a component of crude oil or vehicle fuel, so evaporative losses do not arise. Of 150 compounds identified in gasoline vapour from 13 countries, styrene was not found to be present (CONCAWE, 1987). Styrene is, however, a constituent of vehicle exhaust fumes. Bouscaren et al. (1986) collected values for the styrene content of exhaust fumes; they adopted a value of 1% of the aromatic content of the exhaust gases based on two reports from 1971 and 1984. This figure is for emissions from gasoline-using vehicles; styrene was not identified as a component of exhaust emissions from diesel- and LPG-powered vehicles. The composition of exhaust emissions varies with a number of factors, including the condition of the engine, speed, engine load, presence or absence of a catalytic converter and the ambient temperature. Stump et al. (1990) showed that the aromatic content of the emissions increased at lower temperatures, contributing ~30% at 4.4°C to a total hydrocarbon emission of 0.75 g/km. Taking this as a reasonable worst case and assuming that 1% of the aromatic content is styrene gives a styrene emission rate of 2.3 mg/km. Traffic volume in Western Europe in 1992 was estimated to be $2.2 \cdot 10^{12}$ km (IISRP, 1994); using this figure will overestimate styrene emissions as it includes diesel vehicles. The estimated emissions for Western Europe are 5,060 tonnes; taking 10% of this for the regional release gives 506 tonnes, with the continental release as 4,554 tonnes.

Styrene has been found to be emitted from the exhaust of outboard motors. Jüttner (1994) found that a 4-stroke motor in a test stand basin, running on unleaded gasoline, emitted 9.3 mg of styrene in a 10-minute period. Measurements were also taken from a freshwater lake during heavy boat traffic (Jüttner, 1988). The concentration of styrene rose rapidly with the number of boats. It is not possible to quantify the total release from this source.

3.1.1.7 Summary of release estimates

The releases estimated above are summarised in **Table 3.5**.

Table 3.5 Releases of styrene (tonnes/year)

Source	Local		Regional		Continental	
	Air	Water	Air	Water	Air	Water
Production a)	130	250	130	250	357	686
Polymers:						
GP-, HI-PS	128	0.02	} 263	0.08	} 2,364	0.73
EPS	61	0.38		0.45		4.0
Copolymer ABS a)	38.3	0.23	} 40.5	} 0.25	} 364	} 2.3
Copolymer SAN a)	15.3	0.1				
UPE a)	24	0.59	34	0.84	310	7.6
SBR a)	41	0.25	} 61	} 0.38	} 549	} 3.4
SB latex a,b)	34	0.21				
Polymer processing:						
PS (HI,GP)	0.11		13.2		118	
EPS	0.84		20.9		188	
ABS/SAN	0.04		5.6		50	
SB latex	0.05		8		72	
XSBR latex	0.17		29		262	
SB rubber	0.25		42		378	
UPE	78		1,376		12,384	
Plastics in use:						
EPS			21		189	
Others			12		105	
Disposal:						
Incineration			22.5		203	
Landfill			30	30	270	270
Others:						
Exhausts			506		4,554	
Cigarettes			0.62		5.6	
Total			2,615	282	22,722	974

Notes: a) - largest works is greater than 10% of European figure and so is used for regional estimate
b) - includes all latices

3.1.2 Environmental fate

3.1.2.1 Degradation

Once in the environment, a number of processes can affect the distribution of styrene. The dominant processes are photooxidation, volatilisation and biotransformation. The majority of styrene released into the environment is expected to reach the atmosphere due to its high potential for volatilisation. Styrene is rapidly degraded in the atmosphere by reaction with hydroxyl radicals and tropospheric ozone. Volatilisation from soil and water is rapid and styrene is readily biodegradable. It has been suggested however, that low concentrations of styrene may persist in water. Some bioaccumulation and adsorption to soils and sediments may occur. Styrene has a moderate mobility in soil.

3.1.2.1.1 Abiotic degradation

Photolysis

Styrene does not adsorb solar radiation appreciably at wavelengths greater than 300 nm, therefore degradation of styrene by direct photolysis is unlikely.

Photooxidation

Hydroxyl radicals and tropospheric ozone rapidly degrade styrene in the atmosphere. **Table 3.6** summarises the photodegradation data.

Table 3.6 Photooxidation rate constants for styrene with OH and ozone radicals

Rate constant $cm^3 \cdot molecule^{-1} \cdot s^{-1}$	Half-life (hours) [a]	Method	Reference
OH radicals			
$5.3 \cdot 10^{-11}$	7.2	calculated	Hazardous Substances Database (1993)
$5.3 \pm 0.5 \cdot 10^{-11}$	7.2	smog chamber, relative reaction rate	Bignozzi et al. (1981)
$5.2 \pm 0.5 \cdot 10^{-11}$	7.4	recommended	Atkinson (1985)
Ozone			
$2.16 \cdot 10^{-17}$	12.7	ozone decay rate	Atkinson et al. (1982)
$2.99 \cdot 10^{-17}$	9.2	absolute rate in flow-through system	Bufalini & Altshuller (1965)
$2.7 \cdot 10^{-17}$	10.1	measured	Grosjean (1985)
$1.71 \cdot 10^{-17}$	16.0	ozone decay rate	Tuazon et al. (1993)
OH radicals and ozone			
	2.5 hrs	calculated	Hazardous Substances Database (1993)
	51 mins - 7.3 hrs	calculated	Howard et al. (1991)

Note: [a] half-lives calculated from quoted rate constants using $5 \cdot 10^5$ molecule $\cdot$ cm^{-3} and $7 \cdot 10^{11}$ molecule $\cdot$ cm^{-3} for hydroxyl radical and ozone concentrations respectively.

The values of $5.2 \cdot 10^{-11}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ for k_{OH} and $2.99 \cdot 10^{-17}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ for k_{ozone} will be used in the regional and continental modelling later in this assessment. These give a half-life of 4.0 hours.

Bignozzi et al. (1981) studied the reaction between styrene and hydroxyl radicals in a smog chamber with 65% relative humidity, with NO added to suppress the build up of ozone which would react with styrene in competition. The reaction products found were benzaldehyde and formaldehyde, suggesting that attack took place only on the olefinic moiety of styrene.

Tuazon et al. (1993) monitored the ozone decay rate in the presence of excess styrene. The main products were the same as with hydroxyl radicals, with formaldehyde in 37±5% yield and benzaldehyde in 41±5% yield. Carbon monoxide, carbon dioxide and formic acid were also formed. Grosjean (1985) also found the same two major products together with benzoic acid and a trace of formic acid. They saw no evidence for reaction between these secondary products and ozone under the conditions used (in dry air in the dark). They calculated that equal removal of styrene by reaction with ozone and OH radicals is achieved when the concentration of ozone is 40 ppb if the hydroxyl radical concentration is $5 \cdot 10^5$ $mol \cdot cm^{-3}$ (which is the average level assumed in the TGD). Therefore the reaction with ozone can rapidly become the major loss process, especially in polluted urban air.

Mansour et al. (1985) studied the photodegradation of compounds in water. A relative rate method was used to determine the degradation of styrene by OH radicals in water, produced by the photolysis of H_2O_2. The relative rate constant was $3.37 \cdot 10^9$. Correcting this for an OH concentration of 10^{-17} mol/l, this produces a half-life of 237 days for this degradation route (BUA, 1990).

Organic compounds such as styrene which react readily with hydroxyl radicals in the atmosphere may contribute to the formation of photochemical ozone. However, as noted above styrene also reacts with ozone relatively quickly. Derwent et al. (1998) calculated the photochemical ozone creation potential (POCP) for 120 organic compounds. Relative to ethylene, which has a POCP set to 100, styrene has a POCP of 14.2. For comparison, ethane, which is considered to make a negligible contribution to ozone formation, has a POCP of 12.3. Thus styrene emissions are not expected to contribute significantly to photochemical ozone formation.

Hydrolysis

Styrene contains no hydrolysable groups (Howard et al., 1991).

Summary

The main abiotic routes of degradation are reaction in the atmosphere with hydroxyl radicals and ozone; a half-life of 4.0 hours is estimated.

3.1.2.1.2 Biotic degradation

Styrene can be degraded quite readily in water under aerobic conditions. The biodegradation half-life in water has been estimated to be 2-4 weeks (Howard et al., 1991).

In studies with lake water, aquifer solids, sewage and groundwater, Fu and Alexander (1992) found that the rate and extent of mineralisation (from microbial activity) depended on the type of sample. Extensive degradation in sewage and some soils was observed when the samples presumably were aerobic. Mineralisation was less extensive under waterlogged conditions, but the lack of oxygen may have resulted in the accumulation of organic products. The rate of mineralisation was directly proportional to concentration at 1 mg/kg and below, which suggests first-order kinetics, but the rate was less than directly proportional above 1 mg/kg of soil. The finding that the percentage mineralised per hour decreased in lake water and aquifer sand with decreasing styrene concentrations is consistent with the view that a threshold exists in these environments; however the threshold concentration was below the lowest concentration tested (2.5 μg/l). No evidence was found for a threshold in soil. The authors also investigated the sorption of styrene in a number of soil samples. Although sorption to the soil solids was appreciable, and the degree of sorption was related to the organic matter content of the samples, styrene was extensively mineralised in all but one of the samples. The reason for the lesser extent of mineralisation on the Erie silt loam was suggested to be the lower pH of this sample.

A mixed population of bacteria capable of utilising styrene as a sole carbon source was obtained from landfill soil and enriched (Sielicki et al., 1978). It was found that two different mechanisms were responsible for the disappearance of styrene. The first was oxidation to phenylethanol and phenylacetic acid. They also noted the spontaneous polymerisation of monomer to low molecular weight oligomers, which were then further metabolised. The report suggests that this was due to microbial removal of the inhibitor added to prevent polymerisation, and demonstrated that a styrene-acclimated culture could degrade the inhibitor.

The same mixed population of bacteria was then used to assess the degradation of [8-^{14}C]-styrene in two soils - a heterogeneous landfill soil (0.35% organic matter) and a neutral Californian top soil (2% organic matter). The loss of labelled carbon recovered as $^{14}CO_2$ was used to estimate the percentage decomposition over a 16-week period. From a 200 mg application, 95% degraded in the landfill soil, whereas 87% degraded in the top soil. From a 500 mg application, a significantly smaller percentage degraded.

Degradation of 2.3-4.3% per week and 3.8-12.0% per week in subsurface soil was shown with samples taken directly above and below the water table at two uncontaminated sites in the US (Wilson et al., 1983).

Biofilms were used to model microbiological processes affecting transformations of organic micropollutants in the subsurface. Removal of greater than 99% in an aerobic biofilm column with 20 minutes detention time and 8% removal in a methanogenic biofilm column with a two-day detention time were reported (Bouwer and McCarthy, 1984).

Ready biodegradation

Several tests are available which show that styrene is readily biodegradable.

Ready biodegradability test ISO DIS 9408 (Directive 79/831/EEC Annex V, Part C – manometric respirometry test, equivalent to OECD 301F) was carried out by BASF AG (Ecological laboratory, unpublished data, test no. 388576, 1988). From an initial concentration of 91 mg/l in an activated sludge of domestic origin, 68% of ThOD had degraded after ten days.

The closed bottle test was carried out with an initial concentration of 3,7 and 10 mg/l with bacteria from non-adapted domestic wastewater, first in freshwater and secondly in synthetic seawater (Price et al., 1974). Biodegradation was measured as BOD as a percentage of ThOD. The results were: degradation of 65% and 87% after five days and twenty days respectively in freshwater; and 8% and 80% after five days and twenty days respectively for the synthetic seawater. The closed bottle test is an approved EC test procedure, although this study pre-dates adoption by the EC. The guidelines suggest an initial concentration between 2 mg/l and 5 mg/l, and an inoculum derived from the secondary effluent of a treatment plant or lab-scale unit receiving predominantly domestic sewage. The test as performed matches the guidelines sufficiently to be considered as a valid test.

Another test result of ready biodegradability has been found, using the standard dilution BOD method (APHA Standard Methods No 219) with added alkyl thiourea to prevent nitrification. Magnetic stirring was used for sparingly soluble chemicals including styrene. From an adapted inoculum of predominantly domestic sewage, 80% degradation was observed after five days. From a non-adapted inoculum, 42% degradation occurred in the same period (Bridié et al., 1979).

Kondo et al. (1988) developed a screening method for the biodegradation of chemicals in environmental water using the cultivation method. Degradation of styrene was measured after three days' cultivation, from an initial concentration of 20 mg/l. River water from the Tama River and seawater from Enoshima beach (Japan) were used. Degradation was 100% and 10% in the river and seawater, respectively.

Hüls AG (1986) performed a modified Sturm test. 64% of styrene had degraded after 42 days. As this test requires >60% degradation in 28 days with a 10 day window, this is not a positive result for ready biodegradability.

Inherent biodegradation

The modified MITI test (II) (OECD Guideline 302C) was used to determine the inherent biodegradability of styrene (CITI, 1992). From an initial concentration of 30 mg/l in activated sludge, 100% had degraded after 14 days, leading to the conclusion that styrene is at least inherently biodegradable.

Anaerobic biodegradation

Environment Canada (1993) reports that styrene would degrade more slowly in groundwater than in surface waters. Howard et al. (1991) estimated a half-life in groundwater of between 4 and 30 weeks.

Fu and Alexander (1992) report that anaerobic environment cultures of bacteria have been shown to convert styrene to a series of aromatic, alicyclic and aliphatic products and these probably persist.

Summary

From the limited data available styrene is readily biodegradable under aerobic conditions. There are sufficient results from standard or near-standard tests to consider styrene to be readily biodegradable and meeting the 10-day window criterion. The biodegradation rates for styrene in the various environmental compartments are derived from this in accordance with the TGD. The values are given below:

Compartment	**Half-life**	**Rate**
WWTP	0.69 hours	1 h^{-1}
Surface water	15 days	0.047 d^{-1}
Soil	30 days	0.023 d^{-1}
Sediment	300 days	0.0023 d^{-1}

There is no information on the fate of styrene under anaerobic conditions.

3.1.2.2 Distribution

3.1.2.2.1 Volatilisation

Due to the relatively high vapour pressure and low to moderate water solubility, volatilisation from water to the atmosphere is likely to be an important distribution process. The Henry's law constant has been calculated from the ratio of vapour pressure and solubility as $231.6\ \text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$, or $2.29\cdot10^{-3}\ \text{atm}\cdot\text{m}^3\cdot\text{mol}^{-1}$. Another calculation gives Henry's law constant as $5.2\cdot10^{-3}\ \text{atm}\cdot\text{m}^3\cdot\text{mol}^{-1}$ at 25 °C, indicating rapid volatilisation from surface waters (Singh et al., 1984). BASF (1987) measured an experimental Henry's law constant of $195\ \text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$. A value of $232\ \text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ has been used in the calculations.

The volatilisation half-life of styrene from a body of water one metre deep, with a current velocity of 1 m/s and a wind velocity of 3 m/s is calculated to be about three hours. The USEPA estimated that half-lives of styrene were three days in a pond and thirteen days in an oligotrophic lake (Environment Canada, 1993). Under laboratory conditions, Fu and Alexander (1992) found that styrene volatilised rapidly from shallow layers of lake water, 50% being lost in 1-3 hours.

The half-life for volatilisation of styrene from soil surfaces was estimated to be approximately one minute with the rate of volatilisation decreasing with increasing depth (Environment Canada, 1993). Fu and Alexander (1992) found that volatilisation from soil was slower than from water, with 26% volatilisation from a 1.5 cm depth of soil in 31 days.

3.1.2.2.2 Rain-out

Rain-out is not likely to be a significant process in the fate of styrene (particularly in view of the relatively rapid degradation rate in air and the moderate solubility of styrene).

3.1.2.3 Accumulation

3.1.2.3.1 Bioaccumulation

The value for log *n*-octanol-water partition coefficient (log Kow) is approximately three, and a value of 3.02 is considered representative (see Section 1.3.7).

One report on the measurement of the bioconcentration factor of styrene in fish is available. This gives a result of 13.5 in the goldfish, *Carrasius auratus* (Ogata et al., 1984). This value is lower than would be expected for a substance with a log Kow of 3.02; using the Kow value and the equation for BCF from the TGD gives a BCF of 74. The measured BCF can be lower than that predicted from log Kow, for example if the substance is rapidly metabolised. There are few details of the experimental study available in Ogata et al. (1984); for example, the concentrations used for the individual test substances and the duration of exposure are not included. For all the substances tested this study appears to show lower bioconcentration factors in comparison with other studies (although there are not many alternative values with which to compare the results). Overall this study is not considered to provide sufficient evidence to conclude that accumulation is reduced from that expected from the partition coefficient. In the absence of any other information on metabolism, etc., the bioconcentration factor derived from the partition coefficient will be used, i.e. 74.

As noted in Section 1.4 above, information found in IUCLID for substances such as toluene, xylene, and ethylbenzene shows that they do not accumulate to any great degree in aquatic organisms. By analogy with these substances, and on the basis of the balance of the information available it appears likely that styrene will not accumulate in aquatic organisms. However, a BCF for styrene cannot be calculated by analogy from the data on these substances, and so the value of 74 derived from the log Kow has been used in the assessment as a worst case.

3.1.2.3.2 Adsorption

No measured organic carbon-water partition coefficients (Koc) have been reported for styrene. Using the equation from the TGD for hydrophobic substances and the log Kow of 3.02, a Koc value of 352 is obtained. Values for the partition coefficients between water and soil, sediment and suspended solids based on this Koc value are derived in Appendix A.

Based on the estimated Koc, the mobility of styrene in soil is considered to be moderate. The movement of styrene in a sand aquifer was found to be approximately 80 times slower than that of a non-adsorbing tracer (Environment Canada, 1993). In Fu and Alexander's work (1992) on water and soils, they found that there was significant adsorption to solids, and as expected, the degree of sorption was related to the organic matter content. Sorption seemed to have little effect on the rate of biodegradation.

3.1.3 Aquatic compartment

3.1.3.1 Measured exposure data

While styrene can be detected in water, it is not one of the frequently detected contaminants, nor is it present in large amounts. Levels of styrene measured in surface and drinking water are given in **Table 3.7**.

Information on the levels of styrene in surface waters for 1995 and 1996 has been obtained from the UK Environment Agency. Styrene was not detected in the majority of samples. It is difficult to derive meaningful summary values, as the detection limits vary considerably between locations. In 1995 there were only two positive results from 95 samples, with styrene present at 26 and 9.6 µg/l. The detection limit for 57 samples was 100 µg/l, for four samples it was 2 µg/l and for the other 32 samples it was 0.1 µg/l.

For 1996, one high value of 93 mg/l was recorded, but two other samples from the same site had concentrations below 2.5 µg/l. At a second site the peak value was 2.1 mg/l, but six other samples were below 10 µg/l (five of these below 0.1 µg/l). The sampling points are for the most part influenced by potential sources; the overall picture is that there are occasional elevated levels but the majority of values are below 10 µg/l.

Table 3.7 Levels of styrene in surface water and drinking water

Location	Concentration (µg/l)	Reference
Surface water		
Canada 1985-1991	<0.5	Environment Canada (1993)
River Rhine, 4 locations (Wiesbaden, Köln, Düsseldorf, Wesel). Mean monthly concentrations	<0.01 - 0.11 <0.01 - 0.02 <0.01 - 0.03 <0.01	ARW (1985) ARW (1986) ARW (1987) ARW (1988)
Great Lakes, Canada, 1982-83 [a)] Averages: summer, winter, spring	max: 1.7 <0.1, 0.2, 0.5	Environment Canada (1993) Otson (1987)
Japanese surveys 1977 - 3 samples (dl = 2) 1985 - 27 samples (dl = 0.1) 1986 - 121 samples, 7 positive (dl = 0.03)	nd nd nd - 0.5	Japanese Environment Agency (1991)
Treated drinking water		
Ontario Canada, 1988-90, 86 sources 90 samples positive from >3,000	nd-0.25	Environment Canada (1993)
Great Lakes Canada, 1982-1983 [b)] Averages: summer, winter, spring	0.1, 0.3, 0.5	Otson (1987)

Notes: nd = not detected; dl = detection limit; [a)] = raw water for drinking water treatment plants; [b)] = corresponding treated water

Watts and Moore (1988) measured styrene levels in a river receiving effluent from a WWTP which treated wastewater from plastics manufacturers. The concentration upstream of the discharge was 7.9 ng/l; at 30 m downstream it was 0.0465 µg/l and at 6,500 m downstream it was 0.0191 µg/l. In a subsequent survey of the same river, Tynan et al. (1990) found higher concentrations at the downstream sites of 0.122 µg/l at 30 m and 0.058 µg/l at 6,500 m. The upstream site had a concentration of 0.127 µg/l, suggesting other sources of styrene than the WWTP effluent.

Law et al. (1991) measured levels of styrene in samples from the North and Irish Seas. The highest level found was 1.7 µg/l in the Tees estuary, north-east England, in an unfiltered subsurface sample. The level was below 0.001 µg/l in samples from the River Mersey, the River Thames and Plymouth Sound.

Juttner (1988) sampled the water from the entrance canal to a harbour on Lake Constance. Initial samples were taken at 8.30 am before boat traffic began, with styrene being present at 1 ng/l. As boat traffic passed, the levels of all VOCs rose with the maximum styrene level, 75 ng/l, being measured at 5.30 pm.

A survey of organic contaminants in drinking water in the UK (March to December 1976) was reported by Fielding et al. (1981). Grab samples of raw and treated water were taken at water works treating lowland river water which contained relatively high levels of wastewater. Styrene was identified in four locations (out of 14); these were groundwater, the same groundwater after distribution, surface water (upland reservoir), and surface water (river and lowland reservoir).

Styrene was not detected in drinking water samples collected between 1977 and 1981 from 102 surface water supplies and 12 ground water supplies in the US (Boland, 1981). Krill and

Sonzogni (1986) reported only one positive detection of styrene from 1,791 wells analysed for chemical contamination in Wisconsin. The detection limit in this study was 1 µg/l.

Environment Canada (1993) reported results from an Ontario Ministry of the Environment study on levels in treatment works. Styrene was detected in nine of 274 samples of raw sewage at a maximum concentration of 21.4 µg/l, and in two of 262 samples of primary and secondary effluent at 15 and 13 µg/l. It was also detected in one raw sludge sample (out of 51) at 6,011 µg/kg; it was not detected in treated sludge from 34 monitored plants.

Webber et al. (1996) measured the levels of organic contaminants in sewage sludges from Canada. Liquid sludges were taken from eleven locations: eight were anaerobically digested mixed primary and waste activated material; one was aerobically digested mixed primary and waste activated sludge; one was anaerobically digested primary sludge; and one was raw primary sludge. The styrene concentrations found ranged from not detected (five samples) to 29 µg/kg dry weight.

The only measured levels in sediment are from the Japanese surveys (Japanese Environment Agency, 1991). In 1977, three samples were taken, none of which contained styrene (dl = 6 ppb). In 1985, 21 samples were taken, one of which contained styrene at the detection limit, 0.001 ppb. In 1986, 125 samples were taken, of which 13 were positive, containing styrene at concentrations of 0.5 to 7.5 ppb. No information on site locations was given.

A baseline survey of trace organics in UK groundwater was reported by Kenrick et al. (1985). 32 public and private supply boreholes were sampled in triassic sandstone, chalk, Lincolnshire limestone and great oolite aquifers. From a total of 43 samples, styrene was found only once in the Lincolnshire limestone (confined aquifer) at a concentration of 0.01 µg/l.

The UK Environment Agency has sampled groundwater from a number of locations in the UK, and found only low levels of styrene if it could be detected. In 1995, 179 samples had concentrations below the detection limit of 100 ng/l; four positive samples had a maximum concentration of 2.1 µg/l. In 1996, 111 samples had concentrations less than 100 ng/l and the maximum positive result was 240 ng/l.

High levels have been found where improper disposal has been carried out. Well water close to a site where 2 drums of styrene were buried was found to contain styrene at 0.1-0.2 mg/l and to have a disagreeable odour (Grossman, 1970).

In summary, levels in drinking water and surface water are generally low, with occasional transient higher levels measured near to point sources. Levels in groundwater are very low.

3.1.3.2 Calculation of PECs for the aquatic compartment

3.1.3.2.1 PEClocal for water

In this section the estimates of releases made in previous sections will be used to calculate predicted local concentrations of styrene in water. Following this, calculations based on information from actual sites will be presented.

Production and processing

Estimates of releases to water from the production of styrene were made in Section 3.1.1.1. In order to calculate the predicted concentration in water, account has to be taken of the removal and dilution processes which can occur. These are removal in a wastewater treatment plant (WWTP), dilution of effluent in receiving waters, and adsorption to suspended matter. The TGD assumes that release occurs to a standard WWTP with a flow of 2,000 m^3/day, and that this discharges into a river with a standard dilution by a factor of ten. The concentration in the receiving water may be modified by absorption; however the calculation for styrene using the methods in the TGD shows that this has no significant effect on the aqueous concentrations.

As discussed in Section 3.1.2.1.2, styrene is considered to be readily biodegradable. From EUSES the fate of styrene in the WWTP is estimated as follows:

Degraded:	58.3%
To air:	31.4%
To water:	7.2%
To sludge:	3.1%

The results of applying this to the emissions to WWTP in Section 3.1.1 are in **Table 3.8**.

Table 3.8 Estimated fate in WWTP

Source	Release to wwtp (kg/day)	Amount to sludge (kg/day)	Amount to air (kg/day)	Concentration in effluent (µg/l)	Concentration in receiving water (µg/l)	$PEClocal_{water}$ [c] (µg/l)
Production	833	25.8	262	30,000	11.6 [a]	11.7
Processing:						
GP-,HI-PS	0.05	0.002	0.016	2	0.18	0.23
EPS	1.26	0.039	0.40	45	4.5	4.6
ABS	0.79	0.024	0.25	28	2.84	2.9
SAN [b]	0.32	0.01	0.099	12	1.15	1.2
SB rubber	0.84	0.026	0.26	30	3.02	3.1
SB latex [b]	0.69	0.021	0.22	25	2.49	2.5
UPE	1.96	0.061	0.62	71	7.06	7.1

Notes: [a] - using default river flow for intermediate production from the TGD
[b] - local calculations not included in EUSES
[c] - PEClocal has regional background added (see Section 3.1.3.2)

The calculations were performed with EUSES. (The output has one use pattern for ABS and SAN combined, and one use pattern for SB rubber and latices. The local scenarios are for the largest size of plant in each group, e.g. for ABS; the other values for SAN and SB latices in the following tables were calculated by hand, see Appendix B).

These estimated concentrations are based on emission factors derived from industry data (although the factors are not always specific to the process concerned). The also use the largest expected size of plant carrying out each process. They do not take into account that large production and processing sites may discharge to WWTPs larger than the default size, or that their treated effluent may go to a larger river than the default.

Site-specific PECs

Information has been provided by a number of producers and users of styrene which enables PECs to be calculated for some actual production and processing sites. The detailed information provided and the calculations themselves are not included in this report. They can be made available to Member States Competent Authorities, as a confidential annex, on request. The results are in **Table 3.9**.

Table 3.9 Site-specific PECs

	Code	PEC (µg/l)	Comments
Sites producing styrene	A1	18	discharge to sea – estimated concentration at discharge point
	A2	20	
	A3	0.025	
Sites processing styrene	B1	4.3	default dilution
	B2	0.05	default dilution
	B3	3.8	default river flow, sea discharge
	B4	5.1	
	B5	0.18	default dilution
	B6	<10	total oil and hydrocarbon concentration, measured in sea at 50 m from discharge
	B7	1	default dilution
Sites producing and processing styrene	C1	<0.1	
	C2	<0.02	default dilution
	C3	0.39	default dilution
	C4	<3	
	C5	16	Concentration at edge of mixing zone
	C6	0.2	
	C7	<0.1	default dilution

The sites have been divided into those which produce styrene but do not use it on site, those which use styrene but do not produce it on site, and those which both produce and use styrene. The production sites cover a combined tonnage of 3,489,500 tonnes. The processes included are polystyrene production (all types, covering 1,157,300 tonnes), SB rubber and latex production (covering 148,000 tonnes of styrene use) and UPE resin production (covering 18,000 tonnes of styrene use).

3.1.3.2.2 PECregional and PECcontinental for water and sediment

The regional and continental scale concentrations have been calculated using the EUSES program (see Appendix B). This implements the distribution modelling for the default European environment in the TGD. The release rates used are those given in **Table 3.5**. Releases to water from production and initial processing of styrene were assumed to go to wastewater treatment plants. The releases to water on disposal of styrene-containing products were split 70:30 between wastewater treatment and surface water (Section 3.1.1.5). The resulting concentrations for the aquatic compartment are in **Table 3.10**.

Table 3.10 Regional and continental PECs for the aquatic environment

	Regional	Continental
Water (µg/l)	0.052	0.003
Sediment (µg/kg)	0.37	0.025

3.1.3.2.3 PEClocal for sediment

The concentration in bulk sediment can be calculated from the concentration in the corresponding water body assuming a thermodynamic partitioning equilibrium. The results of these calculations (using EUSES or by hand) are in **Table 3.11**.

Table 3.11 Local concentrations in sediment

Source	$PEClocal_{sed}$ (µg/kg)	Source	$PEClocal_{sed}$ (µg/kg)
Production	98.6	Site specific: A1	152
GP-, HI-PS	1.95	A2	169
EPS	38.7	A3	0.21
ABS	24.3	B1	36.2
SAN	10.1	B2	0.42
SB rubber	26.0	B3	32
SB latex	21.1	B4	43
UPE	60.2	B5	1.52
		B6	<84.3
		B7	8.43
		C1	<0.84
		C2	<0.17
		C3	3.29
		C4	<25
		C5	135
		C6	1.69
		C7	<0.84

The PEC values include the contribution from the regional concentration. Concentrations in the pore water of the sediment can also be calculated using the methods in the TGD. In this case the resulting values are the same as the surface water levels used to calculate the sediment concentrations.

3.1.3.3 Comparison of measured and calculated levels

The calculated levels in water from the generic calculations are similar to or higher than the site-specific levels with a few exceptions, generally where the specific site has a discharge to estuarine or marine waters and the default dilution factor has been used. Most of the measured values are lower; although occasional higher values have been measured these tend to be temporary. However there is no widespread monitoring information with a consistently low detection limit to compare easily with the calculations. (Most of the calculated values would fit well with measurements showing styrene as not detected at 100 μg/l). As the measured data do not allow representative local concentrations to be derived, the generic calculated levels will be taken forward, together with the site-specific values.

The levels measured in the Rhine and in the Great Lakes could be used to indicate a background level of 0.5 μg/l, which is somewhat higher than the calculated regional concentration of 0.052 μg/l. The only levels available in sediment, from Japan, show low levels which are similar to the estimated regional concentration of 0.37 μg/kg.

The calculated levels will be used in the risk characterisation.

3.1.4 Air compartment

3.1.4.1 Measured exposure data

The measured levels of styrene in the atmosphere are summarised in **Table 3.12**.

Bouscaren et al. (1986) have summarised various levels data. In urban air, levels have been reported at 0-6,800 μg/m^3 in Germany, 0.4-1.6 and 1.5 μg/m^3 in the Netherlands.

McKay et al. (1982) measured styrene levels upwind and downwind of reinforced plastics processors at seven locations in the USA. Samples were taken over unspecified periods (estimated to be 3.5 - 18 hours) and at differing distances from each processor depending on the local geography. The range of values found in the upwind samples was 0.29 - 300 μg/m^3; that for the downwind samples was 14.8 - 2934 μg/m^3. The highest values in both cases were measured near the same processor. There did not appear to be any relation between the scale of operations at a site and the levels measured. For the purposes of this assessment the highest values are not considered representative as they were considerably in excess of the other levels measured. Instead the downwind level measured at 122 metres from a plant in Ohio will be taken as representative; this was 80 μg/m^3.

There are many varying measurements in urban air, but the 1988-90 Canadian survey is the largest one reported and should be reasonably representative. The highest daily mean concentration from this survey was 2.35 μg/m^3, and the overall mean from all sites was 0.59 μg/m^3.

Table 3.12 Measured exposure data in air

Location	Concentration (μg/m³)	Reference
Source dominated		
Houston, US. Industrial complex, close to major transport routes. 1987-88	mean: 2.165	Lagrone (1991)
USA. 135 samples	i-q r: 0.17-7.2 med: 2.3	Brodzinsky & Singh (1983)
Contaminated sites	max 67.1	ECETOC (1994)
Urban		
California, 1965	r: 8-63 mean: 21	WHO (1983)
Canada. 586 samples, 1988-90. 18 urban sites	24 hr means: 0.09-2.35 overall mean: 0.59 highest daily max: 32.4	Environment Canada (1993)
New Jersey, California. 6 sets of samples, residential areas	med: 0.28-4.2 max: 1.0-11	Pellizzari et al. (1986)
Los Angeles. Sept-Nov 1981. 16/17 samples positive	r: 2.2-13	Grosjean & Fung (1984)
4 US states, 1981-1984, TEAM study	r: nd-3.8	Wallace (1986)
Delft, Netherlands, 1975	mean: <0.43 max: 3	Bos et al. (1977)
Nagoya, Japan. 4 samples, Nov 1975	r: 0.43-1.7	Hoshika (1977)
Rural		
Canada, 1988-90	max: 3.2	Environment Canada (1993)
Netherlands	0.200	Bouscaren et al. (1986)
Other		
Netherlands, 3 locations, 1979-80 Terschelling – rural Delft – suburban Vlaardingen - source dominated 350 samples from each	mean: 0.09-1.5 max: 0.65-27.7	Guicherit & Schulting (1985)
Ambient air	r: 4.3-21.7	ECETOC (1994)

Notes: i-q = interquartile; med = median; r = range

3.1.4.2 Calculation of PECs for the air compartment

3.1.4.2.1 PEClocal for air

Estimates of the release to air of styrene during production, processing and use of products were made in Sections 3.1.1.1 and 3.1.1.2. The TGD gives a method for calculating the concentration in air at 100 metres from a source; the concentration is proportional to the source strength, so the concentrations are estimated by multiplying the actual emission rate by the concentration from a source of 1 kg day^{-1}. In addition to the direct releases, emissions from wastewater treatment plants also need to be considered. The estimation of the fate of styrene in the WWTP gives a release of 31.4% of the influent amount to air.

The results of applying this to the "generic" calculations are presented in **Table 3.13**, and the results of similar calculations for the specific sites are presented in **Table 3.14**. The values in the Table are PECs and include the regional contribution (see next section). The calculations were performed with EUSES, with additional calculations for some processing steps and the indirect releases from the wastewater treatment plants. (The releases from the processing of polymers appear in the EUSES output as Private Use under the relevant polymer production step, see Appendix B).

Table 3.13 Calculated concentrations of styrene in air

Activity	Emission route	Release rate (kg/day)	$PEClocal_{air}$ ($\mu g/m^3$)	$PEClocal_{air\ ann}$ ($\mu g/m^3$)
Production	direct	433	120	99.0
	via WWTP	262	72.8	59.8
Processing of styrene				
GP, HI-PS	direct	425	118	97.1
	via WWTP	0.016	0.04	0.04
EPS	direct	204	56.7	46.6
	via WWTP	0.88	0.14	0.12
ABS	direct	128	35.4	29.1
	via WWTP	0.55	0.10	0.09
SAN	direct	51	14.2	11.7
	via WWTP	0.22	0.06	0.05
SB rubber	direct	136	37.9	31.2
	via WWTP	0.59	0.10	0.09
SB latex	direct	112	31.2	25.6
	via WWTP	0.48	0.09	0.08
UPE formulation	direct	161	22.3	18.4
	via WWTP	0.83	0.20	0.17
Processing of polymers				
GP, HI-PS	direct	0.38	0.14	0.12
EPS	direct	2.8	0.81	0.66
ABS/SAN	direct	0.12	0.067	0.061
SB latex	direct	0.17	0.080	0.072
XSBR latex	direct	0.57	0.19	0.16
SB rubber	direct	0.84	0.27	0.23
UPE use	direct	260	71.6	59.0

Table 3.14 Concentrations of styrene in air calculated for specific sites

Site code	Emission route	Release rate (kg/day)	$PEClocal_{air}$ ($\mu g/m^3$)	$PEClocal_{air\ ann}$ ($\mu g/m^3$)
A1	direct	47	13.14	10.8
B1	direct	120	33.4	27.4
B3	direct	23.3	6.51	5.35
	via wwtp	0.33	0.13	0.10
B4	direct	271	75.4	62.0
B7	direct	40	11.2	9.17
C1	direct	30	8.37	6.88
C2	direct	110	29.8	24.5
	via wwtp	0.45	0.16	0.13
C3	direct	113	31.4	25.8
	via wwtp	0.4	0.15	0.12
C4	direct	98	27.3	22.4
C5	direct	73	20.3	16.7
C6	direct	372	103	85.0
	via wwtp	58.1	16.1	13.2

Note: only sites for which specific information on releases to air was provided are included here

All the emission rates are based on 300 days of operation per year; the annual average concentrations were calculated by spreading these over 365 days as described in the TGD.

For sites where releases occur via the WWTP as well as directly, the latter always give the higher concentration and so the $PEClocal_{air}$ values are taken from these releases.

3.1.4.2.2 PECregional and PECcontinental for air

Section 3.1.3.2.2 described the methods used to calculate the regional and continental scale concentrations. The results for the air compartment were: $PECregional_{air}$ 0.034 $\mu g/m^3$; $PECcontinental_{air}$ 0.004 $\mu g/m^3$.

3.1.4.3 Comparison of measured and calculated levels

The calculated levels for generic styrene production and processing sites range from 11.6 - 99 $\mu g/m^3$. The values estimated from actual release data are also of a similar order. Concentrations arising from the further processing of styrene-containing polymers, etc., are much lower, with the exception of that from the use of UPE resins. The predicted values for this use are in good agreement with the levels measured in the US.

There are very few measured concentrations for background areas to compare with the PEC regional. Typical levels in urban areas are higher than the regional PEC.

3.1.4.4 Calculation of the deposition fluxes from air emissions

The TGD provides a method for calculating the deposition of a chemical through wet and dry processes and incorporating particulate-adsorbed deposition. For these calculations the direct emissions are combined with the emissions from WWTPs where these occur.

The fraction of chemical associated with particulate material in the air is calculated as $1.5 \cdot 10^{-7}$ (see Appendix A). The resulting estimated deposition rates are in **Table 3.15**. These values are used later in the assessment to estimate concentrations in soil.

Table 3.15 Deposition rates to soil from styrene emission to air

Activity	Combined release rate (kg/day)	Total deposition ($mg \cdot m^{-2} \cdot day^{-1}$)	Annual deposition rate ($mg \cdot m^{-2} \cdot day^{-1}$)
Production	695	0.21	0.17
Processing of styrene			
GP-, HI-PS	425	0.13	0.11
EPS	204	0.061	0.050
ABS	128	0.038	0.031
SAN	51.1	0.015	0.013
SB rubber	136	0.041	0.034
SB latex	112	0.034	0.028
UPE formulation	81	0.024	0.02
Polymer use			
GP-, HI-PS	0.37	$1.1 \cdot 10^{-4}$	$9.3 \cdot 10^{-5}$
EPS	2.80	$8.3 \cdot 10^{-4}$	$6.8 \cdot 10^{-4}$
ABS/SAN	0.13	$3.5 \cdot 10^{-5}$	$2.9 \cdot 10^{-5}$
SB latex	0.17	$5 \cdot 10^{-5}$	$4.1 \cdot 10^{-5}$
XSBR latex	0.57	$1.7 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$
SB rubber	0.83	$2.5 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$
UPE use	260	0.077	0.064

Similar calculations have been performed for specific sites (**Table 3.16**). Where no information on releases to air was available for a site, the appropriate release factors from Sections 3.1.1.1 and 3.1.1.2 were used to estimate a deposition rate from air.

Table 3.16 Deposition rates to soil from styrene emission to air for specific sites

Site code	Combined release rate (kg/day)	Total deposition ($mg \cdot m^{-2} \cdot day^{-1}$)	Annual deposition rate ($mg \cdot m^{-2} \cdot day^{-1}$)
A1	47	0.014	0.012
A2	396	0.023	0.019
A3	219	0.066	0.054
B1	120	0.036	0.030
B2	80	0.024	0.020
B3	24	0.0072	0.0059
B4	271	0.081	0.067
B5	425	0.13	0.11
B6	70	0.021	0.017
B7	40	0.012	0.0099
C1	30	0.009	0.007
C2	107	0.032	0.027
C3	113	0.034	0.028
C4	98	0.029	0.024
C5	73	0.022	0.018
C6	430	0.13	0.11
C7	1610	0.48	0.40

3.1.5 Soil compartment

3.1.5.1 Measured levels in soil

No information on measured levels of styrene in European soils was located. Based on limited data, background concentrations of styrene in soil are very low (Environment Canada, 1993). In a survey of organic compounds in soil in uncontaminated urban areas west of Toronto, styrene was detected in three of five soil samples at Port Credit, Ontario at concentrations of up to 0.2 µg/kg (detection limit 0.05 µg/kg), and was not detected in any of eight samples from Oakville/Burlington, Ontario (detection limit was 5 to 10 µg/kg).

3.1.5.2 Calculation of PECs for soil

3.1.5.2.1 PEClocal for soil

A substance can reach the soil compartment by three routes: direct application, deposition from air and sludge application. No direct application routes have been found for styrene. The substance is released to air, and is adsorbed to sludge in the wastewater treatment plant, and so these two routes to the soil compartment will be assessed.

The three processes of degradation, volatilisation and leaching act on styrene in the soil. Appendix A contains the calculation of the rates of these processes. The overall removal rates for styrene are estimated as: 0.045 day^{-1} for 0.2 m depth soil, and 0.067 day^{-1} for 0.1 m depth soil.

Deposition rates for styrene from air were calculated in Section 3.1.4.4, and emission rates to sludge were estimated in Section 3.1.3.2.1. The concentrations arising in soil as a result of these two routes were calculated using EUSES (see Appendix B). (Site-specific values and those for SAN and latex production were calculated by hand). The removal rates for styrene from soil are such that there is no significant accumulation between annual applications.

The results of the soil concentration calculations are presented in **Table 3.17**. Values are presented for three endpoints: $PEClocal_{soil}$ (averaged over 30 days) for the assessment of effects on the terrestrial ecosystem; $PEClocal_{agr.soil}$ (averaged over 180 days) for the estimation of levels in crops for human consumption; and $PEClocal_{grassland}$ (averaged over 180 days) for the estimation of levels in grass for cattle feed. These concentrations include the contribution from the regional soil concentrations.

Table 3.17 Concentrations of styrene estimated in soil

Process	$PEClocal_{soil}$ (µg/kg)	$PEClocal_{agr.soil}$ (µg/kg)	$PEClocal_{grassland}$ (µg/kg)
Production	26,300	5,920	1,600
Processing			
GP-, HI-PS	8.4	7.2	9.3
EPS	43.0	12.2	6.8
ABS	26.9	7.6	4.3
SAN	11.0	3.1	1.7
SB rubber	28.8	8.2	4.6
SB latex	23.8	6.7	3.8
UPE formulation	63.4	15.3	5.5
Polymer use			
GP-, HI-PS	0.008	0.008	0.01
EPS	0.046	0.046	0.062
ABS/SAN	0.004	0.004	0.004
SB latex	0.005	0.005	0.005
XSBR latex	0.011	0.011	0.014
SB rubber	0.015	0.015	0.020
UPE use	4.2	4.2	5.6

Concentrations for specific sites are in **Table 3.18**. For some sites the sludge from the WWTP is either incinerated or sent to landfill; this has been reflected in the calculations.

Table 3.18 Concentrations of styrene in soil from specific sites

Code	$PEClocal_{soil}$ (µg/kg)	$PEClocal_{agr.soil}$ (µg/kg)	$PEClocal_{grassland}$ (µg/kg)
A1	0.76	0.76	1.02
A2	1.24	1.24	1.67
A3	9.18	4.80	5.08
B1	1.94	1.94	2.60
B2	1.29	1.29	1.73
B3	0.38	0.38	0.51
B4	4.37	4.37	5.87
B5	8.71	7.27	9.31
B6	1.13	1.13	1.52
B7	0.65	0.65	0.87
C1	0.49	0.49	0.65
C2	8.59	3.28	2.74
C3	1.83	1.83	2.46
C4	1.58	1.58	2.12
C5	1.18	1.18	1.58
C6	35.2	13.3	11.0
C7	27.2	26.2	34.9

3.1.5.2.2 PEC regional and PEC continental for soil

The regional and continental concentrations estimated using EUSES are given in **Table 3.19**.

Table 3.19 Regional and continental concentrations of styrene in soil

	Agricultural soil	Natural soil	Industrial soil
Regional (µg/kg)	0.14	0.002	0.13
Continental (µg/kg)	0.005	0.0002	0.013

3.1.5.3 Comparison of measured and calculated levels

Only a few measured levels are available, and these refer to uncontaminated areas. Comparing these to the regional concentrations estimated above, the only positive results, at 0.2 µg/kg, agree with the estimated regional concentrations in agricultural and industrial soils.

Two studies which measured the concentration of styrene in sewage sludge were described in Section 3.1.3.1. In one study, styrene was not detected in treated sludge, and was only detected in one sample of raw sludge, at 6 mg/kg. In the other study the positive results ranged from 0.3 to 29 µg/kg. The calculated concentrations in sludge are much higher than these values; those from the generic production and processing estimations range from 2.0 to 32,700 µg/kg. As there is no specific information about the sources of styrene in the sludges monitored it is difficult to compare these directly.

3.1.6 Secondary poisoning

3.1.6.1 Measured exposure data

Styrene has been measured in a variety of biota from several sources. As well as anthropogenic releases from, for example, industrial processing, which causes contamination of environmental compartments and subsequent exposure of organisms in those compartments, styrene monomer may also leach out of the polymer, especially into fatty foodstuffs. Additionally, it is thought that styrene is a natural constituent of some foods.

Levels of styrene were measured in mussels (*Mytilus edulis*) taken from the Oarai coast in Ibaraki, Japan (Yasuhara and Morita, 1987). They were collected in July 1985 and 1986. Styrene was only identified in the mussels collected in 1986. The tentative concentration was 350 µg/kg.

Whole body concentrations of styrene ranging between 15 and 100 µg/kg were measured in “Splake”, a cross of brook trout and lake trout, and in walleye (*Stizostedion vitreum*) caught in the St Clair River, Canada. Styrene was also detected, but not quantified, in the tissues of several other fish (emerald shiner (*Notropis atherinoides*), black crappie (*Pomoxis nitromaculatus*), bluegill *(Lepomis macrochirus*) and pumpkinseed (*Lepomis gibbosus*)) from the St Clair River. Edible shellfish from Atlantic Canada contained <10.0 µg styrene/kg. In both of these reports, it was not indicated whether the results were expressed on a wet weight or a dry weight basis (Environment Canada, 1993).

Concentrations of styrene in fish were also reported in the Japanese Environment Agency report (1991). In a survey in 1986, 131 samples of fish were taken and styrene was found in 28 of these, at concentrations of 0.5 to 2.3 µg/kg (limit of detection 0.5 µg/kg). No other details were given.

Styrene concentrations have been measured in foodstuffs. These concentrations could arise from naturally occurring styrene or through migration of the monomer from food packaging materials. Miller et al. (1994) cite results from two studies which took precautions to prevent contamination of foods by styrene from plastics. The concentrations found are in **Table 3.20**. It was suggested that the high level of styrene in cinnamon was due to biodegradation or biosynthesis of structurally similar flavourant materials.

An extensive UK survey of styrene monomer levels in styrene-based plastic packaging materials and their contained foods (133) was carried out, examining a wide range of retail foods of different brand names (Gilbert and Startin, 1983). Some of the foods covered were yoghurts, creams, salads, coleslaws, soft cheeses, margarines, hot and cold beverages from dispensing machines, spreads, fresh and cooked meats, candied fruits, fresh strawberries and take-away fast foods. Analysis of the plastic containers showed levels of monomer ranging from 16 to 1,300 mg/kg, although the majority of containers (73%) had styrene levels in the range 100-500 mg/kg and only five plastic tubs had levels exceeding 1,000 mg/kg. Analysis of the food contents of the plastic containers showed levels of monomer ranging from <1 µg/kg to 200 µg/kg, although the majority of foods (77%) had styrene levels below 10 µg/kg and 26% of the total number analysed had levels below 1 µg/kg.

Table 3.20 Levels of styrene in food uncontaminated by contact with packaging (from Miller et al., 1994)

Product	Styrene concentration (µg/kg)	Comment
Blackcurrants	2-6	
Wheat	0.5-2	
Apples, cauliflowers, onions, tomatoes	<1	
Cinnamon	157-39,200	
Wheat	1.2	mean of 3 samples
Peanuts	1.8	mean of 3 samples
Coffee beans	3.6	mean of 5 samples
Strawberries	1.7	mean of 3 samples
Beef	6.1	mean of 3 samples
Oats	0.8,0.9	2 of 4 samples
Peaches	0.3	1 of 3 samples
Tomatoes, peaches, raw milk, chicken	<2	

MAFF (1983) also monitored food products in the UK in 1981. The mean concentrations tended to be higher in dairy products: 26 µg/kg in yoghurt, 22 µg/kg in dessert products, 16 µg/kg in soft cheese, 11 µg/kg in cream and 10 µg/kg in spreads. Lower levels were found in coleslaw, fresh meat, glace fruit, fish, strawberries and take-out foods. Levels in food containers ranged from 197 - 718 mg/kg.

Similar monitoring exercises were carried out in 1992 and 1994 (MAFF, 1995). In the most recent survey, 248 samples of food in a variety of pack types and sizes were analysed. The majority of the samples ranged from below the detection limit (1 µg/kg) to 60 µg/kg. Higher levels were found in some low fat spread samples, up to 100 µg/kg, although other samples of similar materials contained less than 20 µg/kg. Milk and cream products sold in individual portions (~10 g) had styrene contents from 23-223 µg/kg, with a mean of 134 µg/kg. For other food types mean values were less than 30 µg/kg. In general, for each food type higher levels were found for products with a higher fat content or packed in smaller containers. Overall the styrene levels were considered to be similar to those in the previous surveys.

Miller et al. (1994) cited a TNO literature review of surveys of styrene in foodstuffs. The highest concentrations reported were in beer (10-200 µg/kg), coffee (20-360 µg/kg), bilberries (25 µg/kg) and blackcurrants (60 µg/kg). Styrene was detected in 62 food products but was not quantified in most of these.

In a Canadian survey of a wide range of foods, samples of 34 food groups (each a composite of individual food items, combined in approximate proportion to their consumption in the Nutrition Canada Survey), were collected from retail outlets (Environment Canada, 1993). Styrene was not detected in any of the 34 food groups (detection limits 1.0 µg/l for liquids and 0.005 µg/kg for solids).

Asmundo et al. (1986) investigated styrene migration in samples of must and wine fermented and stored in glass reinforced plastic tanks in Sicily. Only small amounts of styrene were detected in must (“mosti-vino rossi”) (trace to 0.05 ppm), and in a few samples of wine (minimum detectable level).

3.1.6.2 Calculated concentrations for indirect exposure

The concentrations of styrene in biota for the various release scenarios were calculated using EUSES; the results are in **Table 3.21**. The estimated human dose for each scenario is also included.

Table 3.21 Calculated concentrations of styrene in biota

Scenario	Concentration (µg/kg)					Human dose a) (mg/kg/day)
	Fish	Plant roots	Plant leaves	Meat	Milk	
Production	704	10,700	11.8	1.7	0.54	0.11
Processing: GP, HI-PS	14.7	13	11.5	0.33	0.11	0.021
EPS	278	22	5.5	0.16	0.051	0.011
ABS/SAN	175	14	3.4	0.1	0.032	0.007
SB rubber/latex	187	15	3.7	0.11	0.034	0.007
UPE resin	433	28	2.2	0.067	0.021	0.005
Use of: GP, HI-PS	3.8	0.014	0.014	$4.5 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$	$3.3 \cdot 10^{-5}$
EPS	3.8	0.084	0.079	$2.3 \cdot 10^{-3}$	$7.3 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$
ABS/SAN	3.8	0.007	0.007	$2.5 \cdot 10^{-4}$	$7.9 \cdot 10^{-5}$	$2.0 \cdot 10^{-5}$
SB rubber/latex	3.8	0.028	0.027	$8.2 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$5.6 \cdot 10^{-5}$
UPE resin use	3.8	7.5	7.0	0.20	0.064	0.013
Regional	3.8	0.25	0.004	$1.6 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$

Note a) - human dose estimate includes intake from air and drinking water as well as from biota

In addition to the calculated levels, the measured levels of styrene in various media can be used to estimate possible uptake in humans. The following values have been selected from those presented in Section 3.1.6.1:

Fish	100 µg/kg (maximum value in fish in Canadian measurements)
Milk	134 µg/kg (mean value from 1994 UK survey, from individual portions)
Other foods	30 µg/kg (upper limit of means, UK 1994 survey)

For air, the value of 80 µg/m^{3} downwind from a reinforced plastics processing site is chosen (Section 3.1.4.1). For water, the value of 10 µg/l is chosen as a reasonable level.

Using these concentrations, a daily intake of 0.019 mg/kg bw/day is estimated.

3.1.6.3 Comparison of measured and calculated levels

It is difficult to compare the measured and modelled levels as in the main they are attributable to different causes. Some of the measured levels in Section 3.1.6.1 above are concerned with styrene as a natural constituent of foods. This has clearly nothing to do with anthropogenic sources, and this effect is not taken account of in EUSES. Other measured levels are due to contamination of foodstuffs due to their proximity to packaging containing styrene monomer. Again the calculated levels do not directly address this route.

The measured levels attributable to environmental contamination are for mussels (350 µg/kg), edible shellfish (<10 µg/g), Canadian fish (15-100 µg/kg) and Japanese fish (2.3 µg/kg). Only the measured concentrations in fish can be compared directly with modelled values; the predicted levels (3.8-711 µg/kg) are of a similar order.

3.2 EFFECTS ASSESSMENT

3.2.1 Aquatic compartment

3.2.1.1 Aquatic toxicity

3.2.1.1.1 Toxicity to fish

Table 3.22 is a summary of the results of acute toxicity tests on various species of fish. These results need to be interpreted with care. Three studies were performed under flow through conditions. In two of these the concentrations were also monitored through the test. The detailed report available for the Springborn study shows that the actual styrene concentrations were only at 60% of the nominal levels, but that they were consistent throughout the study. One other flow through study on rainbow trout with no concentration monitoring has been identified, but the report has not been located. All the other studies are from static tests. In most cases the results are based on nominal concentrations. Bridié et al. (1979b) measured the concentration before and after the test; they kept the exposure to only 24 hours for styrene as longer exposures would lead to low dissolved oxygen levels but the solutions could not be aerated without losing more than 10% of the styrene. They did not indicate whether there were any losses over the course of the exposure, and so no deduction can be made to help in interpreting the other tests. Qureshi et al. (1982) also used a short (24-hour) exposure to reduce the influence of volatilisation; they measured the concentration at the start of the exposure period but not at the end.

The flow-through studies with concentration monitoring are considered to be the most reliable results. The lower of these gives an 96-hour LC_{50} for fathead minnow (*Pimephales promelas*) of 4.02 mg/l. The other result from a flow through study and that from Quereshi et al. give very similar results, and are taken as supporting the chosen value.

3.2.1.1.2 Toxicity to aquatic invertebrates

Table 3.23 is a summary of the acute toxicity results for aquatic invertebrates. Similar considerations apply to these studies as for fish in regard to volatility, although the exposures here are shorter in general. The Springborn (1995a) *Daphnia* study monitored the concentration of styrene during the tests; although the measured concentrations were only on average 18% of the nominal levels they were consistent throughout the study. Springborn (1995b) also conducted a 96-hour test on the amphipod *Hyalella azteca* using a protocol similar to that for *Daphnia*. Here the measured concentrations in the flow through study averaged a consistent 21% of the nominal concentrations. The 96-hour LC_{50} obtained was 9.5 mg/l.

Table 3.22 Acute fish toxicity

Species	Size (mm) / Weight (g)	Dissolved O_2 (mg/l)	Water hardness (mg/l $CaCO_3$)	Water temperature (°C)	pH	Flow/static	Effect concentration (mg/l)	Validity	Ref
Fathead minnow *Pimephales promelas*	29-46 mm (mean 37)	7.4-9.3	35-36	22	6.9-7.2	flow	24 hr LC_{50} 12 (m) 48 hr LC_{50} 12 (m) 96 hr LC_{50} 10 (m)	valid	Springborn (1995)
	0.1 g		52.8	21.3	7.2	flow	96 hr LC_{50} 4.02 (m)	valid	Geiger et al. (1990)
	1-2 g	non-aerated	soft water	25	7.5	static	24 hr LC_{50} 56.7 (n) 48 hr LC_{50} 53.6 (n) 96 hr LC_{50} 46.4 (n)	not valid	Pickering and Henderson (1966)
	1-2 g	non-aerated	hard water	25	8.2	static	24 hr LC_{50} 62.8 (n) 48 hr LC_{50} 62.8 (n) 96 hr LC_{50} 59.3 (n)	not valid	Pickering and Henderson (1966)
		non-aerated		18-22		static	24 hr LC_{50} 32 (n) 48 hr LC_{50} 32 (n) 96 hr LC_{50} 32 (n)	not valid	Mattson et al. (1976)
Bluegill sunfish *Lepomis macrochirus*	1-2 g	non-aerated	soft water	25	7.5	static	24 hr LC_{50} 25.1 (n) 48 hr LC_{50} 25.1 (n) 96 hr LC_{50} 25.1 (n)	not valid	Pickering and Henderson (1966)
Goldfish *Carassius auratus*	1-2 g	non-aerated	soft water	25	7.5	static	24 hr LC_{50} 64.7 (n) 48 hr LC_{50} 64.7 (n) 96 hr LC_{50} 64.7 (n)	not valid	Pickering and Henderson (1966)
		non-aerated		19-21	7.8	static	24 hr LC_{50} 26 (n)	not valid	Bridié et al. (1979b)

Table 3.22 continued overleaf

Table 3.22 continued Acute fish toxicity

Species	Size (mm) / Weight (g)	Dissolved O_2 (mg/l)	Water hardness (mg/l $CaCO_3$)	Water temperature (°C)	pH	Flow/static	Effect concentration (mg/l)	Validity	Ref
Guppy *Lebistes reticulatus*	01-0.2 g	non-aerated	soft water	25	7.5	static	24 hr LC_{50} 74.8 (n) 48 hr LC_{50} 74.8 (n) 96 hr LC_{50} 74.8 (n)	not valid	Pickering and Henderson (1966)
Sheepshead minnow Cyprinodon variegatus	8-15 mm	non-aerated	sea water, salinity 1-3.1%	25-31		static	24 hr LC_{50} 9.1 (n) 48 hr LC_{50} 9.1 (n) 96 hr LC_{50} 9.1 (n)	not valid	Heitmüller et al. (1981)
Golden orfe *Leusciscus idus melanotus*				20			48 hr LC_{50} 17 (n) 48 hr LC_{50} 66 (n)	not valid	Juhnke and Lüdemann (1978)
Rainbow trout Oncorhynchus mykiss	0.5-3.0 g	non-aerated	135	15±1	7.8-8.1	static	24 hr LC_{50} 2.5 (n*)	use with care	Qureshi et al. (1982)
	0.22 g		270	15±1	7.0-7.3	flow	24 hr LC_{50} 6.5 (n) 48 hr LC_{50} 6.3 (n) 96 hr LC_{50} 5.9 (n)	use with care	Abram and Collins (1981)

Most studies are marked as "not valid" because there was no monitoring of concentration. Where a flow-through system was used, this may have reduced the impact of volatilisation on the concentration; hence flow-through studies with no monitoring have been marked as "use with care".

* - concentration measured at start of test but not at end.

Table 3.23 Acute invertebrate toxicity

Species	Test time (hrs)	Test type	Result (mg/l)	Validity	Ref
Water flea *Daphnia magna*	48	EC_{50}	4.7	valid	Springborn (1995a)
	24 24 24	LC_0 (NOEC) EC_{50} EC_{100}	105 182 300	not valid	Bringmann and Kühn (1982)
	24 24 24	LC_0 (NOEC) EC_{50} EC_{100}	130 255 300	not valid	Bringmann and Kühn (1977)
	 24 48	NOEC LC_{50} LC_{50}	<6.8 27 23	not valid	LeBlanc (1980)
	48	LC_{50}	59	not valid	Qureshi et al. (1982)
Amphipod *Hyalella azteca*	96	LC_{50}	9.5	valid	Springborn (1995b)
Brine shrimp *Artemia salina*	24 48	EC_{50} EC_{50}	68 52	not valid	Price et al. (1974)

There are no indications in the other test reports that concentrations were measured. In a study by Qureshi et al. (1982) the styrene level was measured at the start of the exposure. In the two Bringmann and Kühn studies the exposures were carried out in glass beakers loosely covered with filter paper. Le Blanc (1980) covered the test vessels with plastic wrap to reduce the effect of volatilisation. All these studies are considered to be susceptible to volatilisation, and so the Springborn (1995a,b) studies are taken as the only fully valid studies. The lowest EC_{50} for invertebrates is therefore taken as 4.7 mg/l.

3.2.1.1.3 Toxicity to algae

Springborn (1995c) tested the effect of styrene on the green alga *Selenastrum capricornutum* using a test method in accordance with US EPA TSCA Guideline 797.1050 as amended in the Federal Register May 1987, modified to minimise the volatilisation of test compound from the exposure vessels. The flasks were completely filled with test solution to leave no headspace. Concentrations were measured at 0, 24 and 96 hours during the test in the flasks selected for cell counting at these times. The concentrations at the start of the exposure period were below the nominal levels. The pattern in subsequent measurements is not even, but there were no great further reductions in concentration, the variation being less than 20% of the initial measured concentrations. The levels averaged 22-31% of nominal. This test is considered to be valid despite the variation in the concentrations.

The EC_{50} values at 72 and 96 hours calculated in the test report (see below) show an unexpected difference. The data from the report have therefore been examined closely. There is no indication of a lag phase in the controls or the lower concentrations. There does appear to be some variability in the growth rates of the algae when these are calculated over consecutive 24-hour periods, but there is no clear pattern. The increase in cell numbers in the controls over the test period meets the criteria in both the OECD and EU test protocols. These require a minimum increase of 16-fold over the starting numbers of cells, a growth rate of 0.924 d^{-1}; the average growth rate in the controls over 72 hours was 1.19 d^{-1} and over 96 hours it was 1.17 d^{-1}.

The toxicity parameters derived in the study as reported were based on the measured cell densities. This is a measure of the biomass. The mean cell densities (cells/ml) in the exposed vessels were compared with that in the controls and the percentage inhibitions calculated. The percentage inhibitions were probit-transformed and a regression performed against the logarithm-transformed concentrations. The 96-hour EC_{50} based on cell density (EbC_{50}(96-h)) was 0.72 mg/l, with the EC_{10} value (EbC_{10}(96-h)) at the same duration being 0.13 mg/l. The EbC_{50} at 72 hours was 1.4 mg/l.

Overall growth rates for 72 and 96 hours have been calculated, and these have been used to estimate the toxicity parameters. The mean growth rates for each exposure concentration were compared with the control and a percentage inhibition calculated for each concentration. These percentage inhibitions were probit transformed and a regression performed against the logarithm-transformed concentrations. The 96-hour EC_{50} based on growth rate ($E\mu C_{50}$) is 6.3 mg/l, with the 96-hour $E\mu C_{10}$ as 0.28 mg/l. The $E\mu C_{50}$ at 72 hours was 4.9 mg/l.

The toxicity values derived from the effects on growth rate are clearly higher than those based on cell density (biomass). Ratte (1998) described the theoretical calculation of the ratios between the two parameters. A high ratio between EbC_{50} and $E\mu C_{50}$ is expected where the dose-response curve is shallow and the experimental duration is more than around one day. The dose-response curve for styrene is shallow, as was noted in the original test report. Thus the difference between the two parameters is in agreement with the expected behaviour. There is closer agreement between the EC_{10} values from the biomass and growth rate methods (0.13 mg/l for biomass, 0.28 mg/l for growth rate); this is also expected from the theoretical calculations.

Data for a range of similar substances have been collected for comparison with the styrene results. These are presented in **Table 3.24**. The values for toluene and cumene were taken from the risk assessment reports for those substances. Values for the other substances were taken from the submissions in context of the Classification and Labelling of these substances.

The values for styrene toxicity to fish and daphnia fit well into this group of substances. It is also clear that the algal toxicity value derived from the growth rate fits much better than that from biomass in comparison with the other substances. This value also agrees more closely with the value of 5.8 mg/l predicted from the QSAR equation in the TGD (Section 3.2.1.1.5).

Table 3.24 Comparison of aquatic toxicity to some aromatic hydrocarbons

Substance	Log Kow	Fish LC_{50}	Daphnia LC_{50}	Algal EC_{50}
Toluene	2.65	5.4	11.5	10 (NOEC)
o-Xylene	3.12	7.6	3.2	4.7
m-Xylene	3.2	8.4	3.7	4.9
p-Xylene	3.15	2.6	1.4	3.2
Ethylbenzene	3.15	4.2	2.1	4.6
Cumene	3.55	2.7	1	2.6
Propylbenzene	3.57	1.6	2.0	1.8
Styrene	3.02	4.05	4.7	4.9 [a)] or 0.72 [b)]

a) based on growth rate

b) based on biomass

The conclusion is therefore that the EµC$_{50}$ value should be used for styrene; the value from 72 hours is lower than that for 96 hours, hence the EµC$_{50}$ is 4.9 mg/l.

The results of two cell multiplication inhibition tests are reported by Bringmann and Kühn (1978). There are no data on analytical monitoring. The toxicity threshold (equivalent to a NOEC) for *Scenedesmus quadricauda* (green algae) and *Microcystis aeruginosa* (blue green algae) are >200 mg/l after eight days and 67 mg/l after seven days respectively. These results are not considered valid.

3.2.1.1.4 Toxicity to microorganisms

Table 3.25 is a summary of the results of the acute toxicity tests for microorganisms.

Table 3.25 Acute toxicity to microorganisms

Species	Test type	Exposure time	Result (mg/l)	Ref
Entosiphon sulcatum (protozoa)	Cell multiplication test	72 hr	NOEC: >256	Bringmann (1978a)
Uronema parduzci (protozoa)	Cell multiplication test	20 hr	NOEC: 185	Bringmann and Kühn (1980)
Pseudomonas putida (bacteria)	Cell multiplication test	16 hr	NOEC: 72	Bringmann and Kühn (1977b)
Pseudomonas fluroescens (bacteria)	Inhibition of glucose assimilation	16 hr	NOEC: 72	Bringmann (1973)
Photobacterium phosphoreum	Microtox TM test - luminescence inhibition	5 min	EC$_{50}$: 5.4	Qureshi et al. (1982)
Chilomonas paramaecium (protozoa)	Cell multiplication test	48 hr	NOEC: >100	Bringmann et al. (1980)
Spirillum volutans (bacteria)	Motility inhibition test	5 min	MEC$_{90}$ a): 636	Qureshi et al. (1982)
Activated sludge of predominantly domestic sewage	Oxygen consumption inhibition test	30 min	EC$_{50}$: ca 500 EC$_{20}$: ca 140	BASF AG (1988)

a) MEC$_{90}$ = minimum effective concentration to eliminate reversing motility in greater than 90% of cells within 5 minutes

The results in the first four references were originally given as toxicity thresholds, and have been taken to be equivalent to NOECs. There is no information on concentration monitoring in any of the tests included in the table; however, the short-term nature of some of the tests should reduce the influence of volatilisation on the results and they are therefore considered to be suitable to assess the effects of styrene on sewage treatment organisms. Other tests may be affected by volatility, but Section 3.2.1.2.3 shows that they lead to similar PNEC values.

3.2.1.1.5 QSAR predictions of aquatic toxicity

Styrene is considered to exert toxic effects by a non-specific mode of action (Bol et al., 1993) in aquatic species. It is therefore possible to calculate effect concentrations using the methods described in the TGD (Part III, Section 4.1.2.1, equations for non-polar narcosis). The results of these calculations are in **Table 3.26**.

Table 3.26 SAR Predictions of styrene aquatic toxicity

	Short term toxicity (mg/l)		Long term toxicity (mg/l)
	Measured	Predicted	Predicted
Fish	4.05, 10	11	1.0
Daphnia	4.7 (9.5)	6.7	1.0
Algae	4.9	5.8	

The short-term toxicity predictions for fish, *Daphnia* and algae are in good agreement with the valid measured values available.

3.2.1.2 Derivation of aquatic PNECs

3.2.1.2.1 PNEC for water

There is a reasonable amount of data available on the short-term toxicity of styrene to fish, aquatic invertebrates and algae. The base set is therefore complete. In choosing an assessment factor the algal study, although multi-generational, cannot be considered as a chronic study without supporting evidence from other organisms. From the information available the starting point would be to apply a factor of 1000 to the lowest LC_{50} giving a $PNEC_{water}$ of 4.0 µg/l (from the fish acute value of 4.02 mg/l).

However there is evidence to suggest that the factor could be lowered. The values for the LC_{50} to fish, aquatic invertebrates and algae are all similar (within a factor of ten). There are also data from a further species, in addition to the base set requirements, which agree with the other results. Thus there appears to be no great difference in sensitivity between aquatic organisms. There is good agreement between the QSAR predictions and the measured values, and this is indicative that styrene acts by a non-specific mechanism in aquatic species. Therefore a lower assessment factor of 100 will be used on the most sensitive experimental result, giving a $PNEC_{water}$ of 40 µg/l.

3.2.1.2.2 PNEC for sediment

There is no information available on the toxicity of styrene to sediment-dwelling organisms. The equilibrium partitioning method can be used to estimate the PNEC for sediment organisms according to the methods in the TGD. The aquatic PNEC of 40 µg/l leads to a PNEC for sediment organisms of 340 µg/kg.

3.2.1.2.3 PNEC for microorganisms

There is one result from a test on activated sludge, giving an EC_{50} (for oxygen consumption inhibition) of 500 mg/l. The TGD suggests that an assessment factor of 100 should be applied to this result, giving a $PNEC_{microorganisms}$ of 5 mg/l. Most of the other tests reported give no effect concentrations and indicate similar (or lower) sensitivity. Taking the results for *Pseudomonas sp.* and applying a factor of ten to the NOECs gives a PNEC of 7.2 mg/l. The only result which does not fit into a similar range is that from the Microtox test, which appears more sensitive. This test is not considered suitable for assessing the effects on wastewater treatment plants and so it will not be used in this assessment.

3.2.2 Atmosphere

Biotic effects

No information relating to the effects of styrene on plants via exposure through the air has been located. As the air receives the majority of styrene releases to the environment, further investigation of the effects of close analogues of the substance has been undertaken to establish whether styrene might be expected to have an effect on plants via this route.

Aromatic compounds considered as analogues of styrene were benzene, toluene and ethylbenzene. No information was found for the last of these. Both benzene and toluene are being assessed under the Existing Substances Regulation. From the draft risk assessment for benzene, concentrations in the air of the order of 30-160 g/m^3 are required to produce an effect on plants. The effects seen are usually reversible after the exposure has ended. The draft assessment concludes that benzene is not of concern for plants except at very high concentrations.

In the toluene risk assessment a number of studies are presented which show that toluene can have an effect on plants at high concentrations in air. A screening study involving the exposure of a number of plant species to toluene over 14 days found no effects at concentrations of 60 mg/m^3 or below. This value is used in the toluene risk assessment as an indicative level for effects (not a formal PNEC). The assessment concludes that when compared to the estimated air concentrations (up to ~1 mg/m^3), this level indicates that toluene does not present a risk to plants.

Substances containing an alkenyl group could also be considered as analogues. Ethylene itself is known to be a plant hormone and to have effects on growth. Vershueren (1983) includes a number of values for effects on various plant species, covering a wide range of concentrations. The lowest quoted value is 0.002 ppm, which is 2.3 μg/m^3. No indication of the level of effect is included.

The addition of substituents to ethylene appears to reduce the toxicity to plants significantly. The IUCLID for propylene indicates effects at 1000 ppm after three days exposure and effects after two days at 50 ppm. The effects seen were declination in pea seedlings and epinasty (growth promotion) in the petiole of tomato plants respectively; the level of effect is not indicated. The concentrations correspond to 1.7 g/m^3 and 86 mg/m^3 respectively.

For butylene, epinasty in the petiole of tomato plants was also reported, at a concentration of 50,000 ppm (125 g/m^3) over two days.

From the limited amount of information available on the effects of styrene analogues on plants, it is clear that with the exception of ethylene effects are only seen at high concentrations. Ethylene is a special case, and the addition of substituent groups reduces the toxicity markedly. It is also possible that the effects seem in other alkenic substances such as propylene may be due to the presence of ethylene as an impurity. It is therefore concluded that styrene is unlikely to have significant effects on plants except at high concentrations. A PNEC cannot be derived from this information, but the value of 60 mg/m^3 as used for toluene will be considered in the risk characterisation section as a level below which effects would be unlikely.

Abiotic effects

Styrene reacts rapidly with hydroxyl radicals and ozone in the atmosphere. It has a low photochemical ozone creation potential, and so is not expected to contribute to low-level photochemical air pollution.

3.2.3 Terrestrial compartment

Studies on laboratory mammals are discussed in the human health section.

A study on the toxicity of styrene to earthworms (*Eisenia foetida*) was carried out using a method generally conforming to OECD Guideline 207 (Springborn, 1995d). An artificial soil consisting of 70% sand, 20% kaolin colloidal powder and 10% sphagnum peat moss was used. The substance was applied by mixing with a 2:1 soil:water slurry (under a cover to reduce volatilisation) and then mixing with the bulk of the slurry. The test vessels were covered with plastic wrap, with small holes to provide air circulation. Observations were made after seven days, at which time the worms were returned to a fresh medium, and then again after fourteen days. The concentrations in the soil were measured at the start and end of each seven-day period. The initial concentrations averaged 18% of the nominal levels; the levels after seven days showed a significant reduction from these. It also appeared that the concentration in the replacement medium (for days 7-14) reduced to a greater extent than that for the first period, although both started at similar levels.

In the study report the effect concentrations derived are based on the average concentrations in the medium at the start and end of the exposure; these gave a 14-day LC_{50} of 120 mg/kg, and a NOEC for weight change of 44 mg/kg. Alexander (1997) re-evaluated the study in terms of the minimum concentration to which the worms were exposed over the course of the study. He concluded that the NOEC value could be assumed to be 34 mg/kg, if not higher.

Thus, there is only one result for terrestrial organisms and the exposure concentrations are not well defined. The equilibrium partitioning method has therefore been used to estimate a PNEC for styrene. This method is considered to be suitable for a substance like styrene with a moderate log Kow value. The aquatic PNEC of 41 µg/l leads to a $PNEC_{terrestrial}$ of 255 µg/kg in soil (for comparison, an assessment factor of 1,000 on the LC_{50} value from the earthworm study would give a similar result of 120 µg/kg). This value will be used for comparison with the levels in soil.

3.2.4 Secondary poisoning

According to the TGD, the process for deciding whether an assessment of secondary poisoning is necessary involves consideration of the classification of the substance. The current classification of styrene does not include any of the risk phrases that would indicate the need for a secondary poisoning assessment, and therefore no PNEC for secondary poisoning has been derived. In addition, styrene is readily biodegradable and although the log Kow is just above 3, experimental BCF determinations indicate little accumulation (although these studies are not considered fully valid).

3.3 RISK CHARACTERISATION

3.3.1 Aquatic compartment

Predicted environmental concentrations were estimated in Section 3.1.3 for surface water and sediment. Predicted no-effect concentrations for aquatic organisms and sediment-dwelling organisms were estimated in Section 3.2.1 (40 µg/l and 340 µg/kg, respectively). These values are compared in **Table 3.27**. Only the values and ratios for water are presented, the ratios for sediment being the same as those for water (as sediment concentrations were estimated by equilibrium partitioning).

Table 3.27 PEC/PNEC ratios for surface water

Process	Generic PEC (µg/l)	PEC/PNEC	Site code	Site-specific PEC (µg/l)	PEC/PNEC
Production	11.7	0.29	A1	18	0.45
Processing: GP, HI-PS	0.23	0.006	A2	20	0.5
EPS	4.6	0.11	A3	0.025	0.0006
ABS	2.9	0.07	B1	4.3	0.11
SAN	1.2	0.03	B2	0.05	0.001
SB rubber	3.1	0.08	B3	3.8	0.095
SB latex	2.5	0.06	B4	5.1	0.13
UPE resin formulation	7.1	0.18	B5	0.18	0.005
			B6	<10	<0.25
			B7	1	0.03
			C1	<0.1	<0.002
			C2	<0.02	<0.0005
			C3	0.39	0.01
			C4	<3	<0.075
			C5	16	0.4
			C6	0.2	0.005
			C7	<0.1	<0.002

None of the generic scenarios lead to PEC/PNEC ratios greater than one, and all of the ratios estimated for specific sites are less than one.

Conclusion for the aquatic compartment

Conclusion (ii) There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

This conclusion applies to all steps in the production and processing of styrene and the use of styrene-containing products.

3.3.2 Microorganisms in wastewater treatment plants

Estimates of the concentration in wastewater treatment plant effluents were made in Section 3.1.3.2.1. A PNEC of 5 mg/l was derived for microorganisms in WWTPs in Section 3.2.1.2. The resulting PEC/PNEC ratios are in **Table 3.28**. Also included are the concentrations of styrene in the effluent from WWTPs serving specific sites.

Table 3.28 PEC/PNEC ratios for WWTPs

	Generic PEC (µg/l)	PEC/PNEC	Site code	Site-specific PEC (µg/l)	PEC/PNEC
Production	30,000	6	A2	53	0.011
Processing: GP, HI-PS	2	0.0004	A3	5.4	0.001
EPS	45	0.009	B3	500	0.22
ABS	28	0.006	B5	1.8	0.004
SAN	12	0.002	B7	<1000	<0.2
SB rubber	30	0.006	C1	<3	<0.0006
SB latex	25	0.005	C2	<0.2	<0.00005
UPE resin formulation	71	0.014	C3	4	0.0008
			C6	29	0.006
			C7	<1	<0.0002

All the PEC/PNEC ratios are less than one with the exception of the generic production site. This corresponds to the largest size of styrene production site, discharging its effluent to a default wastewater treatment plant of 2,000 m^3/day volume. The production sites which provided specific information cover 93% of styrene production in the EU and are considered to provide a more realistic estimate of the levels of styrene in wastewater treatment plants receiving production waste. Therefore the conclusion for microorganisms in WWTPs is for no concern.

Conclusion for microorganisms in wastewater treatment plants

Conclusion (ii) There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

This conclusion applies to all steps in the production and processing of styrene.

3.3.3 Terrestrial compartment

PEC values for soil were estimated in Section 3.1.5.2, and the PNEC for terrestrial organisms was derived in Section 3.2.3 (255 µg/kg). The resulting PEC/PNEC ratios are in **Table 3.29**.

Only the generic scenario for production gives a PEC/PNEC ratio greater than one. This is due to the assumption of a large site discharging to a standard size WWTP, which produces a very large concentration in the waste sludge and hence in soil. The available site-specific information covers 93% of styrene production sites (codes A and C in the table) and these are considered more representative. Therefore the conclusion is that there is no need for any further information or testing.

Table 3.29 PEC/PNEC ratios for the terrestrial compartment

	Generic PEC (μg/kg)	PEC/PNEC	Site code	Site-specific PEC (μg/kg)	PEC/PNEC
Production	26,300	103	A1	0.76	0.003
Processing: GP, HI-PS	8.4	0.03	A2	1.24	0.005
EPS	43.0	0.17	A3	9.18	0.04
ABS	26.9	0.11	B1	1.94	0.008
SAN	11.0	0.04	B2	1.29	0.005
SB rubber	28.8	0.11	B3	0.38	0.001
SB latex	23.8	0.09	B4	4.37	0.02
UPE resin formulation	63.4	0.25	B5	8.71	0.03
Use of polymer: GP,HI-PS	0.008	$3 \cdot 10^{-5}$	B6	1.13	0.004
EPS	0.046	0.0002	B7	0.65	0.003
ABS/SAN	0.004	$2 \cdot 10^{-5}$	C1	0.49	0.002
SB latex	0.005	$2 \cdot 10^{-5}$	C2	8.59	0.03
XSBR latex	0.011	$4 \cdot 10^{-5}$	C3	1.83	0.007
SB rubber	0.015	$6 \cdot 10^{-5}$	C4	1.58	0.006
UPE resin use	4.2	0.02	C5	1.18	0.005
			C6	35.2	0.14
			C7	27.2	0.11

Conclusion for the terrestrial compartment

Conclusion (ii) There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

This conclusion applies to all steps in the production and use of styrene and the use of styrene-containing products. It should be noted that the same conclusion would apply if the PNEC derived from the earthworm study were used (120 μg/kg).

3.3.4 Air compartment

The levels of styrene in the atmosphere are expected to be low, with the possible exception of the vicinity of major sites. The highest estimated concentration in air is 99 μg/m^3. The possible effects of styrene on plants were discussed in Section 3.2.2 and an indicative level of 60 mg/m^3 (below which effects would not be expected) was proposed. This is around three orders or magnitude above the highest levels estimated. Therefore it is concluded that styrene is unlikely to have any effects on plants at the concentrations estimated in this assessment.

Styrene reacts rapidly with hydroxyl radicals and ozone in the atmosphere. It has a low photochemical ozone creation potential, and so is not expected to contribute to low-level photochemical air pollution.

Conclusion for the air compartment

Conclusion (ii) There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

This conclusion applies to all steps in the production and use of styrene and the use of styrene-containing products.

3.3.5 Secondary poisoning

For secondary poisoning to be a possibility and therefore require assessment, three criteria have to be met. The first is whether indirect exposure to ecosystems can occur. As the bulk of the styrene is released to air and its subsequent distribution includes movement to soil and water then this is possible. The second criterion is an indication of bioaccumulation potential. The log Kow of 3.02 suggests the possibility of accumulation; a measured BCF value of 13.5 is lower than would be expected from the Kow but is not considered to be a valid result. The third criterion is that the chemical be classified on the basis of its mammalian toxicity data. Styrene does not have any of the listed classifications. Therefore there is no need to carry out an assessment of secondary poisoning.

4 HUMAN HEALTH

(will be added later)

5 RESULTS

5.1 INTRODUCTION

Styrene is produced or imported by nine companies in the EU, with an estimated usage of 3,743,000 tonnes in Europe in 1993. It is used mainly as a monomer in a range of polymers and synthetic rubbers; it is also used in unsaturated polyester resins for reinforced plastics.

5.2 ENVIRONMENT

The environmental risk characterisation considers the production of styrene and its use as a monomer in the production of polymers and synthetic rubbers. It also includes the processing of polymers and rubbers into products, and releases of residual monomer from products in use and on disposal. The formulation and use of UPE resins is considered. Calculations for specific sites are included as well as generic assessments.

For the aquatic compartment, including sediment, the PEC/PNEC ratios for all sites and generic scenarios are less than one. The ratios for microorganisms in wastewater treatment plants and for the terrestrial environment are all less than one with the exception of a generic assessment for production; the site-specific calculations for production are considered to be more representative. By comparison with analogous substances, styrene is not expected to have effects on plants through exposure via the air. Styrene is not expected to contribute to low-level ozone formation.

Result

Conclusion (ii) There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

This conclusion applies to all steps in the production and use of styrene and the use of styrene-containing products, for the aquatic compartment (including sediment), to microorganisms in wastewater treatment plants, to the terrestrial compartment and to the air compartment. No assessment of secondary poisoning for predators via the food chain has been carried out.

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ABBREVIATIONS

ADI	Acceptable Daily Intake
AF	Assessment Factor
ASTM	American Society for Testing and Materials
ATP	Adaptation to Technical Progress
AUC	Area Under The Curve
B	Bioaccumulation
BBA	Biologische Bundesanstalt für Land- und Forstwirtschaft
BCF	Bioconcentration Factor
BMC	Benchmark Concentration
BMD	Benchmark Dose
BMF	Biomagnification Factor
BOD	Biochemical Oxygen Demand
bw	body weight / *Bw*, *bw*
C	Corrosive (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)
CA	Chromosome Aberration
CA	Competent Authority
CAS	Chemical Abstract Services
CEC	Commission of the European Communities
CEN	European Standards Organisation / European Committee for Normalisation
CEPE	European Committee for Paints and Inks
CMR	Carcinogenic, Mutagenic and toxic to Reproduction
CNS	Central Nervous System
COD	Chemical Oxygen Demand
CSTEE	Scientific Committee for Toxicity, Ecotoxicity and the Environment (DG SANCO)
CT_{50}	Clearance Time, elimination or depuration expressed as half-life
d.wt	dry weight / dw
dfi	daily food intake
DG	Directorate General
DIN	Deutsche Industrie Norm (German norm)
DNA	DeoxyriboNucleic Acid
DOC	Dissolved Organic Carbon
DT50	Degradation half-life or period required for 50 percent dissipation / degradation
DT90	Period required for 50 percent dissipation / degradation
E	Explosive (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)

EASE	Estimation and Assessment of Substance Exposure Physico-chemical properties [Model]
EbC50	Effect Concentration measured as 50% reduction in biomass growth in algae tests
EC	European Communities
EC10	Effect Concentration measured as 10% effect
EC50	median Effect Concentration
ECB	European Chemicals Bureau
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECVAM	European Centre for the Validation of Alternative Methods
EDC	Endocrine Disrupting Chemical
EEC	European Economic Communities
EINECS	European Inventory of Existing Commercial Chemical Substances
ELINCS	European List of New Chemical Substances
EN	European Norm
EPA	Environmental Protection Agency (USA)
ErC50	Effect Concentration measured as 50% reduction in growth rate in algae tests
ESD	Emission Scenario Document
EU	European Union
EUSES	European Union System for the Evaluation of Substances [software tool in support of the Technical Guidance Document on risk assessment]
F(+)	(Highly) flammable (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)
FAO	Food and Agriculture Organisation of the United Nations
FELS	Fish Early Life Stage
foc	Organic carbon factor (compartment depending)
GLP	Good Laboratory Practice
HEDSET	EC/OECD Harmonised Electronic Data Set (for data collection of existing substances)
HELCOM	Helsinki Commission -Baltic Marine Environment Protection Commission
HPLC	High Pressure Liquid Chromatography
HPVC	High Production Volume Chemical (> 1000 t/a)
IARC	International Agency for Research on Cancer
IC	Industrial Category
IC50	median Immobilisation Concentration or median Inhibitory Concentration
ILO	International Labour Organisation
IPCS	International Programme on Chemical Safety
ISO	International Organisation for Standardisation
IUCLID	International Uniform Chemical Information Database (existing substances)
IUPAC	International Union for Pure and Applied Chemistry
JEFCA	Joint FAO/WHO Expert Committee on Food Additives

JMPR	Joint FAO/WHO Meeting on Pesticide Residues
Koc	organic carbon normalised distribution coefficient
Kow	octanol/water partition coefficient
Kp	solids-water partition coefficient
L(E)C50	median Lethal (Effect) Concentration
LAEL	Lowest Adverse Effect Level
LC50	median Lethal Concentration
LD50	median Lethal Dose
LEV	Local Exhaust Ventilation
LLNA	Local Lymph Node Assay
LOAEL	Lowest Observed Adverse Effect Level
LOEC	Lowest Observed Effect Concentration
LOED	Lowest Observed Effect Dose
LOEL	Lowest Observed Effect Level
MAC	Maximum Allowable Concentration
MATC	Maximum Acceptable Toxic Concentration
MC	Main Category
MITI	Ministry of International Trade and Industry, Japan
MOE	Margin of Exposure
MOS	Margin of Safety
MW	Molecular Weight
N	Dangerous for the environment (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC
NAEL	No Adverse Effect Level
NOAEL	No Observed Adverse Effect Level
NOEL	No Observed Effect Level
NOEC	No Observed Effect Concentration
NTP	National Toxicology Program (USA)
O	Oxidizing (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)
OC	Organic Carbon content
OECD	Organisation for Economic Cooperation and Development
OEL	Occupational Exposure Limit
OJ	Official Journal
OSPAR	Oslo and Paris Convention for the protection of the marine environment of the Northeast Atlantic
P	Persistent
PBT	Persistent, Bioaccumulative and Toxic

PBPK	Physiologically Based PharmacoKinetic modelling
PBTK	Physiologically Based ToxicoKinetic modelling
PEC	Predicted Environmental Concentration
pH	logarithm (to the base 10) (of the hydrogen ion concentration $\{H^+\}$
pKa	logarithm (to the base 10) of the acid dissociation constant
pKb	logarithm (to the base 10) of the base dissociation constant
PNEC	Predicted No Effect Concentration
POP	Persistent Organic Pollutant
PPE	Personal Protective Equipment
QSAR	(Quantitative) Structure-Activity Relationship
R phrases	Risk phrases according to Annex III of Directive 67/548/EEC
RAR	Risk Assessment Report
RC	Risk Characterisation
RfC	Reference Concentration
RfD	Reference Dose
RNA	RiboNucleic Acid
RPE	Respiratory Protective Equipment
RWC	Reasonable Worst Case
S phrases	Safety phrases according to Annex III of Directive 67/548/EEC
SAR	Structure-Activity Relationships
SBR	Standardised birth ratio
SCE	Sister Chromatic Exchange
SDS	Safety Data Sheet
SETAC	Society of Environmental Toxicology And Chemistry
SNIF	Summary Notification Interchange Format (new substances)
SSD	Species Sensitivity Distribution
STP	Sewage Treatment Plant
T(+)	(Very) Toxic (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)
TDI	Tolerable Daily Intake
TG	Test Guideline
TGD	Technical Guidance Document
TNsG	Technical Notes for Guidance (for Biocides)
TNO	The Netherlands Organisation for Applied Scientific Research
ThOD	Theoritical Oxygen Demand
UC	Use Category
UDS	Unscheduled DNA Synthesis
UN	United Nations

UNEP	United Nations Environment Programme
US EPA	Environmental Protection Agency, USA
UV	Ultraviolet Region of Spectrum
UVCB	Unknown or Variable composition, Complex reaction products of Biological material
vB	very Bioaccumulative
VOC	Volatile Organic Compound
vP	very Persistent
vPvB	very Persistent and very Bioaccumulative
v/v	volume per volume ratio
w/w	weight per weight ratio
WHO	World Health Organization
WWTP	Waste Water Treatment Plant
Xn	Harmful (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)
Xi	Irritant (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC)

Appendix A Calculation of chemical properties

This Appendix gives details of the chemical properties derived from the basic data available. It covers partition coefficients, fate in wastewater treatment and other removal processes.

Basic physico-chemical data (as described in Section 1.3)

Boiling point	145.5°C
Vapour pressure	667 Pa
Molecular weight	104.15
Melting point	-30.6°C
Solubility	300 mg/l
Log Kow	3.02

Partition coefficients

Sorption

Koc

Estimated from hydrophobics equation from Section 4.3 of Chapter on QSAR in the TGD.

Equation is: $\log Koc = 0.81 \log Pow + 0.10$

Log Pow = 3.02
log Koc = 2.55
Koc = 352

Solid - Water partition coefficients

From Section 2.3.5 of the TGD (equation 8):

$$Kp_{comp} = Foc_{comp} \cdot Koc \qquad \text{with comp} \in \{\text{soil, sed, susp}\}$$

Using the fraction organic carbon values from Table 3 in the TGD

Kp_{soil} = 7.04 l/kg
Kp_{sed} = 17.6 l/kg
Kp_{susp} = 35.2 l/kg

The dimensionless form of Kp, or the total compartment-water partitioning coefficient, can be derived from equation 9:

$$K_{comp-water} = Fair_{comp} \bullet K_{air-water} + Fwater_{comp} + Fsolid_{comp} \bullet \frac{Kp_{comp}}{1000} \bullet RHOsolid$$

with comp $\in$ {soil, sed, susp}

Using the values of $Fair_{comp}$, $Fwater_{comp}$ and $Fsoil_{comp}$ from Table 3 in the TGD, the value of $K_{air\text{-}water}$ from below and 2,500 kg/m^3 for RHOsolid, gives the following:

$K_{soil\text{-}water}$ = 10.8
$K_{sed\text{-}water}$ = 9.6
$K_{susp\text{-}water}$ = 9.7

Air partition coefficients

Henry's law constant

Section 3.1.2.2 of the risk assessment gives measured and estimated values for the Henry's law constant. The selected values gives H as 232 $Pa \cdot m^3 \cdot mole^{-1}$.

$K_{air\text{-}water}$

The air-water partition coefficient is the dimensionless form of the Henry's law constant, or H/RT. The value for H above leads to $K_{air\text{-}water}$ as 0.1.

Adsorption to aerosol particles

The fraction of chemical associated with aerosol particles can be estimated from equation 5 in the TGD:

$$Fass_{aer} = \frac{CONjunge \bullet SURF_{aer}}{VP + CONjunge \bullet SURF_{aer}}$$

With $CONjunge \bullet SURF_{aer}$ set to 10^{-4} Pa, this gives $Fass_{aer} = 1.5 \cdot 10^{-7}$.

Degradation rates

Hydrolysis

This is discussed in Section 3.1.2.1.1 of the risk assessment; styrene does not hydrolyse under environmental conditions.

Photooxidation

This is discussed in Section 3.1.2.1.1 of the risk assessment, and the value for the half-life taken is 2.63 hours. This corresponds to a rate constant of 6.3 day^{-1}.

Wastewater treatment plant removal

Biodegradation is discussed in Section 3.1.2.1.2. The removal and fate according to EUSES are as follows:

Ready biodegradability:	To air -	31.4%
	To water -	7.2%
	To sludge -	3.1%
	Degraded -	58.2%
	Total removal -	92.8%

Other biodegradation rates

Section 2.3.6 of the TGD gives methods for estimating the biodegradation rates in surface water, soil and sediments. Using these methods for a readily biodegradable substance gives the following results:

	Half-life (days)	Rate constant (day^{-1})
Surface water ($kbio_{water}$)	15	$4.7 \cdot 10^{-2}$
Soil ($kbio_{soil}$)	30	$2.3 \cdot 10^{-2}$
Sediment ($kbio_{sed}$)	300	$2.3 \cdot 10^{-3}$

Removal rates from soil

Volatilisation

The rate constant for volatilisation from soil, k_{volat}, is given by equation 41 in the TGD:

$$\frac{1}{k_{volat}} = \left[\frac{1}{kasl_{air} \bullet K_{air-water}} + \frac{1}{kasl_{soilair} \bullet K_{air-water} + kasl_{soilwater}}\right] \bullet K_{soil-water} \bullet DEPTH_{soil}$$

Taking the values from the TGD as follows:

$kasl_{air}$ =	120 m/day
$kasl_{soilair}$ =	0.48 m/day
$kasl_{soilwater}$ =	$4.8 \cdot 10\text{-}5$ m/day
$DEPTH_{soil}$ =	0.2 or 0.1 m depending on soil type

and the values for partition coefficients from above gives the rate constants:

k_{volat} (0.2) = 0.022 day^{-1}
k_{volat} (0.1) = 0.044 day^{-1}

Leaching

The rate constant for leaching, k_{leach}, is given by equation 42 in the TGD:

$$k_{leach} = \frac{F\,\inf_{soil} \bullet RAINrate}{K_{soil-water} \bullet DEPTH_{soil}}$$

Taking the values from the TGD as follows:

$Finf_{soil}$ = 0.25
RAINrate = $1.92 \cdot 10^{-3}$ m/day
$DEPTH_{soil}$ = 0.2 or 0.1 m depending on soil type

and the value for $K_{soil\text{-}water}$ from above gives the rate constants:

k_{leach} (0.2) = $2.2 \cdot 10^{-4}$ day^{-1}
k_{leach} (0.1) = $4.4 \cdot 10^{-4}$ day^{-1}

<u>Overall removal rate</u>

The overall removal rate is the sum of the three processes volatilisation, leaching and biodegradation. The biodegradation values were derived in Section A1.3.4. The overall results for the two depths are:

k(0.2) = 0.045 day^{-1}
k(0.1) = 0.067 day^{-1}

Appendix B EUSES Output

Notes on EUSES calculations for styrene

The use patterns used in the EUSES calculations are as follows:

Use Pattern 1: *Production* of styrene

Use Pattern 2: *Processing* to polystyrene by mass process (95% of GP- and HI-PS); further processing of polymer under *Private Use*.

Use Pattern 3: *Processing* to polystyrene using suspension process (EPS plus 5% of GP- and HI-PS); further processing of polymer under *Private Use*.

Use Pattern 4: *Processing* to ABS and SAN (using same emission factors); further processing of polymer under *Private Use*.

Use Pattern 5: *Processing* to SB rubber and latex; further processing of polymer under *Private Use*.

Use Pattern 6: *Formulation* of UPE resins; *Processing* of UPE resins.

Use Pattern 7: releases from plastic articles in use and disposal, and indirect emissions from exhausts and cigarettes. These values were entered directly and appear as *Private Use*.

The further processing of the various polymers were entered under Private Use to keep down the numbers of use patterns in the calculations. The fractions of main source were adjusted in order to give the same values as those in the main text (and the regional production tonnage was also adjusted in the same way). In all cases the tonnages are based on styrene so the fractions in formulations are all 1 (but the composition of the products is accounted for in the estimation of the main source fraction in the text).

The regional and continental total emissions were re-entered on the basis that all releases to water from production and initial processing go to waste water treatment, with other releases to water being split 70:30 between waste water and surface water.

Euses Calculations can be viewed as part of the report at the website of the European Chemicals Bureau: http://ecb.jrc.it

European Commission

EUR 20541 EN European Union Risk Assessment Report
Styrene – Part I - Environment, Volume 27

Editors: B.G. Hansen, S.J. Munn, J. de Bruijn, C. Musset, F. Berthault, M. Luotamo, S. Pakalin, S. Vegro, G. Pellegrini, R. Allanou, S. Scheer.

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Environment and quality of life series

The report provides the comprehensive risk assessment of the substance styrene. It has been prepared by the UK in the frame of Council Regulation (EEC) No. 793/93 on the evaluation and control of the risks of existing substances, following the principles for assessment of the risks to man and the environment, laid down in Commission Regulation (EC) No. 1488/94.

The evaluation considers the emissions and the resulting exposure to the environment and the human populations in all life cycle steps. Following the exposure assessment, the environmental risk characterisation for each protection goal in the aquatic, terrestrial and atmospheric compartment has been determined. For human health the scenarios for occupational exposure, consumer exposure and humans exposed via the environment have been examined and the possible risks have been identified.

The environmental risk assessment for styrene concludes that there is at present no concern for the atmosphere, the aquatic ecosystem, the terrestrial ecosystem and for microorganisms in the sewage treatment plant.

European Commission – Joint Research Centre
Institute for Health and Consumer Protection
European Chemicals Bureau (ECB)

European Union Risk Assessment Report

styrene
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