# CHLOROFORM

CAS-No.: 67-66-3

EINECS-No.: 200-663-8

# RISK ASSESSMENT

Final Report (2007)

France

Rapporteur for the risk evaluation of chloroform is the Ministry for the Protection of Nature and the Environment as well as the Ministry of Employment and Social Affairs in co-operation with the Ministry of Public Health. Responsible for the risk evaluation and subsequently for the contents of this report is the rapporteur.

The scientific work on this report has been prepared by the National Institute for Research and Security (INRS) as well as the National Institute for Industrial Environment and Risks (INERIS), by order of the rapporteur.

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## Foreword to Draft Risk Assessment Reports

This Draft Risk Assessment Report is carried out in accordance with Council Regulation (EEC) 793/93[1] on the evaluation and control of the risks of “existing” 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 to the Competent Group of Member State experts for endorsement. Observers from Industry, Consumer Organisations, Trade Unions, Environmental Organisations and certain International Organisations are also invited to attend the meetings. The Risk Assessment Report is then peer-reviewed by the Scientific Committee on Toxicity, Eco-toxicity and the Environment (SCTEE) which gives its opinion to the European Commission on the quality of the risk assessment.

This Draft Risk Assessment Report is currently under discussion in the Competent Group of Member State experts with the aim of reaching consensus. In doing so, the scientific interpretation of the underlying information may change, more information may be included and even the conclusions reached in this draft may change. Competent Group of Member State experts seek as wide a distribution of these drafts as possible, in order to assure as complete and accurate an information basis as possible. The information contained in this Draft Risk Assessment Report therefore does not necessarily provide a sound basis for decision making regarding the hazards, exposures or the risks associated with the priority substance.

**This Draft Risk Assessment Report is the responsibility of the Member State rapporteur. In order to avoid possible misinterpretations or misuse of the findings in this draft, anyone wishing to cite, quote or copy this report must obtain the permission of the Member State rapporteur beforehand.**

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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]

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# 0. OVERALL RESULTS OF THE RISK ASSESSMENT

CAS Number: 67-66-3
EINECS Number: 200-663-8

IUPAC Name : Chloroform

## Environment

This risk assessment has been performed with site-specific data when available and the exposure assessment is therefore only valid for the sites considered in this evaluation. Any change of technology at these sites or any new site will lead to different exposure calculations and thus will have to be evaluate on a case by case basis.

### Conclusions to the risk assessment for the aquatic compartment

**Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account**

Conclusion (iii) is applied to the use of chloroform as a solvent. As the PEC estimation is based on monitoring data and the improvement of the PNEC might not be sufficient to decrease the ratio, it is necessary to limit the risk from now on for this application.

**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**

Conclusion (ii) is applied to all levels of the life cycle of chloroform: production, all uses (except its use as a solvent) and unintended releases of chloroform due to losses as a by-product during chemical manufacturing.

### Conclusions to the risk assessment for the sediment compartment

**Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account**

Conclusion (iii) is applied to the use of chloroform as a solvent. As additional toxicity testings on sediment organisms requested under article 10(2) do not permit to decrease the PEC/PNECratio below 1, it is necessary to limit the risk from now on for this application.

**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**

Conclusion (ii) is applied to all levels of the life cycle of chloroform: production, all uses (except its use as a solvent) and unintended releases of chloroform due to losses as a by-product during chemical manufacturing.

### Conclusions to the risk assessment for the sewage compartment

**Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account**

Conclusion (iii) is applied to production sites A, C, E and J, to all uses and unintended releases. Given that toxicity testings on micro-organisms requested under article 10(2) were not valid, the exposure assessment could not be refined and risks still remain. It is therefore necessary to limit the risk from now on.

## Conclusions to the risk assessment for the atmosphere 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**

## Conclusions to the risk assessment 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**

It should be noticed that the assessment considers that sludge from chloroform and HCFC production sites are not applied on agricultural soils.

## Conclusions to the risk assessment for non-compartment specific effects relevant to the food chain

**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**

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# 1. GENERAL SUBSTANCE INFORMATION

## 1.1. IDENTIFICATION OF THE SUBSTANCE

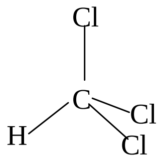
CAS-No.: 67-66-3

EINECS-No.: 200-663-8

Substance name (EINECS name): Chloroform
Synonyms and tradenames : Chloräterid

Formylchlorid
Freon 20
HCC 20
Methane trichloride
Methane, trichloro-
Methenylenchlorür
Methenyl trichloride
Methinchlorid
Methylenchlorür
Methyl trichloride
R 20 (Refrigerant)
TCM
Trichloroform
Trichloromethane
Molecular formula: $CHCl_3$
Molecular weight: 119.5 $g.mol^{-1}$

Structural formula:



## 1.2. PURITY/IMPURITIES, ADDITIVES

Purity : $\geq 99$ % w/w

Impurities : chlorobromomethane (CAS 74-97-5)

carbon tetrachloride (CAS 56-23-5)

chloromethane (CAS 74-87-3) < 0.005 % w/w

1,1-dichloroethylene (CAS 75-35-4) < 0.002 % w/w

others : confidential data

Additives : $\leq 1$ % (confidential data)

## 1.3.PHYSICO-CHEMICAL PROPERTIES

Chloroform is a volatile, heavy, colourless liquid. It is non-flammable and possesses a characteristic sweet odour.

### 1.3.1. Melting point

Only handbook data are available, indicating values between –63.2 and –63.8 °C (Deshon, 1978; Rossberg *et al.*, 1996). No data is available on the used methods. An average value of –63.5°C will be used in this risk assessment.

### 1.3.2. Boiling point

Only handbook data are available, indicating a value of 61.3 °C (Deshon, 1978; Rossberg *et al.*, 1996). No data is available on the used methods. This value will be used in the risk assessment.

### 1.3.3. Relative density

Handbook values of 1,481 to 1,489 kg/m$^3$ are reported (Deshon, 1978; Rossberg *et al.*, 1996), while producers report values of 1,476 to 1,478 kg/m$^3$ at 20 °C (Hoechst, 1996). An average value of 1,480 kg/m$^3$ will be used in the risk assessment.

### 1.3.4. Vapour pressure

The vapour pressure of chloroform has been determined in an equilibrium still from 20 °C to the boiling point (Moelwyn-Hugues and Missen, 1957). At 20°C, a value of 209 hPa has been determined.

The value given by one producer in its safety data sheet is 211 hPa at 20 °C (Hoechst, 1996) without details.

Handbook values of 185 hPa and 212.8 hPa are documented respectively (Weast, 1973; Deshon, 1978). No details on how these values have been obtained are reported.

The value of 209 hPa at 20 °C, the only well documented measurement, will be used in this risk assessment. A vapour pressure of 29.5 kPa is extrapolated by EUSES at 25°C.

The vapour pressure being higher than 0.01 kPa at 293.15 K, chloroform could be considered as a Volatile Organic Compound (VOC).

### 1.3.5. Surface tension

HSDB, 2003 reports a value of 0.0271 N/m at 20°C (Weiss, 1986). Lide, 1997 gives a value of 0.0267 N/m. A rounded value of 0.027 N/m will be retained in this risk assessment.

The values reported in the literature for chloroform tend to indicate that this substance is a surface-active reagent. The fact that chloroform shows surface-active properties could thus lead to the disturbance of analytical method employed to measure some physico-chemical characteristics.

However, there is a difference between the surface activity of traditional surfactants and substances that can reduce the surface activity of solutions, like chloroform. What is observed with chloroform during the surface tension measurements, is the typical non-ideal behaviour of a mixture of a water miscible solvent such as methanol and ethanol. The reason for the observed relationship between surface tension and concentration is the disruption of the hydrogen bonding of the water causing non-linear behaviour of the surface tension against the concentration. In this case, the substance is not migrating to the surface; it is not acting in the traditional surface-active manner. Furthermore, chloroform is miscible with water and does not form micelles but clear solutions.

Therefore, the measurements of the physico-chemical properties are not affected and surface-active properties of chloroform will not be considered in this assessment.

### 1.3.6. Water solubility

8 g/L at 20° C is the value given in the EC Safety data sheet (Hoechst, 1996) without further details.
A value of 8.7 g/L has been measured at 23 °C in sealed bottles without headspace. The aqueous solution was shaken for 12 hours followed by a settling period of at least 2 days. This value represents the mean of 13 measurements (Broholm and Feenstra, 1995).
The value of 8.7 g/L, the only well documented measurement, will be used in the risk assessment. A water solubility of 8.94 g/L is extrapolated by EUSES at 25°C.

### 1.3.7. Henry's law constant

326 Pa.m$^3$/mole at 25° C has been calculated with the QSAR programme developed at the Syracuse Research Corporation (Meylan and Howard, 1995).
According to the TGD, the Henry's law constant can be estimated from the molar mass and the ratio of the vapour pressure and the water solubility which is 394 Pa.m$^3$/mole.
The Henry's law constant was determined by equilibrium partitioning in 158.8 ml serum bottles at two air/water ratios (25 & 100 ml water) in triplicate. The bottles contained simultaneously methanol, tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene, dichloromethane, 1,1-dichloroethane and chloroform. The concentration of the different substances in the headspace was determined by GC/FID. For chloroform, the following results were obtained:

| Temp (°C) | H (Pa.m$^3$/mol) |
|---|---|
| 9.6 | 150 |
| 17.5 | 246 |
| 24.8 | 367 |
| 34.6 | 563 |

The result at 24.8°C is very coherent with the estimations above. Although the presence of other substances in the test system would have had some influence upon the result, the experimental result of 367 Pa.m$^3$/mol will be used in the risk assessment.

### 1.3.8. Partition coefficient octanol water

A logKow of 1.97 has been experimentally determined in bottles totally filled to avoid partitioning with air. The concentration was measured in the water phase only and the value represents the mean of 5 determinations (Hansch and Anderson, 1967).
A value of logKow = 1.52 has been calculated with the QSAR programme developed at the Syracuse Research Corporation (Meylan and Howard, 1995).
The measured value of 1.97 will be used in the risk assessment.

### 1.3.9. Other physical-chemical properties

According to Hoechst, 1996, Deshon, 1978 or Rossberg *et al.*, 1996, chloroform has no flash point, is not flammable and not explosive.

### 1.3.10. Summary

The physical and chemical properties of chloroform used in this risk assessment are summarised in the following table:

**Table 1-1 : Physical and chemical properties of the substance**

| Property | Value |
|---|---|
| Molecular weight | 119.5 g/mol |
| Melting point | -63.5ºC |
| Boiling point | 61.3ºC |
| Relative density | 1.48 at 20ºC |
| Vapour Pressure | 209 hPa at 20ºC |
| Partition coefficient | Log Kow 1.97 |
| Henry's law constant | H = 367 Pa.m3/mol at 25°C |
| Water solubility | 8,700 mg/L at 23ºC |
| Flash point | none |
| Flammability | no |

## 1.4. CLASSIFICATION

### 1.4.1. Current classification

According to Annex I of Directive 67/548/EEC, chloroform is classified as **harmful** and labelled as follows:

| | |
|---|---|
| Symbol: | **Xn** |
| R phrases: | |
| • 1 % ≤ conc. < 5 % | **R 40** [Limited evidence of a carcinogenic effect] |
| • 5% ≤ conc. < 20 % | **R 22** [Harmful if swallowed] **- 40-48/20/22** [Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed] |
| • conc. ≥ 20 % | **R 22-38** [Irritating to skin] **40-48/20/22** |
| S-phrases: | **S 2**: Keep out of the reach of children |
| | **S 36/37**: Wear suitable protective clothing and gloves |

Chloroform is currently not classified as dangerous to the environment.

### 1.4.2. Proposal of rapporteur

Based on the toxicity to fish, invertebrates and algae and the lack of biodegradability in standard test systems, the following classification could be proposed for environmental effects :

R52/53 – Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

S61 – Avoid release to the environment. Refer to special instructions/safety data sheets.

This proposal is based on the acute toxicity with *Oncorhynchus mykiss* (96h-LC 50 = 18 mg/L), *Daphnia magna* (48h-LC 50 = 29 mg/L), the algae *Chlamydomonas reinhardii* (72h-EC 50 = 13.3 mg/L) and the lack of degradation in standard ready biodegradation tests.

However, because the chronic toxicity is above 1 mg/L (Fish NOEC *Oryzias latipes* = 1.463 mg/L), chloroform does not need to be classified for the environmental compartment.

**Therefore, the proposal of the rapporteur is not to classify chloroform as dangerous to the environment.**

# 2. GENERAL INFORMATION ON EXPOSURE

## 2.1. PRODUCTION, IMPORT, EXPORT AND CONSUMPTION VOLUMES

Data from producers/importers are included in the IUCLID-database. These are listed in alphabetical order in Table 2-1.

**Table 2-1: List of producers/importers during 1997-2000**

| |
|---|
| Akzo Nobel Chemicals b.v., (NL) |
| Aragonesas, S.A. (SP) |
| Atofina S.A., (F) |
| Ausimont SpA, (I) |
| Dow Europe S.A., (CH), (prod. : DE) |
| Ercros, S.A. (SP) |
| Ineos Chlor plc, (UK) |
| LII Europe GmbH, (DE) |
| Solvay, S.A., (BE) |

In 2002 the production volume of chloroform in the European Community was estimated to be 302,800 t/a according to producer information available to the CEFIC, 2002).

**Table 2-2: European Production volumes of chloroform (CEFIC, 2001)**

| | 1997 | 1998 | 1999 | 2000 | 2001 | 2002 |
|---|---|---|---|---|---|---|
| Production (in Tonnes) | 253,937[4] | 256,934[4] | 282,061[4] | 301,461 | 303,955 | 302,784 |

EU production volume of 302,800 t/a will be used in this risk assessment.

Besides these production volumes, 14 out of the 15 European countries reported import and export volumes of chloroform.

---

[4] 8 companies from the 9 producing chloroform

**Table 2-3 : Import and export volumes of chloroform in the European Union (CEFIC, 2002)**

| | 1999 | 2000 | 2001 | 2002 |
|---|---|---|---|---|
| Production (in Tonnes) | 282,061 | 301,461 | 303,955 | 302,784 |
| Imports (in Tonnes) | 2,546 | 3,209 | 38 | 18 |
| Exports (in Tonnes | 19,375 | 19,520 | 43,908 | 32,080 |
| Tonnage | **262,232** | **285,150** | **260,085** | **270,722** |

Taking into account imported and exported volumes, is leading to a European tonnage of 285,150 t. in 2000 and 271,000 t in 2002.
The available information regarding use pattern is listed in Table 2-4 (CEFIC, 2001).

**Table 2-4 : Non-feedstock sales and feedstock sales of all European producers for the year 2000.**

| | Figures from (CEFIC, 2001) | Corresponding % of total chloroform sales for 2000 |
|---|---|---|
| Feedstock sales in EU for HCFC22 | 243,385 t | 93.8 % |
| Feedstock sales in EU for dyes and pesticides | 2,282 t | 0.9 % |
| Feedstock sales in EU for other applications | 5,519 t | 2.1 % |
| Total Feedstock sales in EU | 251,186 | 96.8 % |
| Non feedstock sales in EU | 8,277 t | 3.2 % |
| Total Sales | 259,463 t | 100 % |

Figures provided by CEFIC concerning the uses, are only available for the year 2000. However, since the European tonnage did not vary much between 2000 and 2002, it seems realistic to make the assumption that the percentages assigned to each sale are also valid for 2002. Thus, considering the tonnage of 271,000 t as the total use volume for 2002, the different uses will be calculated again using the same proportions as given in Table 2-4 (see Table 2-5).

**Table 2-5 : Production and uses volumes of chloroform calculated to account for a total net trade balance of 271,000 t in 2002.**

| | Figures that will be considered in the RA |
|---|---|
| Production | 302,800 |
| Total Sales = Tonnage | 271,000 |
| Non feedstock sales in EU | 8,700 |
| Total Feedstock sales in EU | 262,300 |
| Feedstock sales in EU for HCFC22 | 254,200 |
| Feedstock sales in EU for dyes and pesticides | 2,400 |
| Feedstock sales in EU for other applications | 5,700 |

## 2.2.PRODUCTION, USES AND UNINTENDED FORMATION

### 2.2.1. Production

Today, two industrial processes are used to produce chloroform (Building Research Establishment, 1994) :

1 / hydrochlorination of methanol
2 / chlorination of methane.

**Hydrochlorination of methanol**

This is a two-stage process in which methanol reacts primarily with hydrogen chloride and the resulting methyl chloride is then chlorinated using chlorine gas. The first reaction occurs in the vapour phase over a catalyst :

$$CH_3OH + HCl \xrightarrow{cat.} CH_3Cl + H_2O$$

The other chloromethanes are then formed by the thermal, non-catalytic chlorination of methylchloride :

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$
$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$
$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

**Chlorination of methane**

A simpler method for the production of chloroform involves the thermal, non-catalytic chlorination of methane. This one stage process is carried out at over 400 °C and 200 kPa pressure to produce a mixture of all four chloromethanes.

The ratio of products can be varied by controlling the feed rates of methane and chlorine and by recycling methane and unwanted lower halocarbons, e.g. methyl chloride (Building Research Establishment, 1994).

### 2.2.2. Uses

Chloroform is used mainly as a raw material in the production of hydrochlorofluorocarbon-22 (HCFC 22).

Future trends in chloroform use may depend on the trends of HCFC 22 manufacture. This HCFC is an ozone depleting substance and its use has been controlled under the Copenhagen Amendment (1992) to the Montreal protocol : a freeze in 1989 consumption of HCFCs was agreed. The last regulation adopted on 29th September 2000 set up a revised reduction program for the production of HCFCs (JOCE L. 244, September 29th, 2000) :

- Freeze : 1997
- 65% reduction on January 1, 2008,
- 80% reduction on January 1, 2014,
- 85% reduction on January 1, 2020,
- no more production of HCFCs on December 31st, 2025 and thereafter.

In the 90s’, the freeze of HCFCs consumption has been translated into a slight freeze in HCFCs production as shown in the following quantities for global HCFC 22 production (personal communication, 2001):

- 1990 : 213,700 t
- 1991 : 236,800 t
- 1992 : 245,700 t

| | |
|---|---|
| - 1993 : | 240,600 t |
| - 1994 : | 239,400 t |

Total HCFC 22 European production is estimated to have been approximately 150,000 tonnes in 1995 with 53,000 tonnes being sold into dispersive end uses (as refrigerant, fire-fighting material, foam blowing agent), 57,000 tonnes being used as chemical feedstock, the remainder being exported from the European Union (E.C., 1997). All the dispersive end uses of HCFC 22 may also be subjected to control in the next following years. This means that there may be a future reduction in demand for chloroform since HCFC 22 production is accounting for 93.8 % of chloroform uses.

At the European level, EU HCFC 22 production seems to have initiated a slight decrease during the last years:

| | |
|---|---|
| - 1995 : | 150,000 t |
| - 1998 : | 177,000 t |
| - 1999 : | 169,000 t |
| - 2000 : | 149,000 t |
| - 2001 : | 140,000 t |
| - 2002 : | 146,000 t |

However, western EU annual capacity for HCFC 22 was still reported to be of 175,500 t in January 2001 (CEFIC, 2001). It was also reported that since 1996, demand for fluorocarbon consumption (in particular HCFC 22) has been growing steadily in Western European countries. In 2005, the total Western European consumption of fluorocarbons is estimated to reach 198,000 tonnes, most of which will be used in refrigerants and air-conditioning, in foams and as fluoropolymer intermediates, whereas this consumption was around 176,000 tonnes in 2000. As there has been only a slight decrease in the HCFCs production since 1995, an average HCFC 22 production volume of **150,000 t/a** will be used in this risk assessment.

Considering the commercial yield of HCFC 22: 1.0 pound of product per 1.51 pounds of chloroform (CEFIC, 2001), the production of HCFC 22 would be 168,400 t in 2002. This figure is not completely in line with the production volume that is provided by Industry for 2002 (146,000 t). According to Industry, the difference between these figures could be attributed to chloroform storage instead of its use for HCFC 22 production.

In conclusion, an HCFC 22 production volume of 150,000 t/a will be used in the risk assessment, which is equivalent to a chloroform use of 226,500 t/a. The difference of 27,700 t between the volume theoretically affected to HCFC 22 production (254,200 t) and the average volume of 226,500 t which seems to be actually used for HCFC 22 production will be affected to stocks of chloroform.

Chloroform is used in other applications including production and extraction solvent, especially in the pharmaceutical industry (for example in the extraction of penicillin and other antibiotics). It is also used as a degreasing agent and as a chemical intermediate in the production of dyes, pesticides and other substances.

The Swedish Chemicals Agency (KEMI ; formerly National Chemicals Inspectorate of Sweden) reported that in 1994 chloroform was mainly used in Sweden as a laboratory chemical and as a raw material in pharmaceutical plant (23 t/a ; www.kemi.se).

The Danish Product Register reports for October 1996, that 291 t/a of chloroform are used in 91 products, the most important product type being solvents (personal communication).

6 products are registered in the Finnish Product Register. No tonnage is given.

According to information transmitted by the US-EPA (personal communication), only 19,691 t/a are used in the USA. These quantities do not include production volumes claimed confidential business information. Other than uses as a general solvent for adhesives, pesticides, fats, oils, etc., chloroform is also registered in the USA for use as an insecticidal fumigant on stored grains and as mildewcide for tobacco seedlings.

In this risk assessment, the following emission scenarios will be considered :

**Table 2-6 : Emission scenarios**

| | Industry Category | Use Category | Quantity used (tonnes/year) |
|---|---|---|---|
| **Use as an intermediate** (HCFC 22, dyes and pesticides production) | 3<br>(Chemical industry : chemicals used in synthesis) | 33<br>(intermediates) | 234,600<br>(HCFC 22 : 226,500<br>dyes & pesticides : 2,400<br>other applications : 5,700) |
| **Use as a solvent** | 2<br>(Chemical industry : basic chemicals) | 48<br>(solvents) | 8,700 |
| **Total uses** | | | 243,300 t/a |
| **Stocks** | - | - | 27,700 |

### 2.2.3. Unintended formation

Exposure to chloroform can occur from sources not covered by the life cycle of the produced/imported chloroform. In accordance with the Technical Recommendation from the European Commission, unintended formations are listed below. The risk assessment will be performed with readily available information on these sources of chloroform.

**Losses as a by-product during chemical manufacturing**

Chloroform is produced and emitted as a by-product in the manufacture of VC/PVC products and other chlorinated bulk chemicals. It is a by-product of Ethylene Monochloride (vinyl chloride, VCM). It is formed during the production of precursor ethylene dichloride (EDC) when produced from ethylene and chlorine by oxychlorination. The production of trichloroethylene and tetrachloroethylene may also result in chloroform emissions (US-EPA, 1984; Building Research Establishment, 1994).

**Water chlorination**

Water is disinfected by chlorination in several different applications. Chloroform is produced by the aqueous reaction of chlorine with various organic compounds in water.

In drinking water, chloroform may be present in the raw water as a result of industrial effluents containing this chemical. In addition, chloroform is formed from the reaction of chlorine with humic materials. The amount of chloroform generated in drinking water is a function of both the amount of humic material present in the raw water and the chlorine feed (US-EPA, 1984). Water utilities are making efforts to avoid by-product formation in the disinfection processes.

Chlorine is also sometimes used to disinfect municipal wastewater. However there is generally a lower concentration of humic compounds, i.e. haloform precursors, in wastewater than in raw water and therefore chlorination of wastewater has been reported to increase chloroform levels only slightly (Building Research Establishment, 1994).

Swimming pool water has been reported as a source of chloroform (Bätjer *et al.*, 1980). In France about 49 % of the swimming pools are disinfected by using chlorine or sodium hypochlorite (Legube *et al.*, 1996). There are some indications that chlorination of swimming pool water might be replaced by ozone treatment (Building Research Establishment, 1994). However it seems that alternative treatments to chlorination have too many drawbacks to be widely used. For example, the use of ozone alone has not a persistent biocidal effect. To be efficient, the ozone treatment must be supplemented with a chlorination treatment which becomes very expensive. The UV treatment has comparable disadvantages and would not lead to a reduced consumption of chlorinated products (Legube *et al.*, 1996).

As there is no evidence until now for a decrease in the use of chlorinated products in the disinfection processes of swimming pools, the more recent available data will be used in this risk assessment without expecting alternative treatments.

Cooling water in power plants and other industrial processes is often chlorinated to prevent the heat exchanger and condensing tubes becoming fouled, which would greatly reduce their efficiency (Building Research Establishment, 1994). Again, the reaction between chlorine and organic material in the water results in chloroform generation.

**Pulp and paper bleaching**

The most important potential for chloroform formation in water is occurring in the pulp and paper industry. Chloroform is produced where wood pulp is bleached with chlorine.

Chloroform is formed from the aqueous reaction of chlorine with organic substances in the wood pulp and is released to air during the bleaching process, the subsequent treatment of effluent, and after the release of the treated effluent to receiving waters (US-EPA, 1984).

**Groundwater**

Chloroform may be formed in groundwater as the result of the degradation of carbon tetrachloride (Laturnus *et al.*, 2000). However this is not expected to be a significant source. The chloroform formation in groundwater will not be estimated in this risk assessment.

**Atmospheric reactions**

The atmospheric degradation of high tonnage chlorinated solvents has been suggested as a major source of chloroform. Both trichlorethylene and perchloroethylene have been implicated.

There are other sources of chloroform releases into the atmosphere (Building Research Establishment, 1994):

- Chloroform has been measured in vehicle exhausts in the United States. Chloroform levels are 100 fold higher in vehicle exhausts of a car using leaded gasoline than in car using unleaded gasoline.
- Chloroform may be found in gases from wastewater sludge incinerators, chlorinated solvents incinerators and from disused or active landfill sites.
- Chloroform may be released from the use of household products (for example cleaning products containing chloroform).

**Natural sources**

Some scientific studies tend to demonstrate that chloroform might be released through natural processes. Some of the chloroform levels measured in the oceans are higher than would be expected from equilibrium calculations (Khalil *et al.*, 1983). It has been suggested that natural production is associated with the oxidation of methyl chloride produced by algal activity and emissions from countryside fires (Su and Godberg, 1976), as cited in Building Research Establishment, 1994.

Although there is no direct evidence of a natural source of chloroform, industrial chloroform releases are not large enough to account for the observed global chloroform burden. Whether known indirect sources of chloroform, such as water chlorination, pulp mill effluents and atmospheric reactions etc., are large enough to account for the observed burden or whether a natural source of chloroform exists is a matter for speculation (Building Research Establishment, 1994).

### 2.2.4. Legislative Controls

***Releases into water:***
Chloroform has been identified as a List I chemical under Council Directive of June 12th 1986 (86/280/EEC) on limit values and quality objectives for discharges of certain dangerous substances included in list 1 of the annex to Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community.

As an organohalogen compound, chloroform may be classified as a List I substance under the Council Directive 80/68/EEC on the protection of groundwater against pollution caused by certain dangerous substances.

***Water Framework Directive:***
According to Decision n° 2455/2001/EC of the European Parliament and of the Council of 20 November 2001, chloroform is included in the list of the 33 priority substances in the field of water policy and amending Directive 2000/60/EC. This list has been established on the basis of a combined monitoring-based and modelling-based priority settings (COMMPS) scheme. The European Commission has recently submitted a proposal for chloroform. Overall Quality Standard for freshwater, transitional, coastal and territorial waters : QS = 2.5 µg/L. This concentration in water aims at guarantying the protection of the pelagic and benthic communities. The proposed QS has been calculated applying the Equilibrium Partitioning Method to the result of the ecotoxicity sediment study of van Vlaardingen and van Beelen, 1992 presented in section 3.2.3. However, it should be indicated that this value is presently only a proposal that still has to be adopted by the European Parliament and the Council.

***Releases into the air:***
In a general scope, chloride and chlorinated compounds are listed in Annex II of Directive 84/360/EEC on the combating of air pollution from industrial plants dated on June 28th 1984. According to article 4 of this directive, all appropriate preventive measures against air pollution, including the application of the best available technology, provided that the application of such measures does not entail excessive costs should be implemented. The competent authority that is delivering the authorization should also check that the industrial plants will not cause significant air pollution and that all emission limits are satisfied.

The regulation is becoming more precise in Directive 96/61/EC concerning integrated pollution prevention and control. Chlorine and chlorinated compounds are listed in annex III for the air compartment, meaning that emission limit values should be defined for these substances in the authorization that is delivered by the competent authorities.

Chloroform is not listed in Annex I of Directive 96/62/EC on Ambient Air Quality Assessment and Management, which is setting limit values and alert thresholds for ambient air.

However, as a volatile organic compound, chloroform may be regulated under other more recent legislations including Directive 99/13/EC on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations. The use of chloroform for the extraction in chemical and pharmaceutical industry may be regulated under this directive: when the consumption of chloroform is above 50 tonnes/year for this activity, the equipment is required to meet an emission limit of 20 mg C/N.m$^{-3}$ in waste gases. Besides, limits to the fugitive and total emissions are set up to 15% of the solvent input for existing installations

(existing installations before the date on which the directive is brought into effect) and limits to the fugitive and total emissions are set up to 5% of the solvent input for new installations. While these limits are immediately applicable for new installations, existing installations are required to meet these limits by 2007.
Chloroform may also be concerned with relevant international legislations for volatile organic compounds: the UN/ECE Convention on Long Range Transboudary Air Pollution (Geneva, 1979) and the Basel Convention and its eight related protocols (1989, entered into force in 1992).

Under the first Convention, Parties are committed to control and to restrain their VOC emissions by 1999 in order to reduce fluxes of these compounds and fluxes of secondary photochemical oxydants and therefore protect Health and the Environment from harmful effects.
Under the Basel Convention, Parties are committed to limit and regulate the production and the transportation of hazardous wastes.

The various European Directives dealing with volatile organic substances are implemented in the French legislation under a range of orders leading to more precise controls for chloroform emissions:

- For air pollution, when fluxes are above 2 kg/h, the concentration of all the volatile organic compounds (VOC) should be below 110 mg/m$^3$. When fluxes are above 0.1 kg/h, concentration of all organic compounds listed in Annex III (and including chloroform) should be below 20 mg/m$^3$. The use of chloroform for the extraction in chemical and pharmaceutical industry is also regulated with the same emission limits as in Directive 99/13/EC on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations (see above). Finally, emission measurements and air monitoring are required when specific VOC emission thresholds are reached.
- For pollution of superficial waters, the threshold concentration in effluents from chloromethane production facilities should be below 1 mg/L. Releases should be below 10g/t and 7.5 g/t of chloromethane produced respectively for facilities using methanol and facilities using chloration of methane.

***Uses :***
According to the European parliament and Council Directive 94/60/EC amending for the 14th time Directive 76/769/EEC chloroform may not be used from 20 June 1996 in concentrations equal to or greater than 0.1 % in substances and preparation placed on the market for sale to the general public. By way of derogation, this provision shall apply neither to medicinal nor veterinary products nor to cosmetic products.
The Commission Directive 96/55/EC replacing the Directive 94/60/EC determines that chloroform may not be used in concentrations equal to or greater than 0.1 % by weight in substances and preparations placed on the market for sale to the general public and/or in diffusive applications such as in surface cleaning and cleaning of fabrics. The provisions entered into force on June 30th 1998.

# 3. ENVIRONMENT

## 3.1.ENVIRONMENTAL EXPOSURE

### 3.1.1. General discussion

The environmental exposure assessment of chloroform will be based on the expected releases of the substance during the following life cycle stages:

**I Production**

**IIa. Use as an intermediate**

- HCFC 22 production
- dyes and pesticides production
- other applications

**IIb. Use as a solvent**

- extraction solvent in chemical and pharmaceutical industry

**IIIa Unintended formation**

- losses as a by product during chemical and VC/PVC products manufacturing

**IIIb**

- Water chlorination
    - drinking water
    - municipal wastewater
    - swimming pools
    - cooling water
- pulp and paper bleaching
- atmospheric reaction of high tonnage chlorinated solvents
- vehicle emissions
- landfills
- incineration processes
- natural sources

For life cycle stages I, IIa and IIb both site-specific and generic emission scenarios are used for calculating the Predicted Environmental Concentrations (PEC) values in the various compartments.

Stage III can be regarded as a diffuse source of chloroform. Except for the losses during chemical and VC/PVC products manufacturing where site-specific information might be found, all the other emissions will be considered in PECregional calculations only.

The releases due to uses in household products will not be considered as a proposal has already been made within the European Community to limit the chloroform concentration to < 0.1 % by weight in substances placed on the market for sale to the general public.

### 3.1.1.1 Releases from production

#### 3.1.1.1.1. Default release estimate

The emission factors proposed in the TGD in table A1.1 (IC2, Main Category 1b) can be used for the whole production of 302,800 tonnes. Vapour pressure being > 10,000 Pa, default emission factors are 0.005 to air, 0.003 to wastewater.
Therefore, the total releases are 1,514 t/a to air and 908 t/a to wastewater. Considering that 10 % of these total releases will occur at a regional scale, the default release estimates are :

| | |
|---|---|
| For the regional scale : | 151 t/a to air |
| | 91 t/a to wastewater |
| For the continental scale : | 1,363 t/a to air |
| | 817 t/a to wastewater |

As there are only ten production sites of chloroform, the 10% rule is not applied. In 1992, all the production sites mentioned in the IUCLID database reported production volumes around 10,000 to 50,000 tonnes/year. In 2000, for 5 companies, the production ranged between 15,000 and 40,000 tonnes/year. As there was still one company that in 1995 reported production volumes up to 50,000 t/a with 300 days/year of emission, the worst case of a site producing 53,615 t/a during 300 days/year is considered in the estimation of the default releases. The default release estimate can be calculated for such a typical site using the same emission factors as for the total releases :

| | |
|---|---|
| Local: | 268 t/a to air |
| | 161 t/a to wastewater |

Local estimations are higher than the regional ones. This situation might come from the generic proportions for the standardised regional environment that might not necessary include the "worst case" of a production site of 50,000 t/a. To take into account the situation when such a site is included in the regional environment, the releases at the regional scale must include the releases at the local scale. This is the reason why local release estimate will be used at the regional scale.
To summarise, the default release estimate during the production of chloroform are :

| | |
|---|---|
| Local : | 268 t/a to air |
| | 161 t/a to wastewater |
| Regional : | 268 t/a to air |
| | 161 t/a to wastewater |
| Continental : | 1,246 t/a to air |
| | 747 t/a to wastewater |

#### 3.1.1.1.2. Industry specific release information

In section 2.2.1 two industrial processes of chloroform production have been introduced. According to US-EPA, 1984, losses to air do not differ between the two procedures. Therefore, no distinction is made between the two different production methods in this assessment. In the same document, an uncontrolled production process loss of 2 kg per tonne plus 3.1 kg per hour fugitive loss due to leaks in process valves, pumps, compressors and pressure relief valves are reported.
The emissions from process fugitive sources do not depend on their size, but only on their number. Therefore the process fugitive emissions are not dependent on plant capacity. Emissions to water were however not specified.

Reynolds and Harrison, 1982 reported a liquid effluent loss of 0.1 - 1 kg per tonne chloroform produced. However, these values are based on estimates obtained from discussions with a number of American and European producers and do not represent accurate assessments.

There are ten major chloroform production sites within the EU with an overall production of 302,800 tonnes in 2002. Three production sites are located on the seaside.
All the ten EU producers informed about specific emissions to water and to air at their production sites. These data are considered as the local emissions during production (***Elocal**$_{production\ water}$* and ***Elocal**$_{production\ air}$*). Emissions linked to handling and storage were also taken into account when available. Production is supposed to occur 365 days/year for all sites except for site C. Release factors ranging from $8*10^{-5}$% to 0.16% to air and $2*10^{-6}$% to 0.0014% to surface water can be derived. This is illustrated in detail in Table 3-1.

**Table 3-1 : Specific emissions to surface water and air during production**

| Site | Production | Emission to air | | | Emission to surface water | | | |
|---|---|---|---|---|---|---|---|---|
| | [t/a] | Local emission to air (kg/d)<br>*Elocal$_{production\ air}$* | Release to air<br>(t/a) | Calculated release factor [%] | Local emission to surface water or sea<br>[kg/d] | Release to surface water or sea<br>[t/a] | Release to wastewater [t/a] | Calculated release factor to surface water [%] |
| A | 19,500 | 83.7 | 30.5 | 0.16 | 0.0077 | 0.0028 | *0.019* | Negligible<br>($1.4*10^{-5}$) |
| B | 15,100 | 0.036 | 0.013 | Negligible ($8*10^{-5}$) | 0.014 | 0.005 (linked to the storage) | 0.005 [1]<br>(no WWTP) | Negligible<br>($3.3*10^{-5}$) |
| C | 53,615 | 7.2 | 2.16 | 0.005 | 0.737 | 0.221 | 0.75 | 0.0004 |
| D | 44,399 | 42 | 15.33 | 0.04 | 0.0078 | 0.0028 | 0.048 | Negligible<br>($6.3*10^{-6}$) |
| E | 28,226 | 4.18 | 1.526 | 0.005 | 0.0017 | 0.0006 | *0.004* | Negligible<br>($2.1*10^{-6}$) |
| F[2] | 35,000 | 21.6 | 7.9 | 0.023 | 0.98 | 0.356 | 0.356 [1]<br>(no WWTP) | 0.0010 |
| G | 27,500 | 3.70 | 1.352 | 0.005 | 1.08 | 0.396 | 2.75 | 0.0014 |
| H | 40,039 | 0.14 | 0.05 | Negligible (0.0001) | 1.45 | 0.53 | ***3.68*** | 0.0013 |
| I | 20,183 | 2.44 | 0.89 | 0.004 | 0.011 | 0.004 | *0.027* | Negligible<br>($2.0*10^{-5}$) |
| J | 11,926 | *nd.* | *nd.* | *nd.* | 0.047 | 0.017 | 0.102 | $1.4*10^{-4}$ |
| **Total** | **295,488** | **166.6** | **60.23** | **0.02** | **4.34** | **1.54** | **7.74** | **$5.2*10^{-4}$** |

*nd.*: no data available

[1] These sites specified that there was no biological wastewater treatment plant but process effluents underwent a steam stripping treatment. However, as no quantitative data is available concerning the efficiency of this treatment, no removal will be considered.

[2] Site F had stopped manufacturing chloroform in 2004 and is being dismantled. Even if the company does no longer produce chloroform, all its data are still presented in this RAR in order to realistically describe the situation in the year 2002.

On site B and H, emissions to air are negligible. For site B, it was reported that all vents were connected to a purification unit before release.

Concerning releases to WWTP, values for sites C, D, G and J, are stemming from measurements in effluents. For production sites A, E, H and I, as no data was available for the removal percentage in STP, releases to wastewater were calculated taking into account a 85.6% removal (see section 3.1.1.5.2). These calculated values are presented in italics in Table 3-1. Releases to surface water for site G were estimated considering the measured releases to wastewater and applying an 85.6% removal (see section 3.1.1.5.2).

For releases to air, well-documented production sites are covering more than 97% of the European chloroform production and a wide range of plant sizes (Table 3-1). Among these 9 production sites, the highest emission factor to air is 0.16%. This highest value is more than 3 times lower than the default value from TGD (0.5%, main category 1b). Therefore, the highest release rate of 0.16% from site A could be considered as a realistic worst-case situation for production site J where no information on releases to air was provided.

The production is supposed to occur 300 days/year (Table B 1.6. of TGD).

**Table 3-2 : Calculated specific emissions to air during production**

| Site | Production [t/a] | Local emission to air [kg/d] $E\ local_{production\ air}$ | Releases to air [t/a] | default release factor [%] |
|---|---|---|---|---|
| J | 11,926 | 63.6 | 19 | 0.16 |

The whole releases at production sites can be summed up to 230.2 kg/d to air and 4.34 kg/d to surface water.

Total production reported in Table 3-1 (295,488 t) is lower than the total production volume reported in section 2: 302, 800 t in 2002. The explanation of this difference of 7,312 t is that global tonnage used in section 2 was available for the year 2002 whereas specific tonnage for the year 2000 was available for 6 of the 10 production sites. For the other 4 production sites, more recent production volumes or, on the contrary, production volumes of 1995 were available.

Considering the 10 EU producers, the sum of the estimated and reported releases is considered as the continental release. As the number of production sites is low, the regional releases due to production are supposed equal to the highest estimated local releases (site A for release to air and site E for release to wastewater (see Table 3-5)).

| | | |
|---|---|---|
| **Regional input:** | **30.5 t/a to air** | **5.1 t/a to wastewater** |
| **Continental input:** | **29.7 t/a to air** | **7.74 t/a to wastewater** |

#### 3.1.1.1.3. Transportation losses

Transport to customer may occur by rail or truck tank or occasionally by vessel. No information has been found regarding losses of chloroform attributed to transportation of the product for its use. The releases during this stage are supposed to be taken into account in the releases calculated during production and uses of the product.

### 3.1.1.2 Releases from use

#### 3.1.1.2.1. Use as an intermediate (life-stage IIa)

##### 3.1.1.2.1.1. Default release estimation

In 2002, 234,600 tonnes of chloroform have been reported to be used as an intermediate (section 2.2.2).
Default release estimates are given in the TGD for chemicals used in synthesis. The release factors during chemical synthesis are 0.005 to air and 0.007 to water (Table A 3.3, Main Category 1c). Thus, total releases of 1,173 t/a to air and 1,642 t/a to water can be calculated.

Production of HCFC 22 is accounting for 96.5 % of the tonnage of chloroform used as intermediate (Table 2-6). As there are only ten HCFC 22 production sites in Europe, the 10% rule is not applied. However, information concerning HCFC 22 production tonnage is available for 6 out of the 10 HCFC 22 production sites, with a highest reported tonnage of 35,000 t/a (*i.e.* 52,850 t/a of chloroform used; see section 2.2.2) over 300 days/year. If we assume a total European HCFC 22 production volume of 150,000 t/a (see section 2.2.2), the 4 remaining production sites for which no data is available, share less than 24,000 t/a.
Thus, the highest tonnage of 52,850 t/a of chloroform used in HCFC 22 production will be considered to estimate the default local release:

| | |
|---|---|
| Local release : | 264 t/a to air |
| | 370 t/a to wastewater |

Furthermore, at the regional scale, chloroform and HCFC 22 are produced by companies distant of more than 100 km. Therefore, local release estimate will be used at the regional scale.
To summarise, the default release estimate during the uses of chloroform as an intermediate are :

| | |
|---|---|
| Local release : | 264 t/a to air |
| | 370 t/a to wastewater |
| Regional release : | 264 t/a to air |
| | 370 t/a to wastewater |
| Continental release : | 909 t/a to air |
| | 1,272 t/a to wastewater |

##### 3.1.1.2.1.2. Industry specific release estimation

<u>HCFC 22 production</u>
The production of HCFC 22 from chloroform can lead to chloroform emissions to the environment. US-EPA, 1984 estimated that an uncontrolled emission to air of 0.59 to 2.5 kg/t HCFC 22 produced takes place. HCFC 22 is produced by the catalytic liquid-phase reaction of anhydrous hydrogen fluoride (HF) and chloroform. Chloroform, HF and chlorine are pumped from storage to the reactor, operating at temperatures ranging from 0 °C to 200 °C and pressures of 100 to 34,000 kPa. Vapour from the reactor is fed to a distillation column, which removes as overheads hydrogen chloride, the desired fluorocarbon products, and some HF (US-EPA, 1984).

In the plants that operate in liquid phase, releases occur from the columns used to neutralise and dry the chlorofluoromethanes produced. The typical $CHCl_3$ concentration in aqueous effluents from HCFC 22 production plants operating in liquid phase is about 63 mg/L. It is calculated that about 50 - 80 kg $CHCl_3$ is emitted to wastewater per 1,000 t production (REIS, 1989).

The plants operating in the gas phase in principle have no water effluent and therefore their contribution of chlorocarbons to the aqueous effluents may be neglected.

It is assumed in this Risk Assessment that all the EU HCFC production takes place in liquid phase.

There are ten HCFC 22 production sites in the EU. CEFIC reported that 96.5 % of chloroform used as an intermediate is used for HCFC 22 production. According to the data from 2002 (Table 2-5), a EU consumption of 254,200 t/a could be assumed for HCFC 22 production.

Although HCFC 22 production volumes provided by industry show an initial increase after 1995, (a total European production volume of 150,000 t was estimated), a decreasing tendency could be observed since 1999 with a reported production volume of 146,000 in 2002 (see section 2.2.2).

The more recent figures will be used in this risk assessment, with a total European HCFC 22 production of 150,000 t (using 226,500 t of chloroform).

**Chloroform emissions from HCFC 22 production plants :**

Emissions from 8 of the 10 European plants where chloroform is used as feedstock for hydrofluorocarbon production are presented thereafter (highest release factors are in bold) :

**Table 3-3 : Chloroform emissions to air and water from HCFC 22 production plants**

| Location | Emissions to air | | Emissions to water | |
|---|---|---|---|---|
| | Reported data (kg/a) | Releases factors (kg/t HCFC 22) | Reported data (kg/a) | Releases factors (kg/t HCFC 22) |
| Site 1, 2001 | 3,800 | 0.17 | 35 | 0.002 |
| Site 2, 1998 | << 1000 | << 0.05 | 100 | 0.005 |
| Site 2, 1999 | << 1000 | << 0.06 | 100 | 0.006 |
| Site 2, 2000 | << 1000 | << 0.05 | 100 | 0.005 |
| Site 3, 2000 | 105 (all vents are connected to recycling circuits. Emissions are mainly linked to the storage) | 0.007 | 170 | 0.011 |
| Site 4 | All the off-gases are collected and sent to the Thermal Oxidation Plant, in which they are converted to CO2, HF and HCl (HF and HCl are removed in a scrubber system) | | 2.02 | **0.058** |
| Site 5, 1998 | 1,400 | About 0.05 | 23 | About 0.05 |
| Site 5, 1999 | 1,400 | About 0.05 | 10 | About 0.05 |
| Site 5, 2000 | 3,700 | About 0.05 | 2.0 | About 0.05 |
| Site 6, 1995 | 4,080 | **0.70** | 0.09 | 0.002 |
| Site 7, 2000 | < 10 | < 0.001 | *nd.* | *nd.* |
| Site 7, 2001 | 5,600 | *nd.* | 0.014 | *nd.* |
| Site 8 | 1,190 | 0.045 | 67 | 0.003 |

*nd.:* no data available

As information is available for 8 of the 10 HCFC 22 production sites, the highest releases factors reported will be used in the risk assessment: 0.0007 to air (site 6) and 0.00006 to wastewater (site 4). At the regional scale, the highest production capacity for one site (35,000 t) will be used:

Local release : 24.5 t/a to air
2.1 t/a to wastewater

Regional release : 24.5 t/a to air
2.1 t/a to wastewater

Continental release : 80.5 t/a to air
6.9 t/a to wastewater

**Integrated manufacturers for chloromethane and fluorocarbon productions.**
Among the ten chloroform production sites, eight sites are not simultaneously producing HCFC 22. The information has been made available either from personal communication (ECSA, 2003) or from the Draft Risk Assessment of Chlorodifluoromethane (E.C., 1997).

For two sites, chloroform and HCFC 22 are produced by two independent companies being situated in very close sites (about 1 km distance between the two sites). Therefore, it could be considered that releases might reach the same river and local emissions to water due to both chloroform and HCFC 22 will be added for these sites. For the air compartment, the releases will be considered separately because the local scenario is estimating the concentration at 100 meters from the source. Finally, for the soil compartment, the contributions of both productions to wet and dry depositions will be added because the local scenario is related to a surrounding area within 1000 m from the source.
In the following table, specific data on chloroform releases during HCFC 22 production over 365 days, are taken into account for both sites.

**Table 3-4 : Local emissions to air and to wastewater during integrated production of chloroform and HCFC 22**

| Site | Emission to air | | | | Emission to wastewater | |
|---|---|---|---|---|---|---|
| | Local emission to air Elocal $_{air}$ (kg/d) | | Releases to air (t/a) | | Local emission to wastewater (kg/d) Elocal $_{water}$ | Releases to wastewater (t/a) |
| | For $C_{local\ air}$ calculation | For $C_{local\ soil}$ calculation | For $C_{local\ air}$ calculation | For $C_{local\ soil}$ calculation | | |
| D[1] | 3.3 | 45.3 | 1.46 | 16.5 | 0.32 | 0.12 |
| E[1] | 2.7 | 6.9 | 1 | 2.5 | 0.28 | 0.1 |
| **Total** | **6** | **52.2** | **2.5** | **19** | **0.6** | **0.2** |

[1] Addition of the emissions to air will only be considered for the soil compartment (addition of the wet and dry depositions in a surrounding area within 1000 m from the source)

For production site D, addition of the emissions to wastewater due to both productions will be considered to determine $PEC_{local,water}$ for the site. For production site E, another integrated scenario presented below will be applied.

Dyes and pesticide production

Chloroform is used as a chemical intermediate in dyes and pesticide production processes.

0.91 % of feedstock sales of chloroform were used in European Union for dyes and pesticides, which corresponds to a volume of 2,400 t/a (Table 2-6).

With an emission factor of 0.5 % to air and 0.7 % to water (Table A3.3, Main Category 1c), total releases of 12 t/a to air and 16.8 t/a to water can be calculated.

As no information on the number of sites using chloroform for the production of dyes and pesticides in Europe was provided, the 10% rule is not applied and the total volume of 2,400 t is used as input in table B3.2. of the TGD.

f main source = 0.3 and number of days = 144 d/a.

Local release : 3.6 t/a to air
5.04 t/a to wastewater

It is assumed that the total EU dyes and pesticide production using chloroform could occur at the regional scale. Therefore, these total releases will be used at the regional level:

Local release : 3.6 t/a to air
5.04 t/a to wastewater
Regional release : 12 t/a to air
16.8 t/a to wastewater

**Integrated manufacturers for chloromethane and dyes / pesticides productions.**

It is possible that some manufacturers have both chloromethanes and dyes or pesticides productions on the same site. Nine production sites confirmed that chloroform was not used on site for this purpose. For the remaining site, an integrated scenario will have to be considered. Given that chloroform and HCFC 22 are also produced at site E, a "worst case" scenario taking into account all these three productions will be used. Consequently, releases to water and air due to production of chloroform, HCFC 22 and dyes / pesticides, will be added for site E.

**Table 3-5 : Local emissions to air and to wastewater during integrated production of chloroform, HCFC 22 and dyes or pesticides**

| Site | Emission to air | | | | Emission to wastewater | |
|---|---|---|---|---|---|---|
| | Local emission to air Elocal $_{air}$ (kg/d) | | Releases to air (t/a) | | Local emission to wastewater (kg/d) Elocal $_{water}$ | Releases to wastewater (t/a) |
| | For $C_{local\ air}$ calculation | For $C_{local\ soil}$ calculation | For $C_{local\ air}$ calculation | For $C_{local\ soil}$ calculation | | |
| **E**[1] | **25** | **31.9** | **3.6** | **6.1** | **35.3** | **5.1** |

[1] Addition of the emissions to air will only be considered for the soil compartment (addition of the wet and dry depositions in a surrounding area within 1000 m from the source)

This worst-case situation will be considered in the risk characterization for production site E:

- For the water compartment, $PEC_{local,water}$ will be calculated using this data.
- For the air compartment, releases will be considered separately because the local scenario is estimating the concentration at 100 meters from the source.
- For the soil compartment, the contributions of chloroform, HCFC 22 and dyes / pesticides productions to wet and dry depositions will be added because the local scenario is related to a surrounding area within 1000 m from the source.

According to this scenario, at production site E, releases to wastewater are the highest compared to the 9 other production sites (see Table 3-1). As the number of production site is low, regional and continental releases to wastewater will be estimated based on this data for site E.

Other applications (considered as confidential)
Chloroform is sold as feedstock for other applications considered as confidential (IC3 / UC33).
2.1 % of feedstock sales of chloroform were used in 2000 in European Union for other applications. A volume of 5,700 t/a is then assumed to be used in 2002 for these confidential applications (Table 2-6).
With an emission factor of 0.5 % to air and 0.7 % to water (Table A 3.3, Main Category 1c), total releases of 28.4 t/a to air and 39.8 t/a to water can be calculated.

For the local scale, it is not expected that such confidential applications might occur in many sites over Europe. Therefore, the 10% rule is not applied and the total volume of 5,700 t is used as input in table B3.2. of the TGD :
f main source = 0.25 and number of days = 300 d/a
Local release : 7. 11 t/a to air
9.96 t/a to wastewater

It is assumed that these total confidential uses could occur at the regional scale, therefore, total releases will be used at the regional level.
To summarise, the default releases estimate during the uses of chloroform for other confidential applications, are :
Local release : 7.11 t/a to air
9.96 t/a to wastewater
Regional release : 28.4 t/a to air
39.8 t/a to wastewater

**- Effluent monitoring**

- A vast number of effluent monitoring was performed in France over the last years. In the following table, the results of measurements performed in the effluents from the chemical industry are summarised.

**Table 3-6 : results of monitoring studies of wastewater effluents from chemical industry**

| Region / year | Number of positive samples [1] | average concentration [µg/L] | highest concentrations [µg/L] | average releases [kg/d] | highest releases [kg/d] | Reference |
|---|---|---|---|---|---|---|
| **Picardie, France / 1992-1998** | 29 | 27 | 239,120,110,100 | 0.030 | 0.271, 0.135, 0.062, 0.043 | DRIRE Picardie, 1996 |
| **Rhône-Alpes, France / 1993 (57 sites were investigated)** | 32 | 1243 | 35475, 1200, 815, 660, 650 | 3.32 | 37.9, 29.0, 19.1, 18.9, 0.34 | INERIS, 1994 |
| **Rhône-Alpes, France / 1998-1999 (58 sites were investigated)** | 50 | 100 | 1088, 1078, 641, 602, 349, 266 | 1.49 | **38.9**, 14.1, 7.0, 4.1, 0.42 | INERIS, 2000 |
| **Franche-Comté, France / 1993-1995** | 1 | 59 | - | 1.5 | - | DRIRE Franche-Comté, 1996 |
| **Poitou-Charente, France / 1996-1998** | 1 | 18 | - | 0.02 | - | DRIRE Poitou-Charentes, 1998 |

[1] When no concentration is available in the monitoring studies, it is not known whether chloroform was not analysed or whether the concentration was below the detection limit.

Releases as high as 38.9 kg/d were measured. 90-percentile values would be approximately 10 kg/d. Even assuming that on-site biological treatment was performed, and using an elimination rate of 85.6 % (cf. section 3.1.1.5.2), a release into raw wastewater of respectively 278 and 69 kg/d can be estimated. This is higher than the quantities estimated above with default release factors. However results from this monitoring programme could be considered as an overestimation of a realistic situation for the following reasons :

- It is not specified on the respective reports whether chloroform was used as an intermediate or as a solvent.
- It is furthermore not indicated whether on-site treatment was performed or not.

The above calculated releases are therefore retained for the risk assessment.

#### 3.1.1.2.2. Use as a solvent (life-stage IIb)

Non feedstock sales of 8,700 t of chloroform in European Union have been estimated for 2002 (Table 2-6). It is suggested that chloroform is mainly used as a solvent in the manufacturing of pharmaceutical and chemical products by chemical synthesis. Each step of the manufacturing process may be a source of chloroform emissions.

#### 3.1.1.2.2.1. Default release estimation

Default release estimates are given in table A3.2 for basic chemicals. The release factors during this use are 0.5 to air and 0.4 to water (1,000 mg/L <water solubility < 10,000 mg/L), vapour pressure ≥ 1,000 Pa).
According to the Technical Guidance Document, 10% of the total use volume i.e. 870 t/a would be used in a region.
As for the local estimation, no details of tonnage produced for individual sites are given. Then, the default values from Table B3.2 will be used. Assuming that the use is well spread over Europe, for a yearly use of 870 tonnes it is assumed that the process occurs for 87 days in a unit representing 40% of the main source.
Therefore the default release estimates are :

Local release : 174 t/a to air
139 t/a to wastewater

Regional release : 433 t/a to air
346 t/a to wastewater

Continental release : 3,900 t/a to air
3,120 t/a to wastewater

#### 3.1.1.2.2.2. Industry specific release estimation

**- Extraction in chemical and pharmaceutical industry**

According to US-EPA, 1984, the magnitude of emissions varies widely among operations. Therefore it is impossible to define specific emission rates for various operations. In this document, no information on water emissions is given. However, industry (ECSA, personal communication, 2006) has provided some qualitative information from six European pharmaceutical industries (location unknown) on releases of chloroform. According to it, quantity of chloroform in treated effluents released to the sea never exceeds 0.5 mg/L and the concentration of chlorinated solvent in untreated wastewater is below 1 mg/L. Moreover, a plant declared that concentrations of chloroform in effluents are below the limit of detection (5 µg/L) and another one stated that all the solvents are incinerated.
As a matter of fact, the representativeness of these data for all the European facilities cannot be established and default values will be used in this risk assessment.

In US-EPA, 1984, it is roughly estimated that 16 % of chloroform used in this industry is emitted to air. Releases to the air can be estimated with a total use of 8700 t/a.
For local uses, emissions to air from 3 pharmaceutical plants from European countries are available for 2000 (CEFIC, 2001):

**Table 3-7 : Emissions of chloroform to air from pharmaceutical plants (kg/y)**

| **Location** | **1998** | **1999** | **2000** |
|---|---|---|---|
| **France** | 3,060 | 1,620 | 187 |
| **The Netherlands** | 130 | 100 | *nd.* |
| **Spain** | *nd.* | 2 | 3 |

*nd.:* no data available

The yearly changes seem to show a continuing reduction at the French site, some reduction at the Dutch sites and negligible emissions at the Spanish. At the local scale, the emissions reported from these 3 sites are far below the estimated ones. The representativeness of these data is however not established and the default values will be preferred.

**- Use as solvent in analytical and research laboratories**

Releases of chloroform between 1 and 2 kg/a to air and about 1 kg/a to water have been measured in a Belgian analytical and research laboratory. These releases could be considered as negligible.

**- Aqueous effluent monitoring**

A vast number of effluent monitoring was performed in France over the last years. In Table 3-6 above, the results of measurements performed in the effluents from the chemical industry are summarised. Releases as high as 38.9 kg/d were measured. 90-percentile values would be approximately 10 kg/d. Assuming that on-site biological treatment was performed, and using an elimination rate of 85.6 % (cf. section 3.1.1.5.2), a release into raw wastewater of respectively 278 and 69 kg/d can be estimated. Although this is much lower than the quantities estimated above with default release factors the results of this monitoring programme could be considered as a “worst case situation” because :

- It is not specified on the respective reports whether chloroform was used as an intermediate or as a solvent. Therefore, chloroform concentrations might come from other releases than the releases due to the specific use of chloroform as a solvent.
- It is furthermore not indicated whether on-site treatment was performed or not.

In comparison with the results of this monitoring programme, default releases estimates seem to greatly overestimate the real situation. However to take into account a worst case situation, the highest measured release into wastewater of 278 kg/d will be assumed on a local scale. The regional and continental releases as estimated above will be retained:

| | |
|---|---|
| Local release : | 24.2 t/a to wastewater |
| Regional release : | 346 t/a to wastewater |
| Continental release : | 3,120 t/a to wastewater |

### 3.1.1.3 Unintended formation (life-stage III)

#### 3.1.1.3.1. Losses as a by-product during chemical manufacturing (life-stage IIIa)

Chloroform is produced and emitted as a by-product in the manufacture of other chlorinated bulk chemicals: ethylene monochloride (VCM), ethylene dichloride (EDC), trichloroethylene (TCE) perchlorethylene (PCE) and other VC/PVC products.

##### 3.1.1.3.1.1. Default release estimation

In Western Europe, ethylene dichloride (1,2-dichloroethane) production was estimated to be approximatively 11.6 million t/a in 2001 (ECSA, Personal communication, 2002). The production of trichloroethylene amounted to 142,000 t/a in 2000 (ECSA, personal communication, 2002), whereas perchlorethylene was produced at a tonnage of 164,000 t in 1994 (E.C., 2003). The whole production of these 3 chlorinated chemicals amounts to 11,906,000 t/a. The production volume of ethylene monochloride is not known.

The TGD does not foresee emission factors due to unintended formation. As this chloroform formation is taking place in chemical synthesis procedure, it seems appropriate to assume the same emission factor as those for production of chemical used in synthesis. 1,2-dichloroethane is mainly used as chemical intermediate in the manufacture of polymers. As this compound is representing 97.4% of the whole production of 11,906,000 t/a, release factors due to production of chemical intermediates will be considered (table A.1.2, Main Category 1b). As chloroform has a vapour pressure of 20,900 Pa, the emission factors are : 0.01 to air and 0.003 to water.

The production of tri- and tetrachloroethylene only happens at a few locations, but there are more than 29 companies in Europe producing EDC and many other plants are involved in VC/PVC productions. Therefore, the 10% rule is applied and a production of 1,190,600t/a will be used as input in the B-table. Then, for the local estimation, a fraction of main source of 0.5 and a duration of production of 300 days/year will be used (Table B1.6).

The releases of chloroform can then be evaluated :

| | |
|---|---|
| Local release : | 5,953 t/a to air<br>1,786 t/a to wastewater |
| Regional release : | 11,906t/a to air<br>3,572 t/a to wastewater |
| Continental release : | 107,154 t/a to air<br>32,146 t/a to wastewater |

##### 3.1.1.3.1.2. Industry specific release estimation

Chloroform is a by-product of EDC in the oxychlorination step. Some goes to the quench water, whence it is removed by stripping, some stays in the crude EDC. Chloroform and EDC are then separated in the EDC purification.

No emission limit is specified for chloroform in the regulations for PVC production from EDC and vinyl chloride (or ethylene monochloride, VCM). Chloroform is regulated as part of the chlorinated hydrocarbons emitted. It is the same for the industry Charter on environmental emissions from the European PVC production units, which does not state a specific limit for chloroform but has a primary objective to reduce EDC and VCM emissions.

Tetrachloroethylene (PCE) and Trichloroethylene (TCE) are produced separately or as coproducts by either oxychlorination of EDC or other C2 chlorinated hydrocarbons.

**Emissions to air :**

US-EPA, 1984 reported uncontrolled emission factors to air of 1.77 kg of chloroform per tonne of EDC formed. This data has been obtained by adding emission factors calculated for each process vent associated with EDC production. However, plants may incinerate vent gases and reduce their chloroform emissions by 98 percent. This emission factor of 1.77 kg/t to air is then a highly worst-case situation. Furthermore, it can be assumed that production processes have been improved since that time. In comparison, a Dutch EDC/VCM plant reported in 1998 an emission of 3.6 g chloroform plus tetrachloroethylene per tonne VCM (EU IPPC draft dated December 2000). Using this emission factor to a total EDC production capacity of 11,600,000 t/a, the total emission due to EDC production is calculated to be 42 t/a.

On the other hand, one facility that produced perchloroethylene (PCE) by EDC chlorination calculated an emission factor to air of 3 kg of chloroform per tonne perchlorethylene produced (US-EPA, 1984). This figure is old and one can assume that production facilities improved their processes since that time. According to information made available by ECSA, there was a significant reduction in chloroform emissions between 1985 and 1999 both due to a decrease in use/import/production of such products between 1993 and 1999 and a significant reduction in emissions. Emission data from about 80 European plants of Euro Chlor member companies among which all major European PVC and chlorinated solvents (PCE, TCE, chloromethanes) producers reported a reduction in air emission of chloroform from 1985 to 1997 by a factor of four to 426 t/year (ECSA, Personal Communication, 2002). We will therefore consider that chloroform releases due to PCE production is 25% the releases reported in 1984 by US-EPA. PCE and trichloroethylene (TCE) are produced separately or as coproducts by either chlorination of EDC or other $C_2$ chlorinated hydrocarbons. The same value of 0.75 kg per tonne produced will be considered in the risk assessment for both PCE and TCE in the absence of any other data. However, in Europe, only one producer is manufacturing PCE and TCE from ethylene dichloride which could give rise to emissions of chloroform (ECSA, personal communication, 2002). A trichloroethylene production site ranges typically from 1,000 to 50,000 t/a whereas tetrachloroethylene plant capacities vary and are in the range of 10,000-50,000 tonnes per annum (E.C., 2001b and E.C., 2001a). Considering that the highest European TCE / PCE from ethylene dichloride production capacity would be 100,000 t/a, releases of chloroform are estimated to be 75 t/a on local scale as well as on regional scale.

In conclusion, total European releases of chloroform to air due to EDC, TCE and PCE productions could be estimated to 117 t/a. This figure is consistent with the total emissions of Euro Chlor members reported for 1997 : 426 t/a (ECSA, personal communication, 2002). A production of 300 days per year will be considered for the manufacture of these chlorinated compounds. Applying the 10% rule, a fraction of main source of 0.5 is applied to EDC production. For TCE / PCE production, as only one site is considered, the total production at this site will be considered for the local and regional releases estimations. The releases for the different scales are :

| | |
|---|---|
| Local release : | 77 t/a to air |
| Regional release : | 79.2 t/a to air |
| Continental release : | 37.8 t/a to air |

***- Air monitoring***
Emissions of chloroform during VC/PVC productions have been reported for 2 European plants, with a capacity ca 350,000 t/a each, ranging from 0.2 to 5 t/a (CEFIC, 2001).
Releases seem to be fluctuating depending on the country, on the year and on the period when the incinerators are out of service. As a matter of fact, the representativeness of these data is not established. Then, the calculated values based on the Dutch plant emissions and the "modified" US-EPA emission factor (section 3.1.1.3.1.2) will be preferred in this risk assessment.

**Emissions to water :**

The OSPAR Decision 98/4 that will apply to existing plants as from January 1st, 2006 gives an overall limit value for discharge of chlorinated hydrocarbons to water at 0.7 g/tonne of EDC purification capacity. As this information is only related to VCM production plants in a future regulation, we will consider a 10 fold higher emission of chloroform to water due to the 11,600,000 t of EDC produced per year.

Besides, in a "Best Available Techniques" (BAT[5]) document related to VCM manufacturing, the emission limit for chloroform in water is set to 1 mg/L before biological treatment, if any. A wastewater stream assumption of 1.5 $m^3$/t VCM will lead to an amount emitted below 1.5 g/t VCM when using Best Available Techniques. As this information is only related to VCM production plants in a future regulation, we will consider a 10 fold higher emission of chloroform to water due to TCE / PCE productions on a 100,000 t production plant.

The total releases calculated with these data is 82.7 t/a. A production of 300 days per year will be considered for the manufacture of these chlorinated compounds. Still applying the 10% rule for EDC production facilities, a fraction of main source of 0.5 is applied. For TCE / PCE production, the total production at one site (100,000 t production capacity) will be considered for the local and regional releases estimations. The releases for the different scales are :

| | |
|---|---|
| Local release : | 5.56 t/a to wastewater |
| Regional release : | 9.62 t/a to wastewater |
| Continental release : | 73.1 t/a to wastewater |

***- Aqueous effluent monitoring***
A vast number of effluent monitoring was performed in France over the last years. In Table 3-6 above, the results of measurements performed in the effluents from the chemical industry are summarised. The origin of the detected chloroform is not specified. Therefore, chloroform concentrations might come from other releases than the releases due to the manufacture of other chlorinated bulk chemicals. It is furthermore not indicated whether on-site treatment was performed or not. Releases as high as 40 kg/d were measured. 90-percentile values would be approximately 10 kg/d. Even assuming that on-site biological treatment was performed, and using an elimination rate of 85.6 % (cf. section 3.1.1.5.2), a release into raw wastewater of respectively 278 and 69 kg/d can be estimated. This is of course higher than the quantities estimated above with the release factor of 7 and 15 g/t chlorinated compound.
Emissions of chloroform during VC/PVC productions have been reported for 5 European plants of which 3 represented a total capacity of 775,000 t/a (CEFIC, 2001):

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[5] Best Available Tecniques (BAT) are reference documents describing materials, products, technology and management systems for chloroform production.

**Table 3-8 : Emissions of chloroform to water as a by-product of VC/DCE production processes (kg/d assuming a production of 300 d/year)**

| Site | 1998 | 1999 | 2000 |
|---|---|---|---|
| K | 0.50 | 0.49 | *nd* |
| L | 0.14 | 0.01 | *nd* |
| M | 0.06 | 0.05 | 0.06 |
| N | 0.32 | 0.22 | 0.15 |
| O | *nd* | *nd* | 0.57 |

*nd*: no data available

Releases of chloroform to water from EDC/VCM production plants before treatment is ranging from 0.05 to 0.6 kg/d. These emissions are much lower than the above estimated figures. However, as these figures are representing less than 20% of the European production facilities by number and less than 10% of the European production capacity, they will not be considered as representative for all the European situations. The scenario with the estimated releases based on the OSPAR decision and on the BAT document is then retained in the risk assessment.

#### 3.1.1.3.2. Water chlorination (life-stage IIIb)

Chloroform may be produced by the aqueous reaction of chlorine with various organic compounds in water. Chloroform is however scarcely measured in chlorinated waters. Integrated parameters like Total Residual Chlorine (TRC, including inorganic and organic chloramines) or Total Residual Oxidants (TRO, collection of reactive halogenated species) are rather measured for analysis methods convenience.

##### 3.1.1.3.2.1. Drinking water

Chlorine tends to react with natural organic material, such as resorcinol-type phenols or alpha-methyl ketones, present in raw water, to produce halo-organic compounds, the most prevalent of which is chloroform. Chloroform production seems to be higher in summer due to increased reaction rates at the higher temperatures. This is despite the lower levels of humic material in the water compared to winter.

The amount of chloroform can be minimised by controlling the pH in the treatment works. Ozonation used as a pre-treatment proved also to be useful for reducing disinfection by-products, especially trihalomethanes (Chang *et al.*, 2002). However, effective removal of algae cells prior to ozonation is necessary because algae can contribute significantly to the formation of disinfection by-products (Plummer and Edzwald, 2001). There are alternative disinfectants such as chlorine dioxide, ozone and chloramines which do not lead to chloroform formation but it is not known to what extent, if any, these have replaced chlorine (Building Research Establishment, 1994).

In their study, Gallard and von Gunten, 2002 investigated the kinetics of chlorination and of Trihalomethanes formation. Four types of European natural waters were treated with chlorine dioxine and ozone to yield a final concentration of 21 µM, which is a typical dose for drinking water treatment. Trihalomethanes were then slowly produced during 3 weeks until a plateau was reached to 194 µg/L for chloroform. This concentration could be considered as an upper limit of chloroform in drinking water because the experimental procedure for chlorinated water sampling was conducted in order to avoid any volatilisation of trihalomethanes during the reaction time.

The authors could also determine a linear relationship between trihalomethanes and chlorine demand: 0.029 mole of chloroform was formed per mole of chlorine consumed.

In another French study on trihalomethanes concentrations in distribution networks with varied treatment processes, chloroform concentrations from 0.6 to 60 µg/L were measured on different points of the network (AGHTM, 2001). These measurements are consistent with the "worst case" scenario presented below.

In the EU risk assessment of sodium hypochlorite (E.C., 2002), chloroform concentration in drinking water due to hypochlorite application was reported to be in the range of 11.7 – 13.4 µg.L$^{-1}$. These values are consistent with the results of the previous French study.

US-EPA, 1984 assumed that chloroform produced in drinking water is transferred to air from leaks in the distribution system and during use. It has been estimated that around 0.041 kg chloroform/10$^{6}$L drinking water treated are produced, assuming that all of the chloroform in drinking water evaporates from the distribution system and during use. In this risk assessment, we will assume that chloroform produced in drinking water is mainly transferred to air and the releases due to drinking water treatment will be considered only for the air compartment.

Considering the mean per capita consumption in the EU of 200 L/day, 364 millions inhabitants (proposed parameters for the continental estimation in TGD, Annex XII, p. 503), and a worst case chlorination of 100 %, total chloroform emission due to chlorination of drinking water can be estimated to be 1,089 t/a.

At the regional scale, the TGD suggest a model with 20 millions inhabitants. The regional input would be 59.9 t/a.

Regional release : 59.9 t/a to air

Continental release : 1,029 t/a to air

###### 3.1.1.3.2.2. Municipal wastewater

Chlorine and the chlorine-containing compounds, calcium and sodium hypochlorite, are used sometimes in the EU to disinfect municipal wastewater before it is discharged to surface water. The amount of chloroform formed is much smaller than the amount formed during the treatment of drinking water because of a lower concentration of humic compounds.

An emission of 0.014 kg chloroform/10$^{6}$l wastewater discharged has been estimated (US-EPA, 1984).

Unlike for drinking water, it is assumed that there is no distribution system that would allow chloroform to evaporate from the disinfected wastewater. Then it can be admitted that all the chloroform is discharged in the receiving surface water.

Assuming on the one hand that the whole consumption volumes are treated and discharged to surface water and on the other hand that all municipal sewage treatment plants in the EU treat their effluents with chlorine, the chloroform emission due to chlorination of wastewater can be estimated:

In Europe, with 364 millions inhabitants, chloroform emission due to chlorination of wastewater could then be estimated to be 372 t/a to water.

The amount of wastewater discharged at the regional scale is estimated to be 20.4 t/a for 20 millions inhabitant at the regional scale.

Regional release : 20.4 t/a to surface water

Continental release : 352 t/a to surface water

###### 3.1.1.3.2.3. Swimming pools

Water used for filling swimming pools does not contain enough haloform precursors to account for chloroform emissions. However the users carry into the pools enough organic matter to explain chloroform formation.

Kim *et al.*, 2002 examined the formation of disinfection by-products by the chlorination of the materials of human origin in a swimming pool model system using two types of water: physically treated surface water and groundwater. Among the disinfection by-products formed, chloroform was a major compound in both ground and surface waters. After 72 hours reaction with different materials of human origin, chloroform average concentration ranged between 12 to 76 µg/L. A longer reaction period (72 h instead of 24 h) or a higher content of organic materials led to increased formation of disinfection by-products. Then the authors suggest that in order to keep the disinfection by-products in chlorinated swimming pools at minimum levels, some mitigation measures such as frequent water change and circulation of pool water through an appropriate filtering system need to be taken.

Chloroform is found both in air and water from the swimming pools that are supposed to be opened 300 days/year.

**Releases to air :**

Total releases of adsorbable organohalides (AOX) have been estimated for indoor swimming pools in France (Legube *et al.*, 1996) 1.4 to 1.8 t/a to air

In France, there are about the same number of indoor swimming pools (1600-1800) as outdoor swimming pools (1900-2100). It is often admitted that outdoor swimming pool water contains higher concentration of AOX than indoor swimming pool water. As no data could be found to check this assertion, a total release of 3.6 t/a to air will be considered in France. This quantity represents the releases of 56.8 million inhabitants and the total EU releases are calculated for 364.32 million inhabitants. It has also been estimated that trihalomethanes (including chloroform) represent 5 to 10% of adsorbable organohalides. Using a worst case of 10 % chloroform in AOX, the total releases of chloroform to air due to swimming pool disinfection processes would be 2.3 t/a. Regional releases are calculated to be 10% of the total with 20 million inhabitants on the regional scale.

**Releases to water :**

Total releases of adsorbable organohalides (AOX) have been estimated for swimming pools in some European countries (Legube *et al.*, 1996) :

| | |
|---|---|
| France | 10 t/a |
| Germany | 30 t/a |
| Netherlands | 9 t/a |
| Spain | 35.5 t/a |

This estimation does not take into account private swimming pools. As the four above countries represent about 50% of the European population, the total EU releases of AOX to water could be evaluated to 169 t/a.

It has also been estimated that trihalomethanes (including chloroform) represent 5 to 10% of adsorbable organohalides. Using a worst case of 10 % chloroform in AOX releases, the total releases of chloroform in water due to swimming pool disinfection processes would be 17 t/a. Regional releases are calculated to be 10% of the total releases with 20 million inhabitants on the regional scale.

To summarize :

Regional release : 0.230 t/a to air
1.7 t/a to wastewater

Continental release : 2.1 t/a to air
15.3 t/a to wastewater

###### 3.1.1.3.2.4. Cooling water

Cooling water in power plants and other industrial processes are disinfected to prevent the heat exchange and condensing tubes becoming fouled, which would reduce their efficiency. When chlorine is used in these disinfection processes chloroform might be generated. A "once-through" cooling system is reported to emit 0.41 kg chloroform per $10^9$ litres of cooling water whereas cooling systems where the water is recycled could emit to the atmosphere 2.3 kg of chloroform per $10^6$ litres of cooling water plus 0.75 kg in effluent per $10^6$ litres of cooling water (US-EPA, 1984). In France, chlorine is no more used in cooling systems of power plants (personal communication). Monochloramine is now used in place of chlorine. Chloroform concentrations in cooling waters of power plants are always below the detection limit (1 µg/L). It is not known how many other industrial processes are still using chlorine in Europe to treat cooling water.

Typical concentrations of chloroform in cooling water were reported in the EU risk assessment of sodium hypochlorite (E.C., 2002): 2.3 – 22.9 µg.$L^{-1}$. However, a proportion of these cooling waters might be treated through wastewater treatment plants before release into the environment.

In the United States, it was suggested that approximately 70% as much chloroform is released from cooling and other water treatments as from drinking and wastewater treatments (Aucott *et al.*, 1999). Assuming that a similar proportion is valid for Europe, the following releases could be estimated :

Regional release : 41.9 t/a to air
84.7 t/a to wastewater

Continental release : 720 t/a to air
1,458 t/a to wastewater

##### 3.1.1.3.3. Other releases

A vast number of effluent monitoring was performed in France over the last years, revealing chloroform concentrations in effluents from a large number of industrial branches. In the following table, the results of measurements performed in the effluents from different industrial branches are summarised. It is not indicated in the respective reports whether on-site treatment was performed or not.

**Table 3-9: Results of monitoring studies of wastewater effluents from different industrial branches, except chemical industry**

| Region / year | Number of positive samples[6] | average concentration [µg/L] | highest concentrations [µg/L] | average releases [kg/d] | highest releases [kg/d] | Reference |
|---|---|---|---|---|---|---|
| **Surface treatment & metal processing** | | | | | | |
| **Picardie, France / 1992-1998** | 33 | 221.5 | 5200; 490; 390; 140 | 0.002 | 0.014; 0.013; 0.013; 0.01; | DRIRE Picardie, 1996 |
| **Rhône-Alpes, France / 1993** | 10 | 45 | 140; 103; 90 | 0.002 | 0.007; 0.005; 0.002 | INERIS, 1994 |
| **Rhône-Alpes, France / 1998-1999** | 35 | 45 | 341; 270; 160; 150 | 0.005 | 0.07; 0.017; 0.016; 0.012 | INERIS, 2000 |
| **Franche-Comté, France / 1993-1995** | 10 | 73 | 350; 95; 90 | **0.109** | 0.99; 0.02; 0.02 | DRIRE Franche-Comté, 1996 |
| **Poitou-Charente, France / 1996-1998** | 4 | 19.5 | 54 | 0.003 | 0.005 | DRIRE Poitou-Charentes, 1998 |
| **Textile industry** | | | | | | |
| **Picardie, France / 1992-1998** | 20 | 16.8 | 95; 47; 35 | 0.014 | 0.09; 0.03; 0.025 | DRIRE Picardie, 1996 |
| **Rhône-Alpes, France / 1993** | 3 | 34 | 73 | 0.026 | 0.045 | INERIS, 1994 |
| **Rhône-Alpes, France / 1998-1999** | 6 | 4.6 | 16 | 0.006 | 0.01 | INERIS, 2000 |
| **Poitou-Charente, France / 1996-1998** | 1 | 4 | - | 0.006 | - | DRIRE Poitou-Charentes, 1998 |
| **Other, e.g. food industry, paint industry, electronics industry, polymer industry, etc** | | | | | | |
| **Picardie, France / 1992-1998** | 33 | 11 | 185; 79; 14; 11 | 0.014 | 0.28; 0.1; 0.015; 0.013 | DRIRE Picardie, 1996 |
| **Rhône-Alpes, France / 1993** | 9 | 92.6 | 420; 325 | 0.042 | 0.28; 0.05 | INERIS, 1994 |
| **Rhône-Alpes, France / 1998-1999** | 17 | 3.1 | 14; 13.6; 11 | 0.002 | 0.009; 0.006; 0.005 | INERIS, 2000 |
| **Other, e.g. food industry, paint industry, electronics industry, polymer industry, etc (continuation)** | | | | | | |
| **Franche-Comté, France / 1993-1995** | 2 | 27.5 | 49 | < 0.001 | - | DRIRE Franche-Comté, 1996 |
| **Poitou-Charente, France / 1996-1998** | 5 | 852 | 3600; 600 | 0.004 | 0.01; 0.06 | DRIRE Poitou-Charentes, 1998 |

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[6] When no concentration is available in the monitoring studies, it is not known whether the substance was not analysed or wheher the concentration was below the detection limit.

While most releases are directly to surface water, some results are related to effluents that are transferred to municipal STPs. Although very high concentrations (up to 5,200 µg/L) have been measured in some effluents, the actual quantities released are rather low (maximum 1 kg/d; maximum average: 0.1 kg/d). The total releases to surface water based on the results in Table 3-9 can be estimated at approx. 2.2 kg/d (keeping only the most recent measurements from the Rhône-Alpes region).
The origin of chloroform in these effluents is not known. For surface treatment and metal processing, one could imagine that chloroform was used as degreasing agent, especially for those measures performed before 1998 when the use as a degreasing agent was still allowed. For the textile industry, the releases could be due to the use of chlorine or sodium hypochlorite as a bleaching agent. In the food industry, the releases could be due to disinfection operations with sodium hypochlorite. The origin of the releases from other industrial branches could not be explained.

Based on the results in Table 3-9, a representative worst-case release into surface water of 0.1 kg/d could be chosen. Only 3 higher values out of 188 were determined. It is furthermore not indicated whether on-site treatment was performed or not. Even assuming that on-site biological treatment was performed, and using an elimination rate of 85.6 % (cf. section 3.1.1.5.2), a release into raw wastewater of respectively 0.7 kg/d can be estimated. The number of inhabitants in the regions covered by the monitoring studies amounted to 10.26 million in 1999 (INSEE, 2000), including the highly industrialised region of Rhône-Alpes. The overall releases could therefore be used for a regional input in the EUSES model. Some releases identified in the monitoring program might though already be covered by estimations made above. Assuming again on-site treatment and using an elimination rate of 85.6 %, the regional releases from other, not further defined, uses or transformation processes would be 15.3 kg/d.
In summary:

| | |
|---|---|
| Regional release : | 5.58 t/a to wastewater |
| Continental release : | 41.9 t/a to wastewater |

#### 3.1.1.3.4. Pulp and paper bleaching (life-stage IIIc)

Chloroform is produced as a by-product during the delignification of wood and other cellulose pulps and the bleaching of paper by chlorine. Other chlorine-containing oxidants used in these processes such as chlorine dioxine ($ClO_2$) also generate chloroform (Aucott *et al.*, 1999). Based on chlorine production capacities and chlorine proportion used for pulp and paper manufacture, chloroform emission factors were derived for Western Europe (Switzerland + 15 European countries). The calculation is taking into account the conversions of many mills to chlorine free paper manufacture. The emission factor is estimated to 0.025 g $CHCl_3.kg^{-1}$ pulp and paper (Aucott *et al.*, 1999).

In the EU risk assessment of sodium hypochlorite, it is assumed that 50 kg NaCLO is used to bleach one tonne of pulp (E.C., 2002). Assuming an NaOCl-AOX conversion of 10%, a 50% removal of AOX formed and a chloroform content of 10% in AOX is giving a chloroform production ratio of 250 g $CHCl_3.kg^{-1}$ pulp, which is higher by a factor of $10^4$ than the previous estimation by Aucott *et al.*, 1999. However, as the proportion of paper manufacturing plants using bleaching process is not known, the previous estimated factor of 0.025 g $CHCl_3.kg^{-1}$ pulp will be used and applied to the European paper production.

Using the global production figures of paper (81.628 x $10^6$ t in 1999) and pulp (34.879 x $10^6$ t in 1999) in Europe plus Switzerland (CEPI, 1999), total releases of chloroform due to this industry is derived:

Total EU releases: 2,900 t/a

The U.S. Toxic Release Inventory (TRI) reported in 1990 a total release of chloroform into the environment of 9,970 t of chloroform from paper or pulp manufacturing facilities. 2.6 % of these releases were transferred to sewage treatment plants and 0.49 % to non incinerating treatment or disposal facilities, including ponds and lagoons. As these non incinerating treatments might ultimately attain the atmosphere, we will consider that only 2.6 % of the global releases of chloroform will be released to wastewater and the remaining 97.4 % will be released to the atmosphere. The specific scenario on pulp, paper and board industry from TGD will be used to assess releases into the environment :

| | |
|---|---|
| Regional release : | 282 t/a to air<br>7.54 t/a to wastewater |
| Continental release : | 2,542 t/a to air<br>67.9 t/a wastewater |

High effluent concentrations have been found, up to 325 µg/L in France corresponding to an annual release of 101 kg/a (INERIS, 1994), and up to 433 µg/L even after treatment (US-EPA, 1980 cited in Building Research Establishment, 1994).

It is not known to which extent these figures are representative of other paper mills. There are moreover various processes for paper and pulp bleaching. The above calculation will be retained in this risk assessment.

#### 3.1.1.3.5. Atmospheric reaction of high tonnage chlorinated solvents

Photolysis of trichloroethylene and reaction of perchloroethylene with hydroxyl radicals may produce chloroform. No details have been found on the conditions in which these processes are supposed to occur.

Trichloroethylene and Perchloroethylene are mainly released to the atmosphere during their use. According to the corresponding EU risk assessment of trichloroethylene (E.C., 2001b), dichloroacethyl chloride can result from chlorine radical reaction with trichloroethylene. Chloroacetyl chloride then reacts further to form chloroacetic acids. However, the initial reaction of chlorine radical with trichloroethylene only accounts for about 3% of trichloroethylene degradation in air. In fact the other main degradation products of trichloroethylene in air are formyl chloride and phosgene.

Some authors argued that the formation of different products depends on the relative concentrations of hydroxyl radicals and chlorine atoms.

However, it does not seem that chloroform is a major product of degradation of trichloroethylene.

In the same way the main products formed through degradation of tetrachloroethylene are phosgene, trichloroacetyl chloride, hydrogen chloride, carbon dioxide and carbon monoxide. Chloroform may be formed too but it does not belong to the major reaction products.

In a recent study, the possible role of perchloroethylene (PCE) in respect of high levels trichloroaceticacid (TCA) was investigated in forest soils in mountainous regions of Central Europe (ECSA, 2003). In the scope of this project, chloroform concentrations were also measured in air to account for the photochemical activity and to investigate degradation processes. During the 6-months site survey, TCA concentration in all soil horizons declined more or less exponentially while PCE concentration in the atmosphere first increased and then decreased (see Figure 3-1). Atmospheric chloroform concentration measured at 40-60 cm above the forest soil varied around 0.10 µg/$m^3$ (see Figure 3-2).

**Figure 3-1 Ambient average PCE concentrations per sampling period**

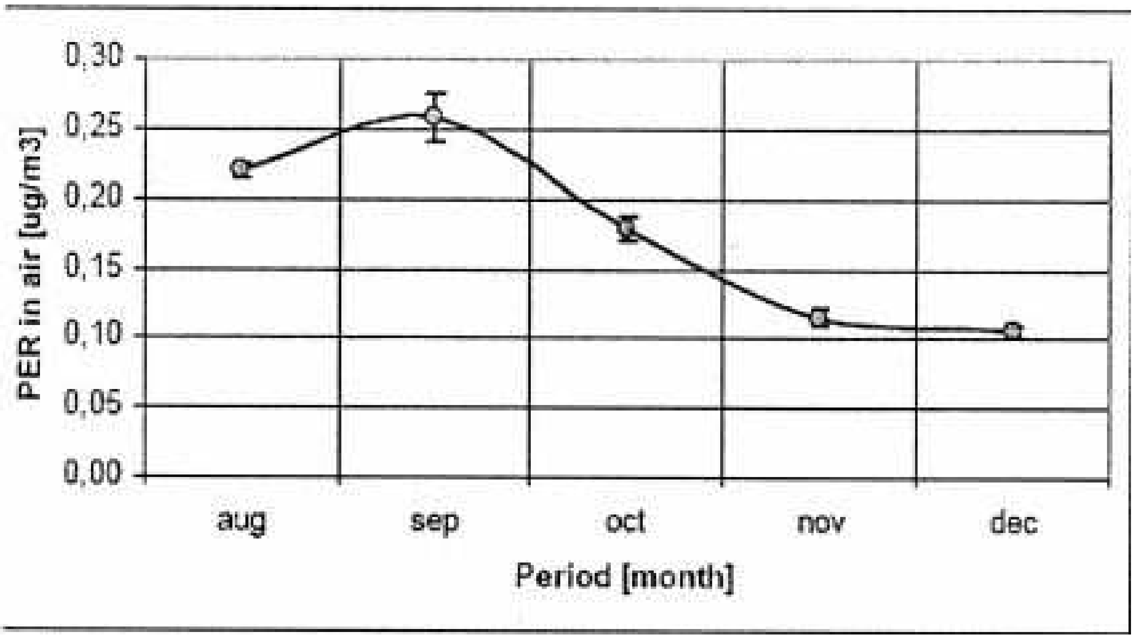
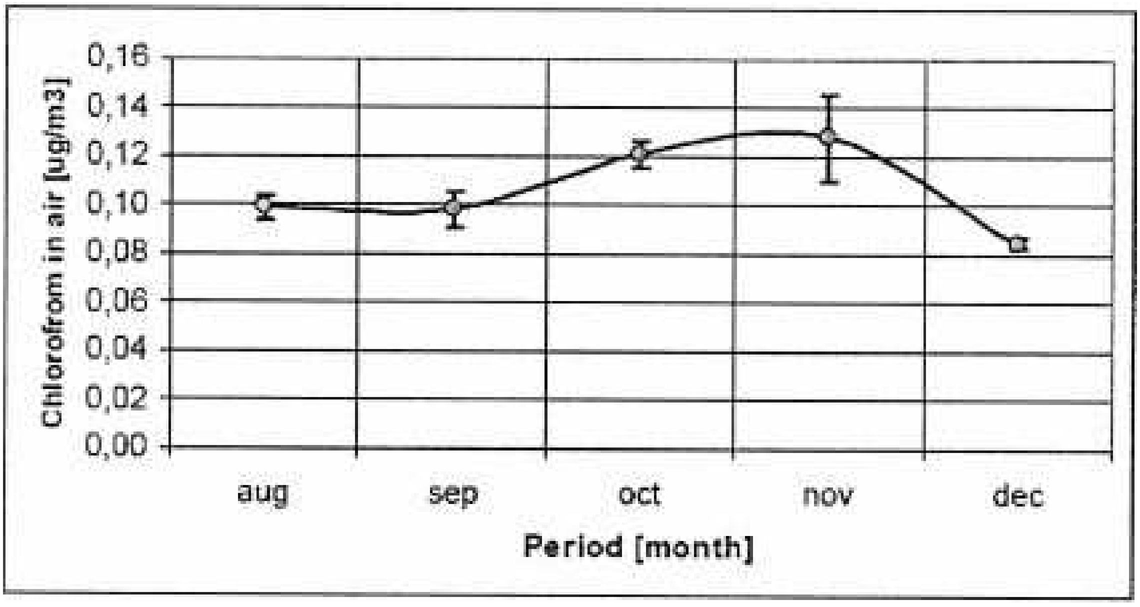


Figure 3-2 Ambient spatial average chloroform concentrations per sampling period



Increases of chloroform concentrations over 0.20 µg/m$^3$ were observed during the autumn in some sites. However, this observation could not be linked to TCA concentrations. It is therefore suggested that atmospheric chloroform concentrations above forest soils are mainly expected to be chlorination products of humic acids (natural processes).

In conclusion, releases of chloroform due to the degradation of tricholoethylene and perchloroethylene will be neglected in the absence of any details on the conditions in which this way of degradation prevails.

#### 3.1.1.3.6. Vehicle emissions

As a result of the decomposition of 1,2-dichloroethane added to fuel as a lead scavenger, exhaust emissions from vehicles may release chloroform into the atmosphere. Chloroform levels in vehicle exhaust have been measured in the United States. For a car using unleaded gasoline chloroform levels about 0.32 – 0.44 µg/m$^3$ have been reported in 1977 (Building Research Establishment, 1994). There are chances that vehicle exhausts characteristics are markedly different nowadays and in European countries. Therefore these data cannot be used for the risk assessment.

#### 3.1.1.3.7. Landfills and incineration processes

Chloroform could be measured in gases from landfills, in air above waste sites containing hazardous products and in exhausts from wastewater sludge incinerators.

In a recent study, the formation of chlorinated hydrocarbons from the reaction of chlorine atoms with carbon at temperatures as high as 200°C was investigated (Khachatryan and Dellinger, 2003). The results have shown that carbon tetrachloride is the major product with chloroform, methylene chloride and methyl chloride being formed in progressively decreasing yields. These findings also proved that chlorinated hydrocarbons including chloroform may be forming in the post combustion cool-zone regions of combustors where they can be emitted without being exposed to destructive conditions.

Chloroform measurements at the exhausts of incinerators are generally not performed but some specific values were found : in the Netherlands, the emission of chloroform from waste disposal was 1.05 t/a to air in 1999 (personal communication). Chloroform was measured in the emission of a municipal waste incineration plant at a concentration of 2.0 µg/m$^3$ (Jay and Stieglitz, 1995). Due to the specificity of each site and to the rapid evolution of incineration processes, it does not seem possible to extrapolate the data for the European countries.

#### 3.1.1.3.8. Natural sources

According to some authors, the observed global chloroform burden can not be fully explained by industrial releases (Building Research Establishment, 1994). Natural source of chloroform should be considered as well.

Many studies were conducted to assess the global atmospheric chlorine cycle and the role of natural processes. To address this issue, emissions of the major reactive chlorine species in the troposphere were calculated. Four major sources were considered: oceanic and terrestrial biogenic emissions, sea-salt production and dechlorination, biomass burning, and anthropogenic emissions (industrial sources, fossil-fuel combustion and incineration).

According to Keene *et al.*, 1999, the major global sources for tropospheric chloroform would be direct emissions from the surface ocean, soils and fungi, although biological processes are not well defined (Keene *et al.*, 1999). Estimated emissions from anthropogenic sources would account for only about 10% of the total emitted from all sources. However, there is still a large inconsistency between the estimated sources and sinks, partly due to sparse observational data currently available.

Although there are very few data for concentrations of chloroform in seawater, these data show a supersaturation suggesting that the oceans are a source of chloroform to the atmosphere. Using a standard model for the exchanges of gases between ocean and the atmosphere, an oceanic emission is estimated to represent half of the total chloroform emissions (Khalil *et al.*, 1999).

Natural production associated with the oxidation of methyl chloride produced by algal activity is also mentioned by other authors (Nightingale *et al.*, 1995 in Environment Canada and Health Canada, 2000). Coastal areas were specifically investigated for chloroform natural emissions. Some algae species were found to release “significant” quantities of chloroform (up to 2,400 ng.g$^{-1}$.h$^{-1}$EuroChlor, 2002). Although some authors tried to calculate the global flux of chloroform from sea shore, they recognized it was empirical (Nightingale *et al.*, 1995 in EuroChlor, 2002). However, the real contribution of the natural process in the global chloroform flux is not known. The supersaturation of chloroform in seawater is therefore not explained and there is no evidence that oceanic emission is a major source for chloroform concentration in the atmosphere.

Besides, global chloroform emissions from biomass burning have been quantified and it was estimated that the amounts emitted from fires represented only 0.4% of their global source strengths (Lobert *et al.*, 1999).

Finally it is also suggested that chlorination of soil organic matter is one possible source of chloroform. Several pathways were suggested for the formation of chloroform above soils (Frank *et al.*, 1989):

(a) wet deposition of airbone trichloromethan,

(b) reaction with chlorocarbon precursors (e.g. tetrachloroethylene),

(c) chlorination of humic acids in soil and emission to air.

(a) With a Henry’s law constant of 275 Pa.m$^3$.mol$^{-1}$ at 20°C, chloroform is unlikely to contribute to wet deposition. Some experimental studies on wet deposition of chlorinated hydrocarbons confirmed that this phenomenon is not an important process that could explain chloroform formation in soils (Frank *et al.*, 1989, ECSA, 2003).

(b) In a recent study (ECSA, 2003), chloroform concentrations in the atmosphere at approx. 40-60 cm above 18 forest soils were measured for a 5 months period (august to december 2002). Test sites with high trichloroaceticacid (TCA) levels were chosen in South –Western Germany and Eastern France. The study was performed to explore the possible role of Perchloroethylene (PCE) in respect of high levels of trichloroaceticacid. However, chloroform concentrations were measured to investigate the photochemical activity of the atmosphere in TCA degradation processes. Results indicated an average chloroform concentration at 0.11 ± 0.02 µg/m$^3$. This concentration was stable except in three test sites where the concentration increased over 0.20 µg/m$^3$ during the autumn. However, these concentrations could not be correlated to the concentration of other chlorinated hydrocarbons indicating that reaction with chlorocarbon precursors is not an important process for the formation of chloroform in soils. The results of this study are not in accordance with a previous study by Haselmann *et al.*, 2000b in ECSA, 2003: the rate of chloroform production in laboratory conditions was doubled by spiking the soils with trichloroacetic acid. These chemical processes might be highly dependent to environmental conditions.

(c) Finally, the source of chloroform in soils and atmospheric air above soils could be explained by the microbially induced halogenation of organic matter in the upper soil layers (Laturnus *et al.*, 2000). Khalil and Rasmussen, 2000 measured chloroform emissions from five soils representing different ecosystems. Emissions ranged from 0 (arctic gras, crops in China) to 52 µg/m$^2$/d, with a middle value of 8 ± 4 µg/m$^2$/d. As the scale of values is extensive and none of the five ecosystems was taken from a European environment, it is not possible to extrapolate the data for Europe. Other studies showed that chloroform was mainly emitted by soils that contain a humic top layer or are covered by wood chips. In the study by Hoekstra *et al.*, 2001, wood degrading areas and soils with a humic layer were found to emit up to 1,000 ng $CHCl_3.m^{-2}.h^{-1}$ and seemed to be the largest chloroform sources over the other studied areas. However, above canopy, all concentration gradients indicated deposition. Other studies reported highly variable rates: 0.1 to 4 µg.m$^{-2}$.d$^{-1}$ in Danish forest soils (Haselmann *et al.*, 2000b). Results from the same group indicated an expected flux of 12 µg.m$^{-2}$.d$^{-1}$ (Haselmann *et al.*, 2000a).

As these processes seem to be highly dependent on environmental conditions, the derivation of the global contribution of these natural processes for chloroform concentrations in air and in soils would need specific measurements all over European ecosystems. With a great uncertainty in extrapolation of a median emission value, Khalil *et al.*, 1999 estimated that chloroform land-based biogenic emission could represent between 15% and 60% of the global emission. At the moment it is not clear whether or not soils in temperate zones contribute significantly to the atmospheric burden.

In conclusion, although one cannot deny that chloroform might be released by natural processes, the global contribution of these phenomena to chloroform emissions to the air and the terrestrial compartments cannot be assessed. All available studies are actually giving empirical calculations based on specific measurements. Therefore, natural emissions of chloroform will be neglected in this risk assessment.

#### 3.1.1.4 Summary of release estimates

In the following table, all releases based on the considerations above are presented.

In the Netherlands, the emission to air of chloroform from the industry was 41.2 t/a in 1999 (personal communication). This value could be compared to the regional emissions that were calculated for industrial activities. Depending on the activity, industrial releases are ranging from 4.35 to 515 t/a (Table 3-9). Emissions from the Netherlands are right in the range of these calculated values. However, it is not known to which industry the Dutch releases are coming from.

**Table 3-10 : Summary of environmental release estimates for chloroform**

| Life cycle stage | Comment | Estimated local release | Estimated regional release | Estimated continental release |
|---|---|---|---|---|
| **Production** | **Site A** | 0.052 kg/d to wastewater [7]<br>83.7 kg/d to air<br>365 d/a | 5.1 t/a to wastewater<br>30.5 t/a to air | 7.74 t/a to wastewater<br>29.7 t/a to air |
| | **Site B** | 0.014 kg/d to wastewater<br>0.036 kg/d to air<br>365 d/a | | |
| | **Site C** | 2.5 kg/d to wastewater<br>7.2 kg/d to air<br>300 d/a | | |
| | **Site D**[8] | 0.32 kg/d to wastewater<br>45.3 kg/d to air<br>365 d/a | | |
| | **Site E**[9] | 35.3 kg/d to wastewater<br>31.9 kg/d to air<br>365 d/a | | |
| | **Site F** | 0.98 kg/d to wastewater<br>21.6 kg/d to air<br>365 d/a | | |

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[7] Releases to wastewater are calculated using emissions from section 3.1.1.1.2 and 85.6% removal

[8] Releases of chloroform considering a simultaneous production of chloroform and HCFC 22 at the local scale

[9] Releases of chloroform considering a simultaneous production of chloroform, HCFC 22 and dyes / pesticides at the local scale

| Life cycle stage | Comment | Estimated local release | Estimated regional release | Estimated continental release |
|---|---|---|---|---|
| | **Site G** | 7.53 kg/d to wastewater<br>3.7 kg/d to air<br>365 d/a | | |
| | **Site H** | 10.1 kg/d to wastewater[10]<br>0.14 kg/d to air<br>365 d/a | | |
| | **Site I** | 0.074 kg/d to wastewater[10]<br>2.44 kg/d to air<br>365 d/a | | |
| | **Site J** | 0.28 kg/d to wastewater<br>63.6 kg/d to air<br>365 d/a | | |
| **Releases from uses** | | | | |
| **Use as an intermediate** | **Use for HCFC 22 production** | 7 kg/d to wastewater<br>81.7 kg/d to air<br>300 d/a | 2.1 t/a to wastewater<br>24.5 t/a to air | 6.9 t/a to wastewater<br>80.5 t/a to air |
| | **Use for dyes and pesticide production** | 35 kg/d to wastewater<br>25kg/d to air<br>144 d/a | 16.8 t/a to wastewater<br>12 t/a to air | |
| | **Other applications** | 33.2 kg/d to wastewater<br>23.7 kg/d to air<br>300 d/a | 39.8 t/a to wastewater<br>28.4 t/a to air | |

---

[10] Releases to wastewater are calculated using emissions from section 3.1.1.1.2 and 85.6% removal

| Life cycle stage | Comment | Estimated local release | Estimated regional release | Estimated continental release |
|---|---|---|---|---|
| **Use as a solvent** | **Extraction solvent in chemical and pharmaceutical industry** | 278 kg/d to wastewater<br>2,000 kg/d to air<br>87 d/a | 346 t/a to wastewater<br>433 t/a to air | 3,120 t/a to wastewater<br>3,900 t/a to air |
| **Unintended formation** | | | | |
| **Losses as a by-product during chemical manufacturing** | **Industry specific release estimation** | 18.5 kg/d to wastewater<br>257 kg/d to air<br>300 d/a | 9.62 t/a to wastewater<br>79.2 t/a to air | 73.1 t/a to wastewater<br>37.8 t/a to air |
| **Water chlorination** | **Drinking water** | | negligible to wastewater<br>59.9 t/a to air | Negligible to wastewater<br>1,029 t/a to air |
| | **Municipal wastewater** | | 20.4 t/a to surface water<br>negligible to air | 352 t/a to surface water<br>negligible to air |
| | **Swimming pools** | | 1.7 t/a to wastewater<br>0.23 t/a to air | 15.3 t/a to wastewater<br>2,1 t/a to air |
| | **Cooling water** | | 84.7 t/a to wastewater<br>41.9 t/a to air | 1,458 t/a to wastewater<br>720 t/a to air |
| | **Other releases** | | 5.58 t/a to wastewater<br>negligible to air | 41.9 t/a to wastewater<br>negligible to air |
| **Pulp and paper bleaching** | | | 7.54 t/a to wastewater<br>282 t/a to air | 67.9 t/a to wastewater<br>2,542 t/a to air |
| **Total emissions[11]** | | | **1.14 t/d to wastewater**<br>**340 kg/d to surface water**<br>**2.72 t/d to air** | **10.5 t/d to wastewater**<br>**3.59 t/d to surface water**<br>**22.8 t/d to air** |

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[11] Total emissions reported by EUSES.

#### 3.1.1.5 Distribution: Steady-state partitioning

Based on the physico-chemical properties of chloroform, the preferred target compartment in the environment at equilibrium is the air compartment (Building Research Establishment, 1994).

##### 3.1.1.5.1. Degradation

###### 3.1.1.5.1.1. Hydrolysis

Pearson and McConnell, 1975 observed that chloroform hydrolyses in contact with water. Dilling *et al.*, 1975 determined experimentally a hydrolysis first order rate of 0.045 $month^{-1}$, which corresponds to a **half-life of 15 months at 25 °C**. The study was conducted for 12 months with a $CHCl_3$ concentration of 1 ppm in light proof pyrex tubes. The pH is not known. Mabey and Mill, 1978and Jeffers *et al.*, 1989 measured lifetimes at different pH values. The half-life at **pH 7 was 1850 years at 25 °C**, at pH 9, 24 years and 0.24 years at pH 11. No acid catalysis was observed.

**Conclusion: hydrolysis is an unimportant fate process at a neutral pH value.**

###### 3.1.1.5.1.2. Photolysis in water

Hubrich and Stuhl, 1980 and Dilling *et al.*, 1975 did not observe any photodegradation of chloroform in water. The test substance was exposed in air-saturated water for one year. No absorption of UV (> 175 nm) or visible light and no absorption under environmental conditions (> 290 nm) were determined.
Zepp *et al.*, 1987 estimated the first order rate by photoejected electrons near the surface water in a lake during July, assuming a concentration of dissolved organic carbon of 4 mg/L. With a first order rate of $1.3 \times 10^{-3}$ $h^{-1}$, a half-life of 533 hours can be derived.
A lack of light absorption has been determined. The observed photolysis by Zepp *et al.*, 1987 is probably only important in the very upper surface layer and depends on the dissolved organic carbon content.

**It is concluded that direct photolysis is not an important fate process.**

###### 3.1.1.5.1.3. Photodegradation in air

The rate of chloroform removal by reaction with hydroxyl radicals has been estimated by many different authors.
Pearson and McConnell, 1975 exposed 2000 - 4000 ppm chloroform in flasks filled with ambient air to diurnal and climatic variations in temperature and radiation. A half-life of 23 weeks (161 days) was determined, which was dramatically reduced in the presence of O or Cl atoms.
Spence *et al.*, 1976 determined a degradation of 75 % after 5 mn irradiation in presence of Cl radicals and air. Chloroform was exposed in a glass chamber with an optical path of 360 m.
Appleby *et al.*, 1976 irradiated a synthetic mixture of trichloroethylene, nitrogen oxide, water vapour and gasoline in Teflon bags. The light source was a fluorescent lamp designed to simulate light of the lower troposphere. Chloroform appeared within two hours of irradiation. The tropospheric stability of chloroform suggests that this compound must be considered as a secondary anthropogenic pollutant, a potential precursor of ozone destroying stratospheric chlorine atoms.
However, according to Building Research Establishment, 1994, chloroform may account for 0.4 % of the chlorine in the upper atmosphere. Once in the stratosphere, chloroform is attacked by hydroxyl radicals, although some may be photolysed by the lower wavelength

radiation present to form ozone depleting species. Chloroform is not covered by the Montreal Protocol and its ozone depleting potential is thus thought to be lower than that of many CFCs.

Crutzen *et al.*, 1978 determined a rate constant of 4.0 x $10^{-10}$ $cm^3$/molecules.s at a sensitizer concentration of 400 molecules/$cm^3$ of O (1D) which is the concentration at 45 km altitude. This result is only relevant for the stratosphere.
Kloepffer and Daniel, 1990 calculated according to Atkinson, 1985 a rate constant of **$k_{OH} = 1 \cdot 10^{-13}$ $cm^3$/molecules.s.** In a review of the atmospheric reactions of chloroform Atkinson, 1985 recommended a rate constant for reaction of hydroxyl radicals with chloroform of **$k_{OH} = 1.03 \cdot 10^{-13}$ $cm^3$/molecules.s**.

Using the specific degradation rate constant with OH radicals of **$1.03 \cdot 10^{-13}$ $cm^3$/molecules.s**, as recommended by Atkinson, 1985, and using a mean OH concentration of 500,000 molecules/$cm^3$, a pseudo first order rate constant for degradation in air can be derived:
**$kdeg_{air}$ [OH] = 0.0044 $d^{-1}$**
Kloepffer and Daniel, 1990 calculated according to Atkinson, 1985 a rate constant of **$k_{NO3} = 2.6 \cdot 10^{-16}$ $cm^3$/molecules.s.** Using a mean $NO_3$-radical concentration of $1 \cdot 10^8$ molecules/$cm^3$, a pseudo first order rate constant for degradation in air can be derived:
**$kdeg_{air}$ [NO3-] = 0.0022 $d^{-1}$**

The overall degradation rate due to $NO_3$ and OH radical concentration is:
**$kdeg_{air}$ [$NO_3$] + [OH] = 0.0066 $d^{-1}$**

An atmospheric **half-life of 105 days** can be deduced for chloroform.

#### 3.1.1.5.1.4. Biodegradation

**Aerobic biodegradation**
*in water:*
The only study performed according to OECD Guideline 301 C (MITI, 1992) **did not show any biodegradation** after 14 days. The initial concentration was 100 mg/L and the test was performed at 25 °C.
Tabak *et al.*, 1981 found chloroform **degradable under aerobic conditions, with gradual adaptation**. Chloroform at concentrations of 5 and 10 mg/L was incubated at 25 °C for 7 days in static cultures inoculated with settled domestic wastewater. The screening was performed by a 7-day static incubation followed by 3 weekly subcultures. Part of the removal of chloroform was due to volatilisation. In this study, the potential for slow biodegradation with a long adaptation period has been reported, it has to be stressed however that an additional carbon source (5 mg/L yeast extract) has been used, also controls have been performed unsatisfactory, the abiotic one being carried out without biomass.
Bouwer *et al.*, 1981 tested chloroform in a concentration of 100 µg/L with primary sewage. Under the test conditions, 20 °C in the dark for 25 weeks, **no biodegradation** was observed. Even with lower initial concentrations (10 µg/L, 30 µg/L) no decomposition under the same conditions could be noticed.
Thomas *et al.*, 2000 found that unlike other trihalomethanes, chloroform added to aquifers does not degrade in either aerobic or anaerobic conditions. The decrease of chloroform that could be observed in wells over aquifer storage and recovery seasons was mainly due to dilution. In the same aquifer, no significant biodegradation of chloroform by the indigenous aquifer microorganisms was observed under aerobic or anaerobic conditions (Thomas *et al.*, 2000). The authors described the specific conditions in which biodegradation could be

observed: aerobic degradation could occur through co-metabolism when sufficient quantity of oxydative co-metabolites (methane, ammonia) and the corresponding bacteria are present.

**In conclusion, the results by Tabak *et al.*, 1981 could not be confirmed under more realistic conditions. Therefore, in this assessment, a first order rate constant for biodegradation in surface water of 0 d-1will be used.**

*in soil:*

**No results from standardised biodegradation systems for soil and sediment are available.**

In a study performed on a sandy soil (Strand and Shippert, 1986), it was found that acclimation to an air-natural gas mixture stimulated the biological oxidation of chloroform to carbon dioxide. Acclimation of the soil was carried out for 3-8 weeks in an atmosphere of 1 % natural gas in air and around 200 ml of dechlorinated tap water/day constantly applied to the soil during this period. Degradation experiments were carried out using around 5 g of the acclimated soil and a chloroform concentration of 31 µg/kg wet soil. Incubations were performed at 22-25°C for 5 days. Chloroform oxidation continued up to 31 days but was inhibited by acetylene and high concentrations of methane, indicating that methane oxidising bacteria may catalyse chloroform oxidation. There was some chloroform oxidation observed in soils that were exposed only to ambient air (which may have included some hydrocarbons) but the rate in the natural gas enriched soils was four times greater.

**In conclusion, these results demonstrate that degradation of chloroform occurs only under certain aerobic conditions by methane-utilising bacteria. However, they cannot be used in the generic assessment. The first order rate constant for aerobic biodegradation in soil and sediment is 0 d-1.**

**Anaerobic biodegradation**

*in water:*

The anaerobic primary degradation of chloroform was studied by Gosset, 1985 in batch studies with an inoculum based on municipal digested sludge at 35 degrees C. At a concentration of 5.1 mg/L, chloroform disappeared within 9 days. The main metabolite was dichloromethane (31%), which remained near constant for 21 days and then disappeared slowly over the remaining 60 days.

Further studies with radiolabelled chloroform indicated that most of the initial disappearance is due to mineralisation:

| Initial $CHCl_3$ conc. (mg/L) | Duration of primary degr. (d) | Final $CO_2$ prod. (%) | $CH_2Cl_2$ prod. (%) |
|---|---|---|---|
| ca. 1.7 | 3 | 43.5 | 34.1 |
| ca. 5 | 5 | 40.3 | 29.9 |
| ca. 17 | 12 | 32.1 | 27.7 |

The quantity of $CH_4$ produced was negligible. Even at 1.7 mg/L, the gas production by the inoculum was inhibited by more than 60%, and by more than 80% at 17 mg/L.

Bouwer *et al.*, 1981 carried out a study on the degradation of chloroform with methanogenic bacteria over 112 days. At an initial concentration of 16 µg/L, 81 % of chloroform was degraded within two weeks. Degradation also occurred with initial concentrations of 34 µg/L (> 70% after 28 days) and 157 µg/L (43 % after 84 days). Degradation at the high concentration of 157 µg/L was less conclusive, but there appears to have been a gradual reduction in chloroform concentration. Removal percentages vary in an important way, as they are based on variable $CHCl_3$ measurements in controls.

Bouwer and McCarty, 1983 found that in seeded cultures under methanogenic conditions, chloroform was almost completely oxidised to $CO_2$. At initial concentrations of 15 and 40 µg/L a lag period of 40 and 20 days was observed respectively. $^{14}C$-measurements confirmed the removal by biooxidation.

Rhee and Speece, 1992 carried out a study with methanogenic bacteria under optimised conditions in a continuous fed anaerobic reactor. The feed contained a primary substrate (either formate, acetate or propionate) so as to maintain a concentration of 2000 mg/L of substrate in the reactor. The concentration of $CHCl_3$ in the influent feed solution were 304, 1230 and 1960 mg/L in formate, acetate and proprionate enrichment cultures, respectively. The feed concentrations were chosen to produce a 50 % reduction in gas production. A degradation of 90, 89 and 93 % after 30 days of continuous operation was observed. The concentrations were monitored in the liquid and gas effluent. The removal by volatilisation was 6.2 - 10 % whereas the removal with the liquid effluent was < 0.08 %, corresponding to concentrations of <0.24, <0.98, <1.57 mg/L.

Fathepure and Vogel, 1991 determined a total decomposition of 83 % after two days in a sequential decomposition process in an anaerobic and aerobic column. A pre-adaptation of 4-6 weeks took place; the aerobic column was working for one year.

**In conclusion, although a certain biodegradation can be mentioned to take place under some anaerobic conditions, chloroform is not considered readily biodegradable in water systems.**

*in sediment:*

van Beelen and van Keulen, 1990 have also shown chloroform to be degraded to $CO_2$ using anaerobic methanogenic sediment. The inoculum was a 20 ml sediment suspension incubated for 64 days without any headspace. 63 % of radiolabelled chloroform at an initial concentration of 4 µg/L was biodegraded. Half-lives of 10 - 14 days at 10 °C and 2.6 days at 20 ° C have been determined. Based on the intermediate results, the biodegradation is supposed to follow 1st order kinetics.

Using an initial concentration of 400 µg/L the final percentage level in carbon dioxide and chloroform are similar to the values of the experiment using an initial concentration of 4 µg/L. However at other time intervals, the percentages of formed $CO_2$ were lower at the higher concentration. Based on the intermediate results, the biodegradation is supposed to follow logarithmic kinetics. Therefore the concentration of 400 µg/L was considered to be above the threshold for growth and adaptation.

van Beelen and van Vlaardingen, 1993 found that $^{14}C$-labelled chloroform was mineralised to $CO_2$ when incubated at low concentrations (2.7-3.4 µg/L) in bottles containing no sandy fresh natural sediments at 20 °C. Chloroform was found to be mineralised in all samples with half-lives in the range 0.9 to 37 days. No mineralisation was observed in the majority of sandy sediment samples.

**In conclusion, chloroform biodegradation is observed in anaerobic sediment. Based on these results, half-lives determined by van Beelen and van Keulen, 1990 are assumed to be valid for the anaerobic part of the sediment and the half-life value of 14 days will be considered here. The TGD proposes to assume that 90 % of the sediment is anaerobic and suggests, when only data is available for the anaerobic part, correcting the half-life value in order to take into consideration the aerobic fraction of the sediment compartment. Therefore, if we consider the whole sediment compartment (90 % anaerobic / 10 % aerobic), only 45 % of the chloroform is biodegraded in 14 days and**

**the actual half-life in sediment is circa 15 days. This value of 15 days will be used in the assessment for the sediment.**

The biodegradation rates for surface water, soil and sediment are therefore estimated, according to the procedure outlined in the TGD.

**Table 3-11: Estimation of biodegradation rate constants in the different compartments**

| Compartment / medium | Biodegradation rate |
|---|---|
| Surface water | $k_{sw} = 0\ d^{-1}$ |
| Sediment | $k_{sed} = 0.046\ d^{-1}$ |
| Soil (aerobic) | $k_{soil} = 0\ d^{-1}$ |

### 3.1.1.5.2. Elimination in sewage treatment plants (STP)

Based on the above cited physical chemical properties (log H = 2.5 and log Pow = 1.97) as well as the biodegradation rate of 0 $h^{-1}$ in a STP, the elimination through biodegradation and distribution can be estimated with the model SIMPLETREAT :

**Table 3-12: Estimation of removal of chloroform in STPs according to SIMPLETREAT:**

| | |
|---|---|
| % to air | 83.9 % |
| % to water | 14.4 % |
| % to sludge | 1.7 % |
| % degraded | 0 % |
| % removal | 85.6 % |

On the other hand, STP monitoring data are available, providing a more realistic description on the behaviour of chloroform in STPs.

The elimination of chloroform was monitored in pilot plants and in full scale STPs (Table 3-13 & Table 3-14).

**Table 3-13: Chloroform removal in full scale STPs :**

| $CHCl_3$ removal [%] | operating parameters: | | | | | Reference |
|---|---|---|---|---|---|---|
| | **Influent conc. [µg/L]** | **Effluent conc. [µg/L]** | **SRT* [days]** | **HRT** [hours]** | **Flow rate [$m^3$/d]** | |
| 86 | 42.8 | 6 | - | - | 757000 | US-EPA, 1982 |
| 62 | 55 | 21 | - | - | 340000 | US-EPA, 1982 |
| 51 | 120 | 59 | - | - | 290000 | US-EPA, 1982 |
| 95 | 26 | 1.3 | - | - | - | Canviro Consultants, 1988 |
| 93 | 32.8 | 2.3 | - | - | - | Canviro Consultants, 1988 |
| 94.5 | 27.3 | 1.5 | - | - | - | Canviro Consultants, 1988 |
| 97.3 | 48 | 1.3 | - | - | - | Canviro Consultants, 1988 |
| 94.5 | 21.8 | 1.2 | - | - | - | Canviro Consultants, 1988 |
| 94.9 | 23.5 | 1.2 | - | - | - | Canviro Consultants, 1988 |
| 92.5 | 29.3 | 2.2 | - | - | - | Canviro Consultants, 1988 |
| 95.4 | 1543 | 71 | - | - | - | NPDES, 1986-1988 |
| 53 | 81 | 38 | - | 5 | 180000 | US-EPA, 1982 |
| 81 | | - | ? | 7.1 | 218000 | Parker *et al.*, 1993 |
| >75 | 4.0 | < 1 | - | - | 44800 | van Luin and van Starkenburg, 1984 |
| 0 | 4.0 | 7.1 | 5.5 | 5.1 | 866800 | Namkung and Rittmann, 1987 |
| 45.4 | 4.4 | 2.4 | 6.7 | 6.1 | 3164300 | Namkung and Rittmann, 1987 |
| 41/61 | 1.7/3.1 | 1.0/1.2 | - | 7.5 | 51840/<br>37152 | Neiheisel *et al.*, 1988 |
| >46/54 | 1.3/1.1 | <0.7/0.6 | - | 3.6 | 8640/<br>6912 | Neiheisel *et al.*, 1988 |
| 39/65 | 3.1/3.7 | 1.9/1.3 | - | 6.0 | 140832/<br>95040 | Neiheisel *et al.*, 1988 |
| 81/72 | 6.9/8.2 | 1.3/2.3 | - | 4.9 | 14688/<br>16416 | Neiheisel *et al.*, 1988 |
| 84/70 | 8.3/7.3 | 1.3/2.2 | - | 6.2 | 253152/<br>245376 | Neiheisel *et al.*, 1988 |
| 98/77 | 30.8/1.3 | 0.5/0.3 | - | 7.4 | 59616/<br>91584 | Neiheisel *et al.*, 1988 |

* SRT: sludge retention time

** HRT: hydraulic retention time

None of the monitored STPs had an anaerobic treatment stage.

**Table 3-14: Chloroform removal in pilot STPs:**

| $CHCl_3$ removal [%] | Operating parameters: | | | | | Reference |
|---|---|---|---|---|---|---|
| | Influent conc. [µg/L] | Effluent conc. [µg/L] | SRT [days] | HRT [hours] | Flow rate [$m^3$/d] | |
| >78 | 33 | <7.2 | 12 | 5.1 | 1.06 | Greeley and Hansen, 1988 |
| 97.4 | 138 | 3.6 | 5.9 | 7.5 | 190 | Petrasek *et al.*, 1983 |
| 98 | 100 | 2 | 7 | 7.5 | 8.2 | Hannah *et al.*, 1988 |
| 86 | 128 | 18 | 7 | 7.5 | 8.2 | Hannah *et al.*, 1986 |
| 91.7 | 43 | 3.6 | 5 | 6.5 | - | Parker *et al.*, 1993 |
| 85 | 293 | 44 | 4 | 7.5 | 190 | Battacharya *et al.*, 1988 |

* SRT: sludge retention time

** HRT: hydraulic retention time

Only during the pilot plant study of Parker *et al.*, 1993 removal percentages by different mechanisms have been determined: 32.5 % was stripped whereas 59.2 % degraded. These results are based on three measurements. Hannah *et al.*, 1986 and Hannah *et al.*, 1988 also measured concentrations in activated sludge and found the same concentrations as in the effluent, indicating no significant adsorption onto sludge.

Comparing these data with the SIMPLETREAT estimation, it becomes clear that the chloroform removal of 85.6 % in STPs is very realistic. In full scale domestic STPs, removal rates between 0 and 98 % have been observed. The lowest removal rates were observed for very low influent concentrations. For point source releases, higher influent concentrations can be expected. If the results from STPs with influent concentrations below 10 µg/L are set aside, removal rates of less than 80% have been observed in only 3 out of 14 full scale STP and in none of the pilot plants, while removal rates of more than 95% were observed in 4 out of 14 full scale STPs and in 2 out of 6 pilot plants.

The higher removals in the pilot plant study might be explained by higher air/water ratios (Namkung and Rittmann, 1987), although not all operating parameters are available for all monitored STPs.

When no site-specific data is available, these results with SIMPLETREAT will be used in the risk assessment.

#### 3.1.1.5.3. Adsorption-Accumulation in soil

In a percolation column study (Wilson *et al.*, 1981) Lincoln fine sand (92 % sand, 5.9 % silt, 2.1 % clay and 0.087 % organic carbon) was tested with initial chloroform concentrations of 0.25 mg/L and 0.9 mg/L. A rapid percolation through the soil was observed whereas 54 % of the test substance volatilised, 41 % was detected in the effluent and 5 % were lost.

A log Koc of 1.9 can be taken from a graph, which corresponds to a Koc value of 79.

In a Cohansey aquifer system with a soil content of 2 % clay, 8 % silt, 90 % sand and 4.4 % organic matter, Uchrin and Mangels, 1986 tested $C^{14}$-labelled chloroform for adsorption.

Depending on the adsorbent mass (predetermined in air dried solids) the following Koc values have been observed:

| Adsorbent mass | 1 g | 5 g | 10 g |
|---|---|---|---|
| **Koc** | 167 | 151 | 86.7 |

The same authors determined with a Potomac-Raretan-Magothy aquifer system (soil content: 5.6 % clay, 24 % silt, 70.4 % sand and 2.2 % organic matter) the following Koc values:

| Adsorbent mass | 1 g | 5 g | 10 g |
|---|---|---|---|
| **Koc** | 398 | 92.5 | 63.4 |

The dependency on adsorbent mass was not explained.
Four different contaminated soil samples have been examined by Liljestrand and Charbeneau, 1987 for chloroform desorption. Soil and water were mixed for 24 hours and 4 - 8 successive extractions were carried out. The following values have been determined:

| | **Organic matter** | **Koc [L/kg]** | **Kp [L/kg]** | **Residual Sorbed Fraction [%]** |
|---|---|---|---|---|
| soil 1 | 0.2 | **65** | 0.13 | - |
| soil 2 | 0.5 | **806** | 4.03 | 1.2 |
| soil 3 | 16.9 | **4.8** | 0.82 | - |
| soil 4 | 0.14 | **1000** | 1.26 | - |

As several data on soil characterisation are missing in this publication, the variations of results cannot be explained.

The OECD Guideline 106 suggests an organic carbon content of 0.6 - 3.5 %. By eliminating the results with soils outside this range, only Koc values of 398, 92.5 and 63.4 l/kg remain (Uchrin and Mangels, 1986). A mean value would be 184.6 l/kg. Using the (Q)SAR relationship recommended in the TGD for hydrophobics, a Koc-value of 50 l/kg is derived. This value is well in line with the measured values.

**In conclusion, a Koc value of 185 will be used in the assessment.**

For the different media, using the standard organic carbon contents proposed in the TGD, the water - solids and total compartments - water partition coefficients can be estimated. The results are presented in the following table.

**Table 3-15: Partition coefficients between different compartments**

| **Compartments** | **OC-content (%) of solid phase** | **Solid_water partition coefficient** | **Total compartment - water part. coefficient** |
|---|---|---|---|
| **soil-water** | 2 | Kp_soil = 3.7 l/kg | Ksoil_water = 5.78 $m^3/m^3$ |
| **sediment - water** | 5 | Kp_sed = 9.25 l/kg | Ksed_water = 5.42 $m^3/m^3$ |
| **suspended matter - water** | 10 | Kp_susp = 18.5 l/kg | Ksusp_water = 5.53 $m^3/m^3$ |

### 3.1.1.6 Bioaccumulation

In the following table, the results from bioaccumulation experiments are summarised:

**Table 3-16 Results from bioaccumulation assays**

| Species | **System** | **Exposure [d]** | **Water conc. [µg/L]** | **Depuration** | **BCF** | **Ref.** |
|---|---|---|---|---|---|---|
| *Cyprinus carpio* | Flow through | 42 | 1000 | - | 1.4 – 4.7 | MITI, 1992 |
| *Cyprinus carpio* | Flow through | 42 | 100 | - | 4.1 – 13 | MITI, 1992 |
| *Oncorhynchus mykiss* | Flow through | 1 | 1000 | Total depuration within 24 h | 3.4 – 10.4 | Anderson and Lustry, 1980 |
| *Lepomis macrochirus* | Flow through | 1 | 1000 | Total depuration within 24 h | 1.6 – 2.5 | Anderson and Lustry, 1980 |
| *Micropterus salmoides* | Flow through | 1 | 1000 | Total depuration within 24 h | 2.1 – 2.2 | Anderson and Lustry, 1980 |
| *Ictalurus punctatus* (1) | Flow through | 1 | 1000 | 91 % depuration within 26 h | 3 – 3.4 | Anderson and Lustry, 1980 |

(1) Equilibrium has not been reached

The test conditions are not available in detail for all tests. The results obtained fall in the range of 1.4 – 13, which is the range obtained by MITI, 1992 in *Cyprinus carpio* at two different water concentrations. In fact, the test systems used in the two studies are very similar, which explains that the results obtained are in the same range.

**For the assessment a worst case BCF of 13 will be used.**

## 3.1.2. Aquatic compartment (including sediment)

### 3.1.2.1 Estimation of local aquatic concentrations

#### 3.1.2.1.1. Estimation of local water and sediment concentrations

The concentration of chloroform in the influent of the STP is calculated using the following formula :

$$Clocal_{inf} = \frac{Elocal_{water} \cdot 10^6}{EFFLUENTstp}$$

Explanation of symbols:

| | |
|---|---|
| $Elocal_{water}$ | local emission rate to (waste) water during emission period [kg/d] |
| EFFLUENTstp | effluent discharge of the STP [l/d] |
| $Clocal_{inf}$ | concentration in untreated water [mg/L] |

The concentration of chloroform in the effluent ($Clocal_{eff}$ ) of a STP is calculated with the formula:

$$\mathbf{Clocal_{eff} = Clocal_{inf} \times \% \text{ not removed STP}}$$

For chloroform it is assumed that 85.6 % elimination occurs in a STP (see above).

From the effluent concentration in the STP, the local concentration in the receiving surface water can be calculated with the equation:

$$\mathbf{Clocal_{water} = Clocal_{eff} / [(1 + Kp\ susp \cdot SUSP \cdot 10^{-6}) \cdot D]}$$

with Kp susp = 18.5 l/kg (see above)
SUSP = 15 mg/L (concentration of suspended matter in river)
D = dilution factor

Due to the low Kp_susp value, the fraction removed by adsorption to suspended matter is negligible and will therefore not be further taken into account.

The concentration of freshly deposited sediment is taken as the PEC for sediment. Therefore, the properties of suspended matter are used:

$$Clocal_{sediment} = (Ksusp\_water/RHOsusp) \cdot Clocal_{water} \cdot 1000 \text{ (wet weight)}$$

According to EUSES (EUSES 2.0.1 Release Notes, http://ecb.jrc.it/), conversion factor based on suspended matter (4.6) is used as conversion factor from wet weight to dry weight for sediment instead of the old one based on sediment bulk density (2.6).

#### 3.1.2.1.2. Production

TGD default figures are indicated in Italics in the following tables.

Effluent discharge rate of STP were available for all production site except for site B, for which TGD default value has been used (2.0E+06 L/d).

Concerning the dilution factor, TGD default values have been used for sites B, C, F and J (see TGD chapter 3 and the emission scenario for intermediates, chapter 7). For the other sites, TGD methodology has been applied: in case of site-specific assessment of the dilution factor, this latter should not exceed 1000 (assumption of complete mixing). Consequently, the dilution factor was set to 1000 for production sites A, E and I, and to its actual value (below 1000) for sites D, G and H.

For all production sites except for sites D and E, chloroform releases presented in the table hereunder are due to the production of chloroform at each site. For production sites D and E, as described in section 3.1.1.2.1.2, integrated scenarii have been considered:

- For site D, chloroform releases are due to the simultaneous production of chloroform and HCFC 22 at this site. Specific values for $EFFLUENT_{STP}$ and removal percentage in STP were available for the chloroform production plant whereas generic data have to be used to integrate HCFC 22 production releases ($EFFLUENT_{STP}$ = 2E+06 and 85.6 % removal). The releases to wastewater have been added (see Table 3-4) as well as the effluent discharge rates of both STPs. This sum is then used to determine the dilution factor, knowing the actual river flow rate.

- For site E, chloroform releases are due to the simultaneous production of chloroform, HCFC 22 and dyes / pesticides at this site. Specific value for $EFFLUENT_{STP}$ was available for the chloroform production plant whereas default value has been used to integrate HCFC 22 and dyes / pesticides productions ($EFFLUENT_{STP}$ = 2E+06). 85.6 % of removal was assumed for each STP. Chloroform releases to wastewater due to production of chloroform, HCFC 22 and dyes / pesticides on the same site have been added (Table 3-5) as well as the effluent discharge rates of the three STPs. This sum is then used to determine the dilution factor, knowing the actual river flow rate.

**Table 3-17 : Local water concentration at each chloroform production site**

| | A | B | C | D | E | F | G | H | I | J |
|---|---|---|---|---|---|---|---|---|---|---|
| **Local emission to surface water or sea (B, C and F) (kg/d)** | 0.0077 | 0.014 | 0.737 | - | - | 0.98 | 1.08 | 1.45 | 0.011 | 0.047 |
| **$Elocal_{water}$**<br>**released to wastewater [kg/d] as reported in** Table 3-1, Table 3.4 **and** Table 3-5 | 0.052 | No WWTP | 2.5 | 0.32 | 35.3 | No WWTP | 7.53 | 10.1 | 0.074 | 0.280 |
| **$EFFLUENT_{STP}$ (L/d)** | 6.0E+04 | *2E+06* | 1.7E+06 | 2.3E+06 | 4.4E+06 | - | 9.5E+07 | 5.1E+07 | 6.7E+05 | 6.5E+05 |
| **Dilution in receiving water** | 1000 | *10*<br>(release to the Mediterranean sea) | *1000*[1]<br>(release to the Mediterranean sea) | 376 | 1000 | *100*<br>(release to the sea) | 262 | 21 | 1000 | *40* |
| **$Clocal_{inf}$ (mg/L)** | 0.867 | 0.007 | 1.447 | 0.139 | 8.07 | 0.49 | 0.079 | 0.198 | 0.111 | 0.432 |
| **$Clocal_{eff}$ (mg/L)** | 0.12 | 0.007 | 0.43 | 0.020 | 1.16 | 0.49 | 0.01 | 0.03 | 0.02 | 0.06 |
| **$Clocal_{water}$ (µg/L)** | **0.12** | **0.68** | **0.43** | **0.05** | **1.16** | **4.90** | **0.043** | **1.34** | **0.016** | **1.56** |
| **$PEClocal_{water}$ (µg/L)** [2] | **0.96** | **1.52** | **1.27** | **0.89** | **1.99** | **5.74** | **0.88** | **2.18** | **0.85** | **2.39** |

[1] Site C declared diluting by 100 its effluents in a lagoon before spilling them into the sea. Thus, its dilution factor is equal to 10*100

[2] Based on PECregional calculated below.

The following $PEClocal_{sediment}$ can be derived :

**Table 3-18 : Local sediment concentrations at each chloroform production site**

| | A | B | C | D | E | F | G | H | I | J |
|---|---|---|---|---|---|---|---|---|---|---|
| **$PEClocal_{sed}$ dry weight [µg/kg]** | **21.3** | **33.7** | **28** | **19.7** | **44.1** | **127** | **19.5** | **48.7** | **18.9** | **52.8** |

### 3.1.2.1.3. All other uses

**Table 3-19 : Local water concentrations during uses of chloroform**

| | HCFC 22 production | Dyes and pesticide production | Other applications | Use as a solvent | Losses as a by product during chemical manufacturing |
|---|---|---|---|---|---|
| **$Elocal_{water}$ released to wastewater [kg/d]** | 7 | 35 | 33.2 | 278 | 18.5 |
| **$Clocal_{inf}$ (mg/L) [1]** | 0.7 | 3.5 | 3.32 | 139 | 1.85 |
| **Elimination in STP** | 85.6 % | | | | |
| **$Clocal_{eff}$ (mg/L)** | 0.10 | 0.50 | 0.48 | 20.02 | 0.27 |
| **Dilution** | 40 | 40 | 40 | 10 | 40 |
| **$Clocal_{water}$ (µg/L)** | **2.52** | **12.6** | **12** | **2001** | **6.7** |
| **$PEClocal_{water}$ (µg/L) [2]** | **3.36** | **13.4** | **12.8** | **2001.9** | **7.5** |

[1] TGD default value of 10,000 $m^3$/d has been applied for all uses (Emission scenario for intermediates, TGD chapter 7) except for “use as solvent” (TGD default value of 2E+6 L/d used).

[2] Based on PEC regional calculated below.

**Table 3-20 : Local sediment concentrations during uses of chloroform**

| | HCFC 22 production | Dyes and pesticide production | Other applications | Use as a solvent | Losses as a by product during chemical manufacturing |
|---|---|---|---|---|---|
| **$PEClocal_{sed}$ dry weight [µg/kg]** | **73.9** | **297** | **282** | **44200** | **165** |

#### 3.1.2.2 Regional and continental concentrations

The EUSES model 2.0.3 has been used to predict regional and continental concentrations of chloroform in water and sediments.
The regional emission of chloroform was set to 1.14 t/d to wastewater, 340 kg/d to surface water and 2.72 t/d to air. Regional PECs could then be calculated :

**PEC regional $_{water}$ = 0.828 µg/L (in surface water)**
**PEC regional $_{sed}$ = 5.35 µg/kg (dry weight)**

The continental estimation takes into account the size of all EU countries together. Emission estimation is based on the EU-wide production volume : 302,800 t of chloroform/year. Continental emission of chloroform was set to 10.5 t/d to wastewater and 3.59 t/d to surface water. Continental PECs are then calculated by EUSES 2.0.3 :

**PEC continental $_{water}$ = 0.109 µg/L (in surface water)**
**PEC continental $_{sed}$ = 0.153 µg/kg (wet weight)**

#### 3.1.2.3 Measured concentrations

An overview of available monitoring results in surface water and sediment is presented in the following tables.

**Table 3-21: Measured average inland surface water concentrations**

| Location | Year of measurement | Mean concentration (µg/L) | Ref. |
|---|---|---|---|
| **Belgium** | | | |
| Meuse, Tailfer | 1992 | 0.2 | RIWA, 1995 |
| **Netherlands:** | | | |
| Meuse, Eijsden | 1992 | 0.9 | RIWA, 1995 |
| Meuse, Keizersveer | 1992 | 0.07 | RIWA, 1995 |
| Rhine, Lobith | 1991 | 0.2 | RIWA, 1993 |
| Rhine, Hagestein | 1991 | 0.3 | RIWA, 1993 |
| Ijsselmeer, Andijk | 1990-91 | < 0.1 | RIWA, 1993 |
| **United Kingdom:** | | | |
| 26 monitoring stations | ca. 1993 | 3.5 (max.55) | DOE, 1993 |
| 210 sites | ca. 1993 | < 0.5 | DOE, 1993 |
| | | 12 sites: >2 | |
| | | 17 sites: 1-2 | |
| | | >180 sites: <1 | |
| Canal water | < 1988 | 12.8-177 | DOE, 1993 |
| 9 regions; 2-45 sites each | 1993-96 | 0.05 - 6.1 (max: 0.3 - 240) | Environment Agency UK, 1997 |
| **Switzerland** | | | |

| Location | Year of measurement | Mean concentration (µg/L) | Ref. |
|---|---|---|---|
| Rhine, Basel | ca. 1982 | 1.19 | Ballschmitter *et al.*, 1988 |
| Typical river | 1981-83 | 0.062(max.1) | Fahrni, 1985 |
| Typical lake | ca. 1984 | < 0.01 | Fahrni, 1985 |
| **Germany, Rhine:** | | | |
| Constanz-Emmerich profile | 1983 | 2 | Ballschmitter *et al.*, 1988 |
| Oehningen | 1991 | N.D | Fleig and Brauch, 1991 |
| Village Neuf | 1991 | 0.1 (max.0.23) | Fleig and Brauch, 1991 |
| Seltz | 1991 | 0.1 (max.0.14) | Fleig and Brauch, 1991 |
| Karlsruhe | 1991 | 0.1 (max.0.45) | Fleig and Brauch, 1991 |
| Worms | 1991 | 1.17 (max. 3) | Fleig and Brauch, 1991 |
| Mainz | 1991 | 0.5 (max.0.98) | Fleig and Brauch, 1991 |
| Bischofsheim | 1991 | 0.36 (max.0.7) | Fleig and Brauch, 1991 |
| Koblenz | 1991 | 0.40 (max.1) | Fleig and Brauch, 1991 |
| Düsseldorf | 1991 | 0.23 (max.0.48) | Fleig and Brauch, 1991 |
| Bimmen | 1991 | 0.15 (max.0.3) | Fleig and Brauch, 1991 |
| Lobith | 1991 | 0.19 (max.0.69) | Fleig and Brauch, 1991 |
| Hessen | 1985-89 | 2.6 (max.9) | Ott, 1990 |
| Bad-Honnef | 1986 | max. 0.4 | LWA, 1987 |
| Köln | 1994 | max. 0.39 | ARW, 1994 |
| Wiesbaden | 1994 | max. 0.40 | ARW, 1994 |
| **Germany, Rhine affluents:** | | | |
| Main, Hessen | 1985-89 | 3.8 (max.12) | Ott, 1990 |
| Sieg | 1986 | < 0.1 | LWA, 1987 |
| Wupper | 1986 | max. 0.4 | LWA, 1987 |
| Ruhr | 1986 | max. 0.1 | LWA, 1987 |
| Ruhr (Duisburg bis Wildshaven) | 1984 | 0.15-15 | Ballschmitter *et al.*, 1988 |
| Emscher | 1986 | max. 0.1 | LWA, 1987 |
| Main, Kahl am Main | 1989 | 3.17 (90%:4.6) | Bayerisches Landesamt für Wasserwirtschaft, 1991 |
| **Germany, Elbe:** | | | |
| Elbe | 1988 | 0.94 (max.2.7) | Malle, 1990 |
| Schnackenburg | 1990 | 0.595 | ARGE Elbe, 1991 |
| Geesthacht | 1981 | 0.594 | ARGE Elbe, 1982 |
| Wedel | 1981 | 0.450 | ARGE Elbe, 1982 |
| Scharhoern | 1981 | 0.168 | ARGE Elbe, 1982 |
| Hamburg harbour | 1983-85 | 1.54 | Freie und Hansestadt Hamburg (Umweltbehörde), 1988 |

| Location | Year of measurement | Mean concentration (µg/L) | Ref. |
|---|---|---|---|
| **Germany, Donau:** | | | |
| Böfinger Halde | 1989 | < 1.017 (90%:1.9) | Bayerisches Landesamt für Wasserwirtschaft, 1991 |
| Jochenstein | 1989 | 0.908 (90%:1.8) | Bayerisches Landesamt für Wasserwirtschaft, 1991 |
| **Germany:** | | | |
| Unterweser | 1985-87 | 0.56(max.5) | Bohlen *et al.*, 1989 |
| Inn, Kirschdorf am Inn | 1989 | < 0.16 (90%:<0.41) | Bayerisches Landesamt für Wasserwirtschaft, 1991 |
| Salzach, Laufen | 1989 | < 1.592 (90%:2.7) | Bayerisches Landesamt für Wasserwirtschaft, 1991 |
| Regnitz, Hausen | 1989 | < 0.177 (90%:0.3) | Bayerisches Landesamt für Wasserwirtschaft, 1991 |
| Sächsische Saale,Joditz | 1989 | < 0.131 (90%:0.3) | Bayerisches Landesamt für Wasserwirtschaft, 1991 |
| Mosel | 1984 | 0.5-1.1 | LWA, 1987 |
| Weser | 1991 | 0.04 | DOE, 1993 |
| Ems | 1991 | 0.06 | DOE, 1993 |
| Bodensee | 1984-90 | 0.01-0.029 | DOE, 1993 |
| Bodensee, Lindau | 1983 | 0.1 | Ballschmitter *et al.*, 1988 |
| Bodensee, Überlingen | 1983 | < 0.05 | Ballschmitter *et al.*, 1988 |
| **Japan** | | | |
| Kako river | 1991 | 0.035 | Yamasaki *et al.*, 1992 |
| Tokyo | 1974 | 0.006 | Morita *et al.*, 1974 |
| areas from all over Japan | 1974 | 1.4-70 | Environment Agency Japan, 1995 |
| | 1975 | 0.09-17 | Environment Agency Japan, 1995 |
| **USA** | | | |
| Ohio R. mainstream | 1977-78 | 0.1-4.6 | Ohio R valley water Sanit. Comm, 1980 |
| Tributaries | 1977-78 | 0.1-22 | Ohio R valley water Sanit. Comm, 1980 |
| Lake Erie | 1975-76 | 9-18 | Konasewich *et al.*, 1978 |
| St Clair R. | 1975-76 | 1-4 | Konasewich *et al.*, 1978 |
| Lake Huron | 1975-76 | 1 | Konasewich *et al.*, 1978 |
| Lake Michigan | 1975-1976 | 1-30 | Konasewich *et al.*, 1978 |
| Niagara Falls | <1979 | 3.1 | Pellizzari *et al.*, 1979 |
| NJ area | <1979 | 14 | Pellizzari *et al.*, 1979 |
| Baton Rouge, LA | <1979 | 20 (max. 394) | Pellizzari *et al.*, 1979 |
| Houston, TX | <1979 | 8.2 (max.8.9) | Pellizzari *et al.*, 1979 |
| Montebello Forebay, CA | 1979-1981 | 5.8-84 | Bookman Edmonston Engineering Inc, 1985 |
| Manasquan river, NJ | 1978-1983 | nd-1570 | US-EPA, 1987 |

For a number of substances, the available data from national monitoring programmes in EU-Member States were aggregated in 1999 (Klein *et al.*, 1999). The final database contained monitoring results covering the years 1994 to 1998.

Monitoring sites related to marine water or groundwater and point sources were eliminated. For chloroform, 11,498 analytical results from 575 sampling stations are available. 4,480 results were above the detection limit (DL).

Because of the heterogeneous data and the varying data quality, sampling stations with more than 90% negative findings were removed. In the same way, data sets with very high detection limits were excluded if more than 80% of the measurements fell below the DL. By this procedure, 334 sampling stations and 5,149 analytical results were excluded. With the remaining data sets, arithmetic means at sampling station level and an EU-level 90-percentile were calculated.

| | |
|---|---|
| 90-percentile: | 1.17 µg/L |
| Median: | 0.28 µg/L |
| Arithmetic mean: | 0.79 µg/L |
| Standard dev.: | 1.61 µg/L |
| N. sampling stations: | 241 |
| N. entries: | 6,349 |
| N. entries > DL: | 4,139 |

**Table 3-22: measured average seawater concentrations**

| Location | Year of measurement | Mean concentration (µg/L) | Ref. |
|---|---|---|---|
| **Northern hemisphere, open ocean** | < 1983 | 0.33-1.09 | Khalil *et al.*, 1983 |
| **Atlantic ocean:** | | | |
| **North-Eastern Atlantic** | 1972 | 0.008 | Murray and Riley, 1973<br>Ernst, 1983 |
| **Between Madeira-Gibraltar (31 °N-18 °W)** | 1985 | 0.0016 | Class and Ballschmiter, 1987 |
| **West African coast (25 °N-18 °W)** | 1985 | 0.0016 | Class and Ballschmiter, 1987 |
| **Pacific ocean:** | | | |
| **Eastern Pacific** | < 1976 | 0.015 | Su and Godberg, 1976 |
| **Open ocean** | < 1979 | < 0.00005 | Singh, 1979 |
| **Gulf of Mexico (only in coastal samples)** | 1977 | 0.04-0.2 | Sauer Jr, 1981 |

**Table 3-23: Average measured concentrations coastal waters and estuaries**

| Location | Year of measurement | Mean concentration (µg/L) | Ref. |
|---|---|---|---|
| **Netherlands/Belgium** | | | |
| **Schelde estuary (Doel)** | 1993 | 0.15 | MVW, 1994 |
| **Netherlands** | | | |
| **Rhine estuary** | 1992 | 0.0048-0.091 | Krijsell and Nightingale, 1993 |
| **Schelde/Maas** | 1993 | < 0.06-0.15 | MVW, 1994 |
| **United Kingdom** | | | |

| Location | Year of measurement | Mean concentration (µg/L) | Ref. |
|---|---|---|---|
| **River estuaries** | 1993-95 | < 0.025-1.5 | MAFF, 1995<br>NRA, 1996 |
| **Baywater** | < 1975 | 1 | Pearson and McConnell, 1975 |
| **Estuarine water** | < 1988 | < 0.02-2.4 | WRC., 1988 |
| **Solent estuary** | < 1991 | 0.01-7.5 | Bianchi *et al.*, 1991 |
| **Mersey estuary** | 1987-90 | 2.7-70 | Rogers *et al.*, 1992 |
| **Humber and Poole estuaries** | 1992 | <0.010-0.0364 | Dawes and Waldock, 1994 |
| **Tees estuary** | 1992 | < 0.010-11.5 | Dawes and Waldock, 1994 |
| **Tyne, Wear and Southampton estuaries** | 1992 | < 0.010-0.242 | Dawes and Waldock, 1994 |
| **Liverpool estuary** | 1992 | 0.0283-0.0889 | Dawes and Waldock, 1994 |
| **Other estuaries (Tweed, Bristol channel, Falmouth, ...)** | 1992 | < 0.010 | Dawes and Waldock, 1994 |
| **France** | | | |
| **Seine estuary** | 1995 | < 1 | Agence de bassin Seine-Normandie, 1995 |
| **Germany** | | | |
| **Ostsee coasts** | 1983 | 0.06-0.17 | Hellmann, 1984 |
| **Nordsee coasts** | 1983 | 0.56-3.8 | Hellmann, 1984 |
| **Unterelbe, Glückstadt** | 1976 | 0.7-1.4 | Bauer, 1981 |
| **Unterelbe, Scharhoern** | 1981-82 | 0.04 | Ballschmitter *et al.*, 1988 |
| **Elbe mouth, St Margarethen** | 1993 | < 0.01-0.09 | Gewässergütebericht Elbe mit Zahlentafeln, 1994 |
| **Weser mouth,Bremerhaven** | 1993 | < 0.02-0.20 | Arbeitsgemeinschaft zur Reinhaltung der Weser, 1994 |
| **Sweden, Stenungsund** | 1988 | 0.0054-0.0148 | Abrahamsson *et al.*, 1989 |
| **USA, California coasts** | < 1976 | 0.009-0.012 | Su and Godberg, 1976 |
| **Gulf of Mexico** | < 1991 | 20-35 | Bianchi *et al.*, 1991 |
| **Maledives, Ziyaaraifushi** | 1986 | 0.0015 | Class and Ballschmiter, 1987 |
| **Coral Sea, Lohifushi** | 1986 | | Class and Ballschmiter, 1987 |
| **high tide**<br>**low tide** | | 0.004<br>0.01 | |

**Table 3-24: Average measured concentrations in sediments**

| Location | Year of measurement | Mean concentration (µg/L) | Ref. |
|---|---|---|---|
| **United Kingdom, Solent estuary** | < 1991 | 23 | Bianchi *et al.*, 1991 |
| **Germany** | | | |
| **Elbesediments** | 1981 | | ARGE Elbe, 1982 |
| **Geesthacht** | | 1.9 | |
| **Wedel** | | 2.3 | |
| **Scharhoern** | | 2.1 | |
| **Hamburg, harbour+Elbe** | 1983-85 | 18.1 | Freie und Hansestadt Hamburg (Umweltbehörde), 1988 |
| **out of harbour +Elbe** | | 3.9 | (Umweltbehörde, 1988) |
| **Rhine sediments** | 1982-83 | ca. 18 | LWA, 1986 |
| **Hitdorf Hafen** | 1987-88 | ca. 90 | Alberti, 1989 |
| **Wesel Hafen** | 1987-88 | ca. 190 | " |
| **Bodensee** | 1984-90 | 50-680 | Landesanstalt für Umweltschutz Baden-Württemberg, 1992 |
| **USA** | | | |
| **STORET database 425 sediment samples** | < 1985 | < 5 (detected in 8%) | Staples *et al.*, 1985 |
| **Pettaquamscutt river estuary (anoxic marine environment)** | < 1983 | | Whelan *et al.*, 1983 |
| **(0-6 cm depth)** | | 64 | |
| **(78-84 cm depth)** | | 1 | |

### 3.1.2.4 Comparison of measured and predicted concentrations

Regarding surface water monitoring, the most complete study has been performed by Klein *et al.*, 1999, aggregating monitoring results from a number of national monitoring programmes in Europe. The median value from this study is three times lower than the estimated regional concentrations. However, the mean concentration from some German rivers is perfectly in line with the estimated regional concentration and some estimated local concentrations are also coherent with high-end measured concentrations.

As the estimated concentrations are tentatively confirmed by the monitoring data, the estimated PECs will be used in the risk characterisation.

The database from monitoring in sediment is not very extensive and the few available data are mostly higher than the estimated regional concentration. However, measured concentrations might be representative of local situations.

### 3.1.3. Atmosphere

#### 3.1.3.1 Estimation of local air concentrations and deposition rates

The concentration in air at 100 m from a point source can be estimated as follows:

$\mathbf{Clocal_{air}\ (mg/m^3) = max\ (Elocal_{air}\ ,\ Estp\_{air})\ x\ Cstd\_air}$

where $Elocal_{air}$ (kg/d) = local direct emission rate to air during episode

$Estp\_{air}$ (kg/d) = local indirect emission to air from the STP = $Fstp_{air} \cdot Elocal_{water}$

$Fstp_{air}$ = 83.9 % (see Table 3-12)

Cstd air $= 2.78 \cdot 10^{-4}$ mg/m$^{3}$ (standard concentration in air at source strength of 1 kg/d)

$$Clocal_{air\ annual} = Clocal_{air} \cdot \frac{T_{emission}}{365}\ mg/m^3$$

Based on its vapour pressure and a log HENRY, the deposition over a radius of 1000 m around the source can be estimated as:

$\mathbf{DEPtotal = (Elocal_{air} + Estp\_{air}) \cdot (Fass_{aer} \cdot DEPstd_{aer} + (1\text{-}Fass_{aer}) \cdot DEPstd_{gas})}$

where: $Fass_{aer} = 4{,}78 \cdot 10^{-9}$ (calculated according to the TGD)
(Fraction of the chemical bound to aerosol)

$DEPstd_{aer} = 1 \cdot 10^{-2}\ mg.m^{-2}.d^{-1}$
(Standard deposition flux of aerosol-bound compounds at a source strength of 1 kg/d)

$DEPstd_{gas} = 3 \cdot 10^{-4}\ mg.m^{-2}.d^{-1}$
(Deposition flux of gaseous compounds (log HENRY > 2) at source strength of 1 kg/d)

##### 3.1.3.1.1. Production

Nine over the ten production companies have provided specific data on how measurements or estimations have been performed.
The tables hereunder describe the three following scenarios:

1. Only chloroform is produced on site (Table 3-25)
2. Chloroform and HCFC 22 are produced simultaneously at sites D (Addition of the releases to air due to both productions will be only considered for the soil compartment) (Table 3-26)
3. Chloroform, HCFC 22 and dyes / pesticides are produced simultaneously at site E (Releases to air due to the three productions are added. This scenario will be only considered for the soil compartment) (Table 3-27)

**Table 3-25 : Local concentration in air at each production site during chloroform production periods and emission**

| | A | B | C | D | E | F | G | H | I | J |
|---|---|---|---|---|---|---|---|---|---|---|
| $Elocal_{air}$ (kg/d) | 83.7<br>[1] | 0.036 | 7.2<br>[2] | 42<br>[3] | 4.18 | 21.6<br>[4] | 3.7<br>[5] | 0.14 | 2.44 | 63.6 |
| $Elocal_{water}$ released to wastewater [kg/d] | 0.052 | 0.014 | 2.5 | 0.32 | 0.01 | 0.98 | 7.53 | 10.1 | 0.074 | 0.28 |
| $Estp_{air}$ (kg/d) | 0.044 | 0.012 | 1.76 | 0.27 | 0.008 | 0.82 | 6.32 | 8.47 | 0.06 | 0.24 |
| $Clocal_{air}$ ($\mu g.m^{-3}$) | 23.3 | 0.01 | 2.00 | 11.7 | 1.16 | 6.00 | 1.76 | 2.36 | 0.68 | 17.7 |
| $Clocal_{air\ annual}$ ($\mu g.m^{-3}$) | 23.3 | 0.01 | 1.64 | 11.7 | 1.16 | 6.00 | 1.76 | 2.36 | 0.68 | 17.7 |
| **$PEClocal_{air,ann}$ [6]** | **23.4** | **0.15** | **1.8** | **11.8** | **1.3** | **6.2** | **1.9** | **2.5** | **0.8** | **17.8** |
| **DEPtotal [µg/m² x d]** | **25.1** | **0.01** | **2.8** | **12.7** | **1.3** | **6.7** | **3.0** | **2.6** | **0.75** | **19.2** |

[1] Mainly linked to storage and handling.

[2] Weekly atmosphere analysis performed in 6 different areas.

[3] Based on 153 measurements performed 3 to 5 times per week; max. value monitored in 2004 in exposure measurements in the plant 0.3 mg/m3 (mean value = 0.05 mg/m3, 136 values lower than the detection limit 0.05 mg/m3).

[4] Based on measurements of most critical air outlets and calculation models, all approved by national competent authority; waste gas incinerator; max. value monitored in 1995 in exposure measurements in the plant (n=90) 1.8 mg/m3 (90 % percentile 0.2 mg/m3, detection limit 1 mg/m3).

[5] Calculated theoretical emission from diffuse sources, VDI guideline 2440.

[6] Based on $PEC_{regional,\ air}$ calculated below.

**Table 3-26 : Local concentration in air at production site D during integrated production of chloroform and HCFC 22**

| **Production site D** | **For the air compartment** | **For the soil compartment** |
|---|---|---|
| **Elocal $_{air}$ (kg/d)** | 3.3 | 45.3 |
| **Elocal$_{water}$**<br>**released to wastewater [kg/d]** | 0.32 | 0.32 |
| **Estp $_{air}$ (kg/d)** | 0.268 | 0.27 |
| **Clocal$_{air}$**<br>**(µg.m$^{-3}$)** | 0.92 | 12.59 |
| **Clocal$_{air\ annual}$**<br>**(µg.m$^{-3}$)** | 0.92 | 12.59 |
| **PEClocal $_{air,ann}$[6]** | 1.06 | **12.74** |
| **DEPtotal**<br>**[µg/m$^2$ x d] [6]** | 1.07 | **13.67** |

[6] Based on PEC$_{regional,\ air}$ calculated below

**Table 3-27 : Local concentration in air at production site E during integrated production of chloroform, HCFC 22 and dyes / pesticides**

| **Production site E** | **For the soil compartment** |
|---|---|
| **Elocal $_{air}$ (kg/d)** | 31.9 |
| **Elocal$_{water}$**<br>**released to wastewater [kg/d]** | 35.3 |
| **Estp $_{air}$ (kg/d)** | 29.6 |
| **Clocal$_{air}$**<br>**(µg.m$^{-3}$)** | 8.87 |
| **Clocal$_{air\ annual}$**<br>**(µg.m$^{-3}$)** | 8.87 |
| **PEClocal $_{air,ann}$[6]** | **9.01** |
| **DEPtotal**<br>**[µg/m$^2$ x d] [6]** | **18.46** |

[6] Based on PEC$_{regional,\ air}$ calculated below

#### 3.1.3.1.2. All other uses

**Table 3-28: Local air concentrations during uses of chloroform**

| | HCFC 22 production | Dyes and pesticide production | Other applications | Use as a solvent | Losses as a by product during chemical manufacturing |
|---|---|---|---|---|---|
| **$Elocal_{air}$ (kg/d)** | 81.7 | 25 | 23.7 | 2,000 | 257 |
| **$Elocal_{water}$ released to wastewater [kg/d]** | 7 | 35 | 33.2 | 278 | 18.5 |
| **$Estp_{air}$ (kg/d)** | 5.9 | 29.4 | 27.9 | 233 | 15.5 |
| **$Clocal_{air}$ (µg.m$^{-3}$)** | 22.7 | 8.2 | 7.7 | 556 | 71.4 |
| **$Clocal_{air\ annual}$ (µg.m$^{-3}$)** | 18.7 | 3.2 | 6.4 | 132.5 | 58.7 |
| **$PEClocal_{air,\ ann}$[6]** | **18.8** | **3.4** | **6.5** | **132.7** | **58.9** |
| **DEPtotal [µg/m² x d]** | **26.3** | **16.3** | **15.5** | **670** | **81.8** |

[6] Based on PECregional, air calculated below

### 3.1.3.2 Regional and continental concentrations

The EUSES model has been used to predict regional and continental concentrations of chloroform in air.
The regional emission of chloroform was set to 2.72 t/d to air. Regional PEC could then be calculated:

$$\textbf{PEC regional}_{air} = 0.145\ \mu g.m^{-3}$$

The continental estimation takes into account the size of all EU countries together. Emission estimation is based on the EU-wide production volume: 302,800 t of chloroform/year. Continental emission of chloroform to air was set to 22.8 t/d. Continental PECs are then calculated by EUSES :

$$\textbf{PEC continental}_{air} = 0.0746\ \mu g.m^{-3}$$

### 3.1.3.3 Measured concentrations

An overview of measured concentrations is presented in the following tables.

**Table 3-29: Average measured concentrations in air in remote areas**

| Location | Year of measurement | Mean concentration (µg/m³) | Ref. |
|---|---|---|---|
| **Northern hemisphere** | 1974 | 130 | Cox *et al.*, 1976 |
| | 1981 | 102 | Singh *et al.*, 1983 |
| **Southern hemisphere** | 1974 | < 15 | Cox *et al.*, 1976 |
| | 1981 | 54 | Singh *et al.*, 1983 |
| **Atlantic ocean:** | | | |
| **Open sea** | < 1989 | 60-110 | Bruckmann *et al.*, 1989 |
| **Between England and** | 1972 | 1.7 | Murray and Riley, 1973 |
| **North-Western Africa** | 1973 | 92 | Lovelock, 1974 |
| **Northern Atlantic** | 1982-85 | 100-250 | Class and Ballschmiter, 1986 |
| **North-Eastern Atlantic** | < 1987 | 59-110 | Tille and Bächmann, 1987 |
| **Arctic** | | | |
| **Norway coasts; summer** | 1982 | 80 | Hov *et al.*, 1984 |
| **spring** | 1983 | 132 | |
| **23.8 °N-25.3 °N** | 1991-92 | 15.3 | Schauffler *et al.*, 1993 |
| **Norway, Spitzberg** | < 1990 | 98 | Müller and Oehme, 1990 |
| **USA, Alaska, Point Barrow** | 1981 | 195 | van der Heijden *et al.*, 1986 |
| **Northern hemisphere** | | | |
| **Madeira, Pico Arieiro (1810 m)** | 1982 | 100 | Kirschmer and Ballschmiter, 1983 |
| **Madeira, Porto Santo (100 m)** | 1982 | 110 | “ |
| **Bermuda** | 1985 | 75 | Ballschmitter *et al.*, 1988 |
| **USA,at 2360 m** | 1976 | 85 | Singh, 1977 |
| **Pacific ocean:** | | | |
| **North-Western Pacific** | 1976 | 44 | van der Heijden *et al.*, 1986 |
| **Marshall Islands (NH)** | 1981 | 130 | van der Heijden *et al.*, 1986 |
| **Equatorial Pacific (15 °N-10 °S/144 °W-165 °W)** | 1990 | 41 | Atlas *et al.*, 1993 |
| **North-Eastern Pacific (0-40 °N)** | 1981 | 105 | van der Heijden *et al.*, 1986 |
| **South-Eastern Pacific (0-40 °S)** | 1981 | 55 | van der Heijden *et al.*, 1986 |
| **South-Eastern Pacific (30-40 °S/138-146 °E)** | 1981 | 105 | van der Heijden *et al.*, 1986 |
| **Coastal sites near San Francisco** | 1975 | 116 | Singh *et al.*, 1977 |
| **Southern hemisphere** | | | |
| **South Pole** | 1979-81 | 78 | Khalil *et al.*, 1983 |

| Location | Year of measurement | Mean concentration (µg/m³) | Ref. |
|---|---|---|---|
| **Cape Town** | 1974 | < 15 | van der Heijden *et al.*, 1986 |
| **South-Africa** | 1977 | < 15 | van der Heijden *et al.*, 1986 |
| **Samoa Islands** | 1981 | 110 | Khalil *et al.*, 1983 |

**Table 3-30: Average measured concentrations in air in rural areas**

| Location | Year of measurement | Mean concentration (µg/ m³) | Ref. |
|---|---|---|---|
| France, Brittany | 1985 | 0.105 | Ballschmitter *et al.*, 1988 |
| Netherlands | 1991 | | RIVM, 1993 |
| Wijnandsrade | | 0.11 | |
| Zegveld | | 0.08 | |
| Witteveen | | 0.12 | |
| United-Kingdom | < 1973 | 0.004 | Murray and Riley, 1973 |
| | < 1975 | 0.12-0.59 | Pearson and McConnell, 1975 |
| Ireland, Cork | 1974 | 0.132 | Lovelock, 1974 |
| Germany | | | |
| German Alps, Hochgrat (1800 m) | 1982 | 0.103 | Kirschmer and Ballschmiter, 1983 |
| Schwäbische Alb, Asch | 1985 | 0.33(max.0.69) | Güthner *et al.*, 1990 |
| Oberfranken, Hof | 1985 | < 0.7 | Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen, 1986 |
| South-Western Germany, | 1987 | 0.05-0.5 | Frank *et al.*, 1989 |
| Nordschwarzwald, | 1988 | 0.2 | Frank *et al.*, 1991 |
| Berchtesgaden | 1989-90 | 0.18 | “ |
| Freudenstadt | 1990 | 0.6 | “ |
| Fichtelberg | 1990 | 0.3 | “ |
| Deuselbach, Hunsrück, 420m | 1987-1996 | 0.10-0.15 | Müller, 1995<br>Müller, 1996 |
| Schauinsland, Black Forrest, 1205 m | 1987-1996 | 0.07-0.11 | ‘’ |
| Norway, Birkenes | < 1990 | 0.073 | Müller and Oehme, 1990 |
| Finland, rural | 1987 | 0.063 | Kroneld, 1989 |
| USA | | | |
| rural background | 1980-81 | 0.097 | Singh *et al.*, 1982 |
| rural Pullmann, WA | 1974-75 | 0.1 | Grimsrud and Rasmussen, 1975 |
| Talladega national forest, AL | 1977 | 0.5 | Holzer *et al.*, 1977 |

| Location | Year of measurement | Mean concentration (µg/ m³) | Ref. |
|---|---|---|---|
| Magna, UT | 1976-78 | 0 | Pellizzari, 1978 |
| | <1983 | 0.19 | |
| South-Western Germany (8 sites) and Norhern France (2 sites) | 2002 | 0.11 ± 0.02 | ECSA, 2003 |

**Table 3-31: Average measured concentrations in air in urban and suburban areas**

| Location | Year of measurement | Mean concentration (µg/ m³) | Ref. |
|---|---|---|---|
| **Belgium, Brussels** | 1974-75 | 2.39-14.6 | Su and Godberg, 1976 |
| **Netherlands** | 1980 | 0.01-1 (max.36.6) | Guicherit and Schulting, 1985 |
| | 1979-81 | 0.15 (max.10) | Den Hartog, 1980-81 |
| **Apeldoorn** | 1991 | 0.13 | RIVM, 1993 |
| **Dordrecht** | 1991 | 0.14 | " |
| **Rotterdam** | 1991 | 0.16 | " |
| **United-Kingdom** | | | |
| **Runcorn works perimeter** | < 1975 | 11.9-47.4 | Pearson and McConnell, 1975 |
| **Liverpool and Manchester cities** | < 1975 | 3.6-9.5 | " |
| **Southampton, commuting route** | < 1991 | 1 | Bevan *et al.*, 1991 |
| **Southampton town centre** | < 1991 | < 0.2 | " |
| **Germany** | | | |
| **Bremen** | 1979 | 0.12 | Bätjer *et al.*, 1980 |
| **Bremerhaven** | 1979 | 0.03 | " |
| **Köln** | 1980 | 0.07 | Anonym, 1987 |
| **Koblenz** | 1983 | 0.05-1.6 | Hellmann, 1987 |
| **Ulm** | 1982-85 | 0.85 | Class and Ballschmiter, 1986 |
| **Göppingen** | 1986 | 0.16-0.69 | Hecht *et al.*, 1987 |
| **Petersberg (suburban)** | 1986-87 | 1.14 | Heil *et al.*, 1989 |
| **Hamburg** | 1986-87 | 0.2-0.6 | Bruckmann *et al.*, 1989 |
| **Essen** | 1988 | 0.23 | " |
| **Berlin** | 1990 | 0.26 | Berliner Senatsverwaltung für Stadtenwicklung und Umweltschutz Berlin, 1991 |
| **Leipzig, Tübingen, Freudenstadt** | 1990 | 0.6-0.95 (max.30) | Frank *et al.*, 1991 |
| **Offenbach** | 1987-1996 | 0.11-0.22 | Müller, 1995; Müller, 1996 |
| **Italy, Turin (winter)** | 1987-88 | 0.83 | Gilli *et al.*, 1990 |
| **(summer)** | 1988 | 0.14 | |

| Location | Year of measurement | Mean concentration (µg/m$^3$) | Ref. |
|---|---|---|---|
| **Finland, industrial site** | 1987 | 95 | Kroneld, 1989 |
| **France (Paris)** | 2000 | 0.9 (mean of 128 measurements)<br>min: < 0.3<br>median: 0.7<br>95th percentile: 2.2<br>max: 3.2 | Personal communication Laboratoire d'Hygiène de la Ville de Paris (2002) |
| **USA** | | | |
| **industrial sites, Iberville Parish, LA** | 1977 | 0.4-5.9 | Pellizzari, 1982 |
| **Vicinity of chemical plants in NJ** | 1976-1978 | 0.13-0.77 | Pellizzari, 1978 |
| **11 highly industrialized locations** | 1976-1978 | 0 -53.8 | Pellizzari, 1978 |
| **Waste disposal site, Kin-Buc, NJ** | 1976 | | Pellizzari, 1982 |
| **vapor phase organics:** | | trace-6.4 | |
| **ambient air** | | 0.9-28 | |
| **Old Love canal** | 1978 | (1-110) 30 | Barkley *et al.*, 1980 |
| **Houston, TX** | 1980-81 | 2.055 | Singh *et al.*, 1982 |
| **St. Louis, MO** | 1980-81 | 0.335 | " |
| **Denver, Co** | 1980-81 | 0.899 | " |
| **Riverside, CA** | 1980-81 | 3.415 | " |
| **Staten Island, NY** | 1980-81 | 0.709 | " |
| **Pittsburgh, PA** | 1980-81 | 0.471 | " |
| **Chicago, IL** | 1980-81 | 0.393 | " |
| **Tuscaloosa, AL** | 1977 | 3.96 | Holzer *et al.*, 1977 |
| **Los Angeles, CA** | 1978 | 0. | Singh *et al.*, 1981 |
| **Phoenix, AR** | 1978 | 0.6 | " |
| **Oakland, CA** | 1978 | 0.16 | " |
| **Niagara Falls, NY** | 1979 | 89 | Pellizzari *et al.*, 1979 |
| **NJ area** | 1979 | 47 | " |
| **Baton Rouge, LA** | 1979 | 5.5 | " |
| **Houston, TX** | 1979 | 1 | " |
| **Rutherford, NJ** | 1978 | 23 (max. 150) | Bozzelli and Kebbekus, 1982 |
| **Residential** | | 30 (max.90) | |
| **east, industrial** | | 25 (max. 153) | |
| **north, industrial** | | 14 (max. 33) | |
| **west, industrial** | | 22 (max. 50) | |
| **Newark, NJ** | 1978 | 19 (max. 37) | " |

| Location | Year of measurement | Mean concentration (µg/ m³) | Ref. |
|---|---|---|---|
| **Middlesex, NJ** | 1978 | 11 (max. 14) | " |
| **Sommerset, NJ** | 1978 | 0 | " |
| **Summerville, NJ** | 1978 | 25 (max. 50) | " |
| **Overall (1739 measure points)** | <1983 | 1.3 | Brodinsky and Singh, 1983 |
| **Industrial (306 measure points)** | | 11 | |
| **Japan, Tokyo** | 1974 | 35-1320 | Ohta et al., 1974 |
| **measurements all over Japan** | 1979 | 0.11-24.8 | Environment Agency Japan, 1995 |
| | 1980 | 0.08-22.8 | |
| | 1983 | 0.05-10.9 | |
| | 1991 | 0.037-5.3 | |
| | 1992 | nd-3.2 | |

**Table 3-32: Average measured concentrations in precipitations**

| Location | Year of measurement | Mean concentration (µg/L) | Ref. |
|---|---|---|---|
| **United Kingdom, rainwater** | < 1975 | < 0.2 | Pearson and McConnell, 1975 |
| | **Germany** | | |
| **Hesse, pine forests, rainwater** | 1989 | 0.039-0.097 | Renner *et al.*, 1990 |
| **fields, rainwater** | 1989 | 0.011-0.017 | |
| **Koblenz, rainwater** | 1982-83 | 0.6-0.9 | Hellmann, 1984 |
| **Schwäbische Alb, rainwater** | 1985 | 0.025 | Ballschmitter *et al.*, 1988 |
| **Kolmbach, Odenwald, rainwater** | 1987-88 | 0.014-0.520 | Kubin *et al.*, 1989 |
| **Kolmbach, Odenwald,mist** | 1988 | 0.79 | |
| **Ulm, rainwater** | 1985 | 0.025 | Class and Ballschmiter, 1986 |
| **USA, Alaska, snow** | < 1976 | 0.094 | Su and Godberg, 1976 |
| **Los Angeles, rainwater** | 1982 | 0.25 | Kawamura and Kaplan, 1983 |
| **Japan** | 1974 | 10-118 | Environment Agency Japan, 1995 |
| | 1975 | 0.1-43 | Environment Agency Japan, 1995 |

### 3.1.3.4 Comparison of measured and predicted concentrations

Concentrations in remote and rural areas are usually between 0.05 and 0.2 µg/m3. In urban or suburban areas, recent measured chloroform concentrations are usually below 5 µg/m3, while concentrations measured recently in the vicinity of industrial areas reached up to 95 µg/m3. The estimated regional concentration is coherent with many urban concentrations. However, it may underestimate the actual concentrations of highly industrialised areas where concentration far above 1 µg/$m^3$ were measured at many locations. Such a difference between the measured concentrations and the estimated PEC might be explained by the oldness of the measures (eighties, nineties) compared to the releases volumes from 1995 – 2000 that were used to estimate the PEC. Since the eighties, it can be assumed that the releases of chlorinated solvents have been significantly reduced. This assumption is confirmed by the measurements all over Japan that show a significant decrease in the measured concentrations from 1979 to 1992. No other data can support this assumption. However, with recent measurements, we can observe that the estimated regional concentration may also underestimate the actual concentrations of highly urbanised area: 0.26 µg.$m^{-3}$ in Berlin in 1990, 0.6 – 0.95 µg.$m^{-3}$ in Leipzig - Tübingen in 1990, 0.83 µg.$m^{-3}$ in Turin in 1987-88 and 0.9 µg.$m^{-3}$ in Paris in 2000. These higher concentrations might be due to the presence of chloroform precursors in such urbanised area. In particular, trichloroethylene and tetrachloroethylene were also detected at high concentrations in Paris in 2000 (Personal communication, Laboratoire d'Hygiène de la Ville de Paris, 2002): mean concentrations were respectively 2.0 and 2.3 µg.$m^{-3}$. These results could imply that trichloroethylene and tetrachloroethylene might be preferred precursors for chloroform formation in highly urbanised areas. Another explanation could be the emissions from chlorination of drinking and cooling water in urban areas, which does not seem to have been reduced over the last decennia.

## 3.1.4. Terrestrial compartment

### 3.1.4.1 Estimation of local concentrations in soil.

Because of the low bioaccumulation potential of chloroform, the PEC in agricultural soil will be considered. The release of chloroform to the terrestrial compartment is small. Chloroform is not expected to adsorb to soil to any significant extent. Using the EUSES model, local concentrations in soil are estimated. These concentrations are the results of emission and atmospheric deposition.

According to the European regulation, biological sludge containing dangerous substances is identified as hazardous waste when the waste contains more than a certain percentage, which is specific to each hazardous property. In the case of chloroform biological sludge containing more than 1% of chloroform should be considered as dangerous waste and cannot be used in agriculture.

However, for most chloroform production sites, chloroform is not the only dangerous substance in the biological sludge. Therefore it is standard practise to consider sludge from chemical industries as dangerous waste and not to use it in agriculture. In addition, producers also confirmed this statement.

Therefore, the application of sludge from sewage treatment plants was not taken into account in the calculation of the local concentrations in soils. However, these local concentrations in soils could be assimilated to long-term steady state concentrations.

#### 3.1.4.1.1. Production

For all production sites except for sites D and E, chloroform releases presented in Table 3-33 are due to the production of chloroform at each site. For production sites D and E, as described in section 3.1.1.2.1.2, integrated scenarii have been considered:

- For site D, chloroform releases are due to the simultaneous production of chloroform and HCFC 22 at this site. Releases to wastewater and to air due to both productions have been added (see Table 3-4).
- For site E, chloroform releases are due to the simultaneous production of chloroform, HCFC 22 and dyes / pesticides at this site. Releases to wastewater and to air due to the three productions have been added (see Table 3-5).

**Table 3-33 : Local concentration in soil at each production site during emission period and chloroform production**

| | A | B | C | D | E | F | G | H | I | J |
|---|---|---|---|---|---|---|---|---|---|---|
| **DEPtotal** **[µg/m$^2$ x d]** | 25.1 | 0.01 | 2.8 | 13.7 | 18.5 | 6.7 | 3.0 | 2.2 | 0.75 | 19.2 |
| **Temission [d/a]** | 365 | 365 | 300 | 365 | 365 | 365 | 365 | 365 | 365 | 365 |
| **$DEPtotal_{annual}$** **[µg/m$^2$ x d]** | 25.1 | 0.01 | 2.3 | 13.7 | 18.5 | 6.7 | 3.0 | 2.2 | 0.75 | 19.2 |
| **$Clocal_{soil}$** **[µg/kg] (ww)** | **1.15** | **0.0005** | **0.10** | **0.62** | **0.84** | **0.30** | **0.14** | **0.12** | **0.03** | **0.87** |
| **$PEClocal_{soil}$** **[µg/kg] (ww)** [1] | **1.16** | **0.01** | **0.12** | **0.64** | **0.85** | **0.31** | **0.15** | **0.13** | **0.05** | **0.89** |

[1] Based on PECregional $_{natural\ soil}$ calculated below.

#### 3.1.4.1.2. All other uses

**Table 3-34: Local soil concentrations during uses of chloroform**

| | HCFC 22 production | Dyes and pesticide production | Other applications | Use as a solvent | Losses as a by product during chemical manufacturing |
|---|---|---|---|---|---|
| **DEPtotal [µg/m² x d]** | 26.3 | 16.3 | 15.5 | 670.0 | 81.6 |
| **Temission [d/a]** | 300 | 144 | 300 | 87 | 300 |
| **$\text{DEPtotal}_{\text{annual}}$ [µg/m² x d]** | 21.6 | 6.4 | 12.7 | 159.7 | 67.1 |
| **$\text{Clocal}_{\text{soil}}$ [µg/kg] (ww)** | **0.99** | **0.29** | **0.58** | **7.25** | **3.07** |
| **$\text{PEClocal}_{\text{soil}}$ [µg/kg] (ww) [1]** | **0.995** | **0.30** | **0.59** | **7.26** | **3.08** |

[1] Based on $\text{PECregional}_{\text{natural soil}}$ calculated below

### 3.1.4.2 Regional and continental concentrations

The EUSES model 2.0.3 has been used to predict regional and continental concentrations of chloroform in soil. Regional PECs are calculated :

**PEC regional $_{\text{soil}}$ = 1.86 µg.kg$^{-1}$ (ww)**

**PEC regional $_{\text{natural soil}}$ = 11.5 ng.kg$^{-1}$ (ww)**

**PEC regional $_{\text{soil pore water}}$ = 549 ng.L$^{-1}$**

The continental estimation takes into account the size of all EU countries together. Emission estimation is based on the EU-wide production volume : 302,800 t of chloroform/year. Continental PECs are then calculated by EUSES 2.0.3 :

**PEC continental soil = 0.202 µg.kg-1 (ww)**

**PEC continental natural soil = 5.22 ng.kg-1 (ww)**

**PEC continental soil pore water = 59.6 ng.L-1**

### 3.1.4.3 Measured concentrations

An overview of available monitoring results in soil and groundwater is presented in the following tables.

**Table 3-35: Average measured concentrations in soil**

| SOIL | | | |
|---|---|---|---|
| **Location** | **Year of measurement** | **Mean concentration (mg/kg dw)** | **Ref.** |
| Netherlands | < 1989 | | Kliest *et al.*, 1989 |
| uncontaminated site | | 13 | |
| near to a garage | | < 5 | |
| near to a waste dump site | | < 5 | |
| Germany, Hamburg | 1983-85 | 0.0044 | Freie und Hansestadt Hamburg |

| | | | |
|---|---|---|---|
| | | | (Umweltbehörde), 1988 |
| SOIL-AIR | | | |
| Location | Year of measurement | Mean concentration (µg/m3) | Ref. |
| United Kingdom, disused fire station site | < 1991 | <= 770 | Eastwood *et al.*, 1991. |
| Germany | | | |
| Berchtesgaden | 1989 | 0.145-1.030 | Frank *et al.*, 1991 |
| Forests in South Germany | 1987 | | Frank *et al.*, 1989 |
| Mauzenberg | | 11.9-77.4 | |
| Bernstein | | 0.4-1.8 | |
| Schönbuch | | 0.4-7.2 | |
| SOIL PERCOLATION WATER | | | |
| Location | Year of measurement | Mean concentration (µg/L) | Ref. |
| Germany, Hesse forests | 1989 | | Renner *et al.*, 1990 |
| pine forests | | 0.017-0.087 | |
| fields | | 0.030-0.540 | |

**Table 3-36: Average measured concentrations in groundwater**

| Location | **Year of measurement** | **Mean concentration (µg/L)** | **Ref.** |
|---|---|---|---|
| Netherlands, 29 deepwells | ca. 1980 | >=0.1(in 8/29) | van der Heijden *et al.*, 1986 |
| **United Kingdom** | | | |
| Groundwater | < 1988 | 0.16 | WRC., 1988 |
| 36 groundwater sites | < 1984 | < 0.1-4.6 (in 35/36) | Folkard, 1984 |
| groundwater from site of disused fire station | < 1991 | 12.8-20.8 | Eastwood *et al.*, 1991. |
| Birmingham aquifer | 1986-88 | | Rivett *et al.*, 1990b |
| 59 supply boreholes | | >=0.02(in 53%) | Rivett *et al.*, 1990a |
| | | 5%: 0.02-0.1 | |
| | | 31%: 0.2-1 | |
| | | 17%: 1.1-10 | |
| 15 monitoring wells | | <= 20 | |
| Coventry area | < 1993 | > 1 (in 43%) | Burston *et al.*, 1993 |
| 42 boreholes (18: industrial water supplies, 20: public water supplies, 4: agricultural purposes) | | (mean: 2.1) | Nazari *et al.*, 1993 |
| **Germany** | | | |
| Rhine-Sieg area, groundwater | < 1984 | <= 3 | Schoeler *et al.*, 1984 |
| Hessen, groundwater | 1988-89 | 0.01-2.5 | Renner and Mühlhausen, 1989 |
| Bremen, groundwater | 1978-79 | 2.0 | Lahl *et al.*, 1981 |
| mixed groundwater/treated surface water from Weser river | 1978-79 | 0.3 | |

| | | | |
|---|---|---|---|
| Switzerland | 1981-83 | 0.021(max.1.2) | Fahrni, 1985 |
| Spain, Galicia | < 1992 | 9-48 | Freiria-Gandara *et al.*, 1992 |
| USA, Pittman, Nevada [contaminated site] | < 1987 | nd-866 | Kerfoot, 1987 |
| Montebello Forebay, CA | < 1984 | | Bookman Edmonston Engineering Inc, 1985 |
| unchlorinated well water | | < 0.2-2.6 | ” |
| chlorinated well water | | < 0.1 -1.6 | “ |
| reclaimed water | | 5.8 – 84 | “ |
| imported water sources | | 0.2-29 | “ |

#### 3.1.4.4 Comparison of measured and predicted concentrations

There are not sufficient measured concentrations in soil available for a meaningful comparison.

### 3.1.5. Non compartment specific exposure relevant to the food chain

Because of the low bioaccumulation potential of chloroform (BCF = 13), the potential for secondary poisoning can be considered to be negligible.
This is furthermore confirmed by the monitoring data available from marine aquatic biota as well as in birds as presented in Table 3-37 and Table 3-38.

**Table 3-37: Average measured concentrations in marine biota from around the United Kingdom**

| **Organism / organ** | **L (*)** | **Level (µg/kg)** | **Ref.** |
|---|---|---|---|
| **Plankton** | (1) | 0.02-0.9 (w) | R1 |
| | (2) | 5 (w) | R1 |
| **Ragworm (Nereis diversicolor)** | (3) | ND | R1 |
| **Mussel (Mytilus edulis)** | (1) | 9-10 (w) | R1 |
| | (4) | 8 (w) | R1 |
| | (5) | 3 (w) | R1 |
| **Whelk (Buccinum u.)** | | | |
| **digestive gland** | (6) | 117 (d) | R2 |
| **muscle** | (6) | 129 (d) | R2 |
| **Mussel (Modiolus m.)** | | | |
| **digestive tissue** | (6) | 56 (d) | R2 |
| **mantle** | (6) | 438 (d) | R2 |
| **muscle** | (6) | 200 (d) | R2 |

| **Organism / organ** | **L (*)** | **Level (µg/kg)** | **Ref.** |
|---|---|---|---|
| **Scallop (Pecten m.)** | | | |
| **gill** | (6) | 1040 (d) | R2 |
| **mantle** | (6) | 224 (d) | R2 |
| **muscle** | (6) | 440 (d) | R2 |
| **ovary** | (6) | 720 (d) | R2 |
| **testis** | (6) | 448 (d) | R2 |
| **Cockle (Cerastoderma edule)** | (1) | 4-150 (w) | R1 |
| **Oyster (Ostrea edulis)** | (5) | 3 (w) | R1 |
| **Whelk (Buccinum undatum)** | (5) | 10 (w) | R1 |
| **Slipper limpet (Crepidula fornicata)** | (5) | 6 (d) | R1 |
| **Crab (Cancer pagurus)** | (7) | ND | R1 |
| | (1) | 3-115 (w) | R1 |
| | (4) | 180 (w) | R1 |
| **Shore crab (Carcinus maenas)** | (4) | 15 (w) | R1 |
| **Hermit crab** | (4) | 73 (w) | R1 |
| **(Eupagurus bernhardus)** | (5) | 20 (w) | R1 |
| **Shrimp (Crangon crangon)** | (4) | 45 (w) | R1 |
| **Starfish (Asterias rubens)** | (5) | 13 (w) | R1 |
| **Sunstar (Solaster sp.)** | (5) | 3 (w) | R1 |
| **Sea urchin (Echinus esculentus)** | (5) | 2 (w) | R1 |
| **Flounder (Platychthys f.)** | | | |
| **flesh** | (1) | 21 (w) | R1 |
| **liver** | (1) | 6 (w) | R1 |
| **Eel (Conger c.)** | | | |
| **gill** | (6) | 50 (d) | R2 |
| **gut** | (6) | 43 (d) | R2 |
| **liver** | (6) | 474 (d) | R2 |
| **muscle** | (6) | 219 (d) | R2 |
| **Cod (Gadus m.)** | | | |
| **brain** | (6) | 167 (d) | R2 |
| **gill** | (6) | 156 (d) | R2 |
| **heart** | (6) | 67 (d) | R2 |
| **liver** | (6) | 19 (d) | R2 |
| **muscle** | (6) | 168 (d) | R2 |
| **skeletal tissue** | (6) | 29 (d) | R2 |
| **stomach** | (6) | 7 (d) | R2 |

| Organism / organ | L (*) | Level (µg/kg) | Ref. |
|---|---|---|---|
| **Coalfish (Pollachius b.)** | | | |
| **alimentary canal** | (6) | 51 (d) | R2 |
| **gill** | (6) | 294 (d) | R2 |
| **heart** | (6) | 112 (d) | R2 |
| **liver** | (6) | 851 (d) | R2 |
| **muscle** | (6) | 168 (d) | R2 |
| **Dogfish (Scylliorhinus c.)** | | | |
| **brain** | (6) | 404 (d) | R2 |
| **gill** | (6) | 755 (d) | R2 |
| **gut** | (6) | 544 (d) | R2 |
| **heart** | (6) | 210 (d) | R2 |
| **liver** | (6) | 76 (d) | R2 |
| **muscle** | (6) | 649 (d) | R2 |
| **spleen** | (6) | 80 (d) | R2 |
| **Mackerel (Scomber s.)** | | | |
| **flesh** | (1) | 50 (w) | R1 |
| **liver** | (1) | 18 (w) | R1 |
| **flesh** | (2) | 5 (w) | R1 |
| **Dab (Limanda l.) / flesh** | (5) | 23 (w) | R1 |
| **Plaice (Pleuronectes p.) / flesh** | (5) | 17 (w) | R1 |
| **Sole (Solea s.)/flesh** | | | |
| **flesh** | (5) | 26 (w) | R1 |
| **guts** | (5) | 9 (w) | R1 |
| **Red gurnard (Aspitrigla c.)** | | | |
| **flesh** | (5) | 21 (w) | R1 |
| **guts** | (5) | 2 (w) | R1 |
| **Scad (Trachurus t.) / flesh** | (5) | 48 (w) | R1 |
| **Pout (Trisopterus l.) / flesh** | (5) | 15 (w) | R1 |
| **Spurdog (Squalus a.) / flesh** | (5) | 110 (w) | R1 |
| **Sprat (Clupea s.) / flesh** | (2) | 5 (w) | R1 |
| **Grey seal (Halichoerus g.) / blubber** | (8) | 7.6-22 (w) | R1 |

(*): Locations: (1): Liverpool Bay; (2): Torbay; (3): Mersey Estuary; (4): Firth of Forth; (5): Thames Estuary;

(6): Irish Sea; (7): Tees Bay; (8): Farne Isles

ND : not detectable; (d): dry weight basis; (w): wet weight basis

References: R1: Pearson and McConnell, 1975; R2: Dickson and Riley, 1976

### Table 3-38: Average measured concentrations in birds from around the United Kingdom (Pearson and McConnell, 1975)

| Organism / organ | Location | Level (µg/kg wet weight) |
|---|---|---|
| **Gannet (Sula bassana)** | Irish Sea | |
| **liver** | | 7.4 |
| **eggs** | | 1.9-2.0 |
| **Shag (Phalacrocerax a.) / eggs** | Irish Sea | 0.7 |
| **Razorbill (Alca torda) / eggs** | Irish Sea | 6.6-19.7 |
| **Guillemot (Uria aalge) / eggs** | Irish Sea | 8-65 |
| **Kittiwake (Rissa t.)** | | |
| **eggs** | North Sea | 58 |
| **liver** | Frodsham Marsh | 17.3 |
| **kidney** | Merseyside | 8.4 |
| **Moorhen (Gallinula c.)** | Merseyside | |
| **liver** | | 1.3 |
| **muscle** | | 8.2 |
| **eggs** | | 19.5-29 |
| **Mallard (Anas p.) / eggs** | Merseyside | 10-22 |

## 3.2. EFFECTS ASSESSMENT: HAZARD IDENTIFICATION AND DOSE (CONCENTRATION) - RESPONSE (EFFECT) ASSESSMENT

### 3.2.1. Aquatic compartment

Results have been obtained with various fish species. In general, chloroform toxicity measurements are limited by its high volatility, which has to be considered sufficiently during testing.

#### 3.2.1.1 Acute and prolonged toxicity to aquatic vertebrates (fish and amphibians)

**Table 3-39: acute toxicity results towards fish**

| Species | Method | Endpoint (duration) | Reliability index[12] | Remarks | Reference |
|---|---|---|---|---|---|
| ***Limanda limanda*** | | LC 50 (96 h) = 28 mg/L | 4 | Flow-through system, analytical monitoring<br>No details on the experimental conditions | Pearson and McConnell, 1975 |
| ***Lepomis macrochirus*** | | LC 50 (96 h) = 18 mg/L<br>(mean LC 50 of 5 tests) | 3 | Daily analytical monitoring. No clear dose-effect relation.<br>High mortality due to *Columnaris* infection in the control and the lower concentration | Anderson and Lustry, 1980 |
| ***Poecelia reticulata*** | US EPA, 1971 | LC 50 (96 h) = 300 mg/L | 3 | No analytical monitoring<br>static test, insufficient documentation | Hazdra *et al.*, 1979 |
| ***Leuciscusidus*** | DIN 38412 | LC 0 (48 h) = 51 mg/L<br>LC 50 (48 h) = 92 mg/L<br>LC 100 (48 h) = 151 mg/L | 3 | The test system is not appropriate for volatile substances | Knie *et al.*, 1983 |
| ***Leuciscusidus melatonus*** | DIN 38412 | LC 0 (48 h) = 147 mg/L<br>LC 50 (48 h) = 162 mg/L<br>LC 100 (48 h) = 176 mg/L | 3 | No analytical monitoring<br>The test system is not appropriate for volatile substances | Juhnke and Lüdemann, 1978 |
| ***Oncorhynchus mykiss*** | | LC 50 (48 h) = 20 mg/L | 3 | No analytical monitoring. Insufficient documentation | Slooff, 1979 |

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[12] Reliability index:

Reliability index 1 : Valid: method and description in accordance with test guidelines and with accurate actual concentrations measurements

Reliability index 2 : Valid with restriction: falling short of highest standards concerning protocol or reporting

Reliability index 3 : Not valid

Reliability index 4 : Validity cannot be established due to missing information

| Species | Method | Endpoint (duration) | Reliability index[12] | Remarks | Reference |
|---|---|---|---|---|---|
| ***Brachydanio rerio*** | | LC 50 (48 h) = 100 mg/L | 3 | No analytical monitoring. Insufficient documentation | Slooff, 1979 |
| ***Oryzias latipes*** | Testing methods for industrial and wastewater, Japan | LC 50 (48 h) = 117 mg/L | 3 | No analytical monitoring<br>Semi-static system | MITI, 1992 |
| ***Cyprinus carpio*** | | LC 50 (3-5 d) = 97 mg/L<br>(toxicity to carp embryos) | 2 | Semi-static system<br>2 initial concentrations are measured.<br>LC 50 value is corrected with estimated mean concentration during the static period | Mattice *et al.*, 1981 |
| ***Ictalurus punctatus***<br>**(juvenile catfish)** | | LC 50 (96 h) = 75 mg/L | 2 | Daily analytical monitoring.<br>Flow-through toxicant delivery system | Anderson and Lustry, 1980 |
| ***Pimephales promelas*** | US-EPA | LC 50 (96) = 71 mg/L | 2 | Flow-through system, daily analytical monitoring | Geiger *et al.*, 1990 |
| ***Pimephales promelas*** | ASTM, 1980 | Fry : LC 50 (96 h) = 129 mg/L<br>Juvenile : LC 50 (96 h) = 171 mg/L<br>Subadults : LC 50 (96 h) = 103 mg/L | 2 | static, closed system<br>, no analytical monitoring | Mayes *et al.*, 1983 |
| ***Oncorhyn-chus mykiss*** | | LC 50 (96 h) = 18 mg/L (mean LC 50 of 5 tests) | 2 | Daily analytical monitoring.<br>Flow-through toxicant delivery system | Anderson and Lustry, 1980 |
| ***Micropterus salmoides*** | | LC 50 (96 h) = 51 mg/L (mean LC 50 of 3 tests) | 2 | Daily analytical monitoring.<br>Flow-through toxicant delivery system | Anderson and Lustry, 1980 |
| ***Poecelia reticulata*** | | experimental : LC 50 (14 d) = 102 mg/L<br>calculated : LC 50 (14d) = 154 mg/L | 2 | No analytical monitoring<br>Semi-static system<br>Use of solvent | Könemann, 1981 |
| ***Brachydanio rerio*** | OECD 203 | LC50 (96h) =121 mg/L | 1 | Flow-through test (6 renewals per day) with analytical monitoring | Röderer, 1990 |

Slooff, 1979 performed acute toxicity tests with *Brachydanio rerio*. Ten fish were exposed for 48 hours in 10 L aquaria with a dynamic closed system (6L/h). The fish were not fed. No measurement of the concentrations is mentioned. At least three concentrations were tested but there is no precision about the range of concentrations nor the confidence limits of the results. The test is too short and the result is used as an indicative range of concentrations that could lead to acute toxicity towards fish.

The acute toxicity of chloroform to four species of freshwater fish has been studied in flow-through 96-hours toxicity tests by Anderson and Lustry, 1980. Test concentrations have been checked by daily measurement. Behaviour of the fish is depending upon the species : trout and catfish tend to exhibit an initial tolerance to chloroform with mortality increasing later whereas mortality rate of bluegill and largemouth bass were high during the first day.

As columnaris infection on fish caused high mortality rate in the control and in the low concentration aquarium, the results for *Lepomis macrochirus* could not be considered.

Könemann, 1981 conducted acute toxicity tests on 72 industrial pollutants using guppies (*Poecilia reticulata*) and compared the results with values that have been obtained with the QSAR method. Tests were performed in semi-static conditions for 14 days on 8 fishes per concentration. The concentrations increased in geometric progression with a ratio of 1.8. Both final experimental and calculated LC 50 results are given and the model seems to fit well with the chloroform substance, as the ratio $\frac{calculatedLC50}{\exp erimentalLC50}$ is 1.5. As the article is reporting results of 72 industrial chemicals, experimental conditions are reported in general and nothing is known about the specific conditions for chloroform (which solvent is used, solvent control, control results...). Nor is the concentration / effect relation reported.

The objective of the study from Mayes *et al.*, 1983 was to examine the influence of age on the acute toxic response of fathead minnow exposed to nine organic compounds including chloroform. 96 h-LC 50 of the three stages of the fish are reported. The subadults seem to be the most sensitive to chloroform.

In the six validated studies, the LC 50 range from 18 mg/L for *Oncorhynchus mykiss* to 171 mg/L for *Pimephales promelas*.

The first value 96 h-LC 50 = 18 mg/L is retained all the more as the study was performed with daily analytical monitoring and a flow-through toxicant delivery system.

### Chronic toxicity to fish and amphibians

Chronic toxicity results in determining the mortality at post hatching are shown in the following table.

**Table 3-40 : Chronic Toxicity results towards fish and amphibians**

| Species | Method | Endpoint (duration) (95 % confidence limit) | Reliability index | Remarks | Reference |
|---|---|---|---|---|---|
| ***Pimephales promelas:*** | | LC 50 (9 d) > 58 mg/L | 3 | Flow through; exposure period: 9 days; analytical monitoring | Black *et al.*, 1982 |
| ***Oncorhynchus mykiss*** | | LC 10 = 83.2 µg/L<br>(9.4 - 251.4 µg/L) | 3 | Flow through; exposure period: 27 days; analytical monitoring | cited by Black *et al.*, 1982 |
| ***Oncorhynchus mykiss*** | | LC 1 (27 d) = 0.0062 mg/L LC50 (27 d)=2.03mg/L (water hardness = 48 mg/L)<br>LC 1 (27 d) = 0.0049 mg/L LC50 (27 d)=1.24mg/L (water hardness = 210 mg/L) | 3 | Flow through; exposure period : 27 days; analytical monitoring | Birge *et al.*, 1979 |
| ***Oncorhynchus mykiss*** | | LOEC (24 h ) = 20 mg/L<br>(increasing of the respiration frequency) | 3 | No analytical monitoring, Uncommon endpoint<br>Flow-through closed dynamic system | Slooff, 1979 |

| Species | Method | Endpoint (duration)<br>(95 % confidence limit) | Reliability index | Remarks | Reference |
|---|---|---|---|---|---|
| ***Poecilia sphenops*** | | NOEC (60 d) < 1.5 mg/L (mortality, distress, inhibition of growth and fatty change of the liver) | 3 | Semi-static system (complete renewal every 2 weeks)<br>No analytical monitoring<br>2 concentrations, no replicate, only 6 fish per concentration | Loekle *et al.*, 1983 |
| ***Oryzias latipes*** | | LOEC (6/9 months) = 1.464 mg/L<br>NOEC (6/9 months) = 0.151 mg/L<br>NOEC (6/9 months) > 1.463 mg/L | 1 | Flow-through exposure system with weekly analyses<br>Lesions in gallbladder and abnormalities of the bile ducts<br>Length, growth | Toussaint *et al.*, 2001 |
| ***Brachydanio rerio*** | | LOEC (14 d) =13 mg/L,<br>NOEC (14 d) = 6.1 mg/L (position of the fish in the aquaria) | 3 | Flow-through system (6 renewals per day) with analytical monitoring | Röderer, 1990 |
| ***Rana temporaria**** | | LC 50 (5 d) = 16.95 mg/L (11.05 – 28.91 mg/L) | 3 | Flow through; exposure period: 5 days; analytical monitoring | Black *et al.*, 1982 |
| ***Ambystoma gracile**** | | LC 50 (5 d) = 21.58 mg/L (13.25 – 41.77 mg/L) | 3 | Flow through; exposure period: 5 days; analytical monitoring | Black *et al.*, 1982 |
| ***Xenopus laevis**** | | LC 50 (5 d) > 68 mg/L | 3 | Flow through; exposure period: 5 days; analytical monitoring | Black *et al.*, 1982 |
| ***Hyla crucifer**** | | LC 50 (7 d) = 0.27 mg/L (0.19 – 0.37 mg/L)<br>LC 10 (7 d) = 17.7 µg/L (9.9 – 28.1 µg/L<br>LC 1 (7 d) = 1.9 µg/L (0.8 - 3.9 µg/L) | 3 | Flow through; exposure period: 7 days; analytical monitoring | Birge *et al.*, 1980 |
| ***Bufo fowleri**** | | LC 50 (7 d) = 35.14 mg/L (18.37 – 92.25 mg/L) | 3 | Flow through; exposure period: 7 days; *analytical monitoring* | Birge *et al.*, 1980 |
| ***Rana pipiens**** | | LC50 (9 d) =4.16mg/L (1.96 – 7.06 mg/L)<br>LC 10 (9 d) = 383.4 µg/L (60.1 - 985 µg/L)<br>LC 1 (9 d) = 54.9 µg/L (3.1 – 225 µg/L) | 3 | Flow through; exposure period: 9 days; analytical monitoring | Birge *et al.*, 1980 |
| ***Rana palustris**** | | LC 50 (8 d) = 20.55 mg/L (11.53 - 43.83 mg/L) | 3 | Flow through; exposure period: 8 days; *analytical monitoring* | Birge *et al.*, 1980 |

* *amphibians*

Slooff, 1979 studied chronic toxicity of 13 compounds. He used rainbow trouts to detect the concentration at which a respiration frequency of at least three fourth of the test fish exceed the predetermined individual critical values. The uncommon endpoint, the lack of precision of the experimental conditions and of the results, prevent us from considering the chronic results as valid.

Chronic effects have been determined in a early life stage test with fish and amphibians for chloroform (Birge *et al.*, 1979; Black *et al.*, 1982; Birge *et al.*, 1980). Volatility was effectively prevented in a dynamic closed through system. The test water was monitored daily for chloroform.

NOEC values for the fish and amphibian species could not be determined for the following reasons:

- The only chronic result of the study is a LC 1, which is not usable in the risk assessment. The results are very low because the toxic effect curve is plane. As survival data are control-adjusted it is not possible to use the data to calculate any EC 10 or NOEC.
- Control survival is only 72 %
- Confidence limit cannot be determined because of the big ratio between test concentrations (3.3 to 17).
- No replicate has been performed in the study

In the study by Loekle *et al.*, 1983, adult black mollies, *Poecilia sphenops* were exposed for a 60-day test period to water contaminated with chloroform. 100% of fish exposed to 7.4 mg/L and 67% of fish exposed to 1.5 mg/L of chloroform either died or were distressed (inability to swim, to feed or react to a stimulus). In addition a decline in weight could be measured at both concentrations. Finally, chloroform induced a striking change in liver morphology (increase of fat accumulation). Because the test was “semi-static” with a complete renewal of water every two weeks, concentrations of chloroform could not be maintained throughout the experiment. In addition, no replicate was performed and there were only 6 fish per concentration. Therefore, the result could not be used in the derivation of a PNEC.

In the study from Röderer, 1990, the most sensitive endpoint used for the derivation of the NOEC was the position of the fish in the aquaria. It cannot be used in the risk assessment. No other chronic endpoint is available in this study.

The only chronic valid study has been published by Toussaint *et al.*, 2001. 14-day-old fry Japanese Medaka fish were continuously exposed to chloroform in a flow-through system for 6 and 9 months. Mean measured test concentrations were 0.017 ± 0.004 mg/L, 0.151 ± 0.034 mg/L and 1.463 ± 0.242 mg/L. Endpoints were growth, survival, hepatocarcinogenicity, hepatocellular proliferation, histopathology and intrahepatic chloroform concentration.

After 6 months exposure, there was a suggestion of growth and length reductions, but these results were statistically not significant. At 9 months, no reduction in growth was found for length or weight. Chloroform did not either appear to bioconcentrate in fish livers.

Chronic toxicity effects could be found on histopathology of gallbladder (lesions) and bile ducts (abnormalities) after 6 and 9 months exposure at 1.463 mg/L (Toussaint *et al.*, 2001). There were significant differences between males and females in their response to chloroform, the later being more significantly affected: after 6 months exposure at the highest concentration (1.463 mg/L), a significative effect was found only on one endpoint in the males (proliferation or hyperplasia of bile ducts of the liver). In contrast, at the same concentration, female exhibited nine significant findings in the bile ducts of the liver and the gallbladder (bile duct hyperplasia, bile duct epithelium hyperplasia, dilatation of the bile ducts, concretions in the lumen, inflamations around bile ducts, concretions in the lumen of the gallbladder, gallbladder and cystic duct hyperplasia and cystic duct dilatation). After 9 months exposure males exhibited higher incidence of dilatation of the cystic duct of the gallbladder and a tendency toward a significantly higher incidence of epithelium hyperplasia of the gallbladder. At 1.463 mg/L, females responded with a higher incidence for 3 of the 9 endpoints already significantly affected after 6 months plus a significative effect on the inflammation of the wall of the gallbladder (granulomatous inflammation). At the lower concentration of 0.151 mg/L, these hepathological findings were not found to occur at such a higher incidence (only bile duct dilatation was found at a higher incidence after 9 months exposure).

Pathology findings were dissimilar between this study and other studies with mammalians. As an example, biliary concretions that are observed on mammalians are usually caused by infection while in the case of fish, the reason for the occurrence of concretions in the gallbladder and the bile ducts is unknown. These dissimilarities could be attributed to the different routes of exposure, different exposed concentrations and obviously to the choice of the animal model.

In conclusion, despite there was no effect on growth, this study is demonstrating that a chloroform concentration of 1.463 mg/L is causing significant effects on histopathology of gallbladder (lesions) and bile ducts (abnormalities). Although these findings should be considered ecotoxicologically significant, this effect concentration will be considered as a NOEC because of the very specific effects that were observed at this concentration and the uncertainty about effects at the population level (it is not proved that there might be effects on population level with longer exposure periods).

Finally, the NOEC = 1.463 mg/L will be considered in this risk assessment to take into account the abnormalities and all other effects that were observed on the fish.

Therefore, the only valid chronic result on fish is : **NOEC = 1.463 mg/L.**

#### 3.2.1.2 Acute and prolonged toxicity to invertebrates

Several studies have been realised determining acute effects on invertebrates.
**For acute effects:**

**Table 3-41 : Acute toxicity results towards invertebrates**

| Species | Method | Endpoint (duration) | Reliability index | Remarks | Reference |
|---|---|---|---|---|---|
| ***Panaeus duorarum*** | | LC 50 (96 h) = 81.5 mg/L | 4 | Insufficient documentation on test method | US-EPA, 1980 |
| ***Daphnia magna*** | Static three-brood test, Cowgill & Milazzo, 1989 | LC 50 (48 h) = 353 mg/L | 3 | No analytical monitoring.<br>Volatility is not sufficiently taken into account<br>Organisms are fed during the test | Cowgill and Milazzo, 1991 |
| ***Ceriodaphnia dubia*** | Static three-brood test, Cowgill & Milazzo, 1989 | LC 50 (48 h) = 290 mg/L | 3 | No analytical monitoring.<br>Volatility is not sufficiently taken into account<br>Organisms are fed during the test | Cowgill and Milazzo, 1991 |
| ***Daphnia magna*** | ASTM subcommitte on safety to aquatic organisms | LC 50 (48 h) = 65.7 mg/L (geometric mean of 3 results) | 3 | No analytical monitoring<br>Volatility is not sufficiently taken into account | Gersich *et al.*, 1986 |

| **Species** | **Method** | **Endpoint (duration)** | **Reliability index** | **Remarks** | **Reference** |
|---|---|---|---|---|---|
| ***Daphnia magna*** | DIN 38412 | LC 0 (24 h) = 62 mg/L<br>LC 50 (24 h) = 290 mg/L<br>LC 100 (24h) = 500 mg/L | 3 | No analytical monitoring.<br>Test system is not appropriate to volatile substances | Knie *et al.*, 1983 |
| ***Crassostrea virginica*** | | LC 50 (48 h) = 0.385 mg/L (estimated from a graph) | 3 | Analytical monitoring at a median concentration: 100µg/L The result is based on a calculated time-weighted mean concentration that is taking into account the loss of chloroform) | Stewart *et al.*, 1979 |
| ***Crassostrea gigas*** | | EC 50 (48 h) = 152.5 mg/L<br>NOEC (48 h) = 50.4 mg/L | 1 | Analytical monitoring at every tested concentration (48h losses were below 12%). Larvae with incompletely developed shells were counted dead | WRc-NSF, 2002 |
| ***Daphnia magna*** | US-EPA-660/3, 1975 | LC 50 (48 h) = 29 mg/L | 2 | No analytical monitoring<br>Closed vessels | LeBlanc, 1980 |
| ***Daphnia magna*** | Bobra et al., 1983 | LC 50 (48 h) = 79 mg/L | 2 | No analytical monitoring<br>Static closed test,<br>No air-spaces in exposure chambers to minimize volatilisation daphnids 4-5 days old | Abernethy *et al.*, 1986 |
| ***Daphnia magna*** | DIN 38412 | LC 50 (24 h) = 79 mg/L<br>LC 0 (48 h) = 48 mg/L | 2 | Nominal concentration<br>Static closed test | Kühn *et al.*, 1989 |
| ***Artemia salina*** | | EC 50 (24 h) = 31.1 mg/L (25% ASW)<br>EC 50 (24 h) = 37 mg/L (25% ASW) (immobilisation of stage II nauplii) | 2 | No monitoring but the volatility is sufficiently taken into consideration<br>ASW = Artificial Sea Water | Foster and Tullis, 1985 |

There was no analytical monitoring in any test performed with daphnia. The tests in which volatility has not been taken sufficiently into account have not been considered as valid (reliability ≥ 3). Among the other tests with a reliability of 2, the results on the *Daphnia magna* tests are homogeneous with a 48 h-LC 50 between 29 and 90 mg/L.

These results are supported by the quantitative structure-activity relationships (QSARs) that were calculated by Hermens *et al.* Relationships between toxicity and hydrophobicity (Kow) were calculated with a computer program for 19 chemicals with anaesthetic (Hermens *et al.*, 1984). The equation was then applied to derive the toxicity of 31 other substances including chloroform for daphnia. : 79 mg/L < LC 50-48h < 105 mg/L.

*Artemia salina* cysts proved to be of a similar range of sensitivity as daphnia (24 h-EC 50 from 31 to 37 mg/L depending of the salinity of the artificial medium).

A test with an analytical monitoring has been performed on larvae of the oyster *Crassostrea virginica* : 15,000 freshly spawned and fertilised oyster eggs were exposed to chloroform in 1.1 l beakers (Stewart *et al.*, 1979). In the 100 µg/L test system, the initial concentration fell to 14 µg/L at the end of the test. The test has been performed 5 times and the 48 h-LC 50 could be estimated about 1 mg/L from a graph. This estimated result is based on initial concentration. Suggesting that the loss of chloroform is the same at 100 and 1000 µg/L and using the measured concentration after 5 and 48 hours in the 100 µg/L solution, a time-weighted mean concentration of 385 µg/L is calculated. This value is 100 fold lower than the lowest valid result on Daphnia (29 mg/L). However, this article is short: testing methods and endpoints were not that much described. In addition, the study is not specific to chloroform: several disinfection byproducts were assessed.

Because of these uncertainties in methodology and because the lowest result was based on a graphical extrapolation and an assumption about the loss of substance during the course of exposure, another study with a better maintenance of the exposure level was conducted in 2002.

The test was conducted with oyster embryos according to ASTM Method E724-94 (WRc-NSF, 2002). Fertilised ova were exposed during 48 hours to chloroform nominal concentrations ranging from 2.8 to 278 mg/L. During this period, the embryos were supposed to develop to D-shaped larvae. Under a subsequent microscopic examination, larvae with incompletely developed shells were counted as dead because a retarded development would likely reduce survival. Concentrations were measured at the beginning and at the end of the test. Losses of chloroform during the preparation of the test vessels were <30% and losses of chloroform during the 48h test was <12%. With the results, a clear dose-response relationship could be established and some endpoints calculated based on measured concentrations :
48 h-EC50 = 152.5 mg/L, LOEC = 80.4 mg/L, NOEC = 50.4 mg/L.

A test was simultaneously performed with a reference substance, zinc.
The result, 24 h-EC50 = 0.4 mg Zn.L$^{-1}$ was consistent with the historical control chart of the laboratory. The proportion of abnormal embryos in the control vessels was < 30%. Therefore, the test could be considered as valid.
The difference in the results from the test by Stewart *et al* with the new test by WRc could be explained by several factors :

1) In the study by Stewart *et al.*, 1979, assumption had to be made to derive concentrations taking into account a decrease of the substance during the test. Losses of the substances might have been overestimated. In addition, chemical analyses of chloroform might have been improved since the test by Stewart,

2) In the oyster tests, microscopy examination needs trained persons. Even with trained persons, interpretation of the endpoints might be slightly different from one to the other laboratory : some are considering the larvae as abnormal only if they could not observe the D-form whereas other are taking into account any abnormal aspect with an accurate observation. Such differences in endpoints might partly explain the gap between both results. In Stewart *et al.*, 1979 study, the effects were based on whether the D-shaped were alive or dead. No information is given in the paper as to how this was carried but it is assumed it is based on whether the organisms were motile in the unfixed sample. Since chloroform has narcotic properties, larvae in the Stewart *et al.* paper could have been considered to be dead when in fact they were immobile because they were narcotised. In the study conducted by WRc-NSF, 2002, the assessment of the proportion of larvae in a sample which have developed to the D-shaped is made after the organisms are fixed with formaldehyde. Therefore, endpoints of both studies are not directly comparable.

Considering all the technical shortcomings in the study by Stewart *et al.*, 1979, the results of this older test can not be used. Results from the test by WRc will be preferably considered. In this new test, test conditions are completely described, analytical measurements were performed at every concentration and the methodology was close to an international standardised method (ASTM). In addition the 48h-EC 50 seems to fit more closely to other acute toxicity results on invertebrates (LC 50-48h ranging from 29 to 79 mg/L for *Daphnia magna*).

**For chronic effects:**

**Table 3-42 : Chronic toxicity results towards invertebrates**

| Species | Method | Endpoint (duration) | Reliability | Remarks | Reference |
|---|---|---|---|---|---|
| ***Daphnia magna*** | Static three-brood test, Cowgill & Milazzo, 1989 | NOEC (10 d) = 120 mg/L (mortality, brood size and progeny) | 3 | No analytical monitoring. Volatility is not sufficiently taken into account. | Cowgill and Milazzo, 1991 |
| ***Cerio-daphnia dubia*** | Static three-brood test, Cowgill & Milazzo, 1989 | NOEC (9 d) = 3.4 mg/L (mortality) | 3 | No analytical monitoring.<br>Volatility is not sufficiently taken into account | Cowgill and Milazzo, 1991 |
| ***Daphnia magna*** | Hermens, 1984 | EC 50 (16 d) = 59.9 mg/L<br>NOEC (16 d) = 15 mg/L (growth) | 2 | endpoint : length (uncommon) analytical monitoring | Hermens *et al.*, 1985 |
| ***Daphnia magna*** | German Federal Environ-mental Agency, 1984 | NOEC (21 d) = 6.3 mg/L<br>(reproduction) | 1 | Analytical monitoring<br>NOEC refers to the parent animal mortality, the reproduction rate and the appearance of first offsprings. | Kühn *et al.*, 1989 |

The study from Cowgill and Milazzo, 1991 is not considered as the volatility of the substance is not sufficiently taken into account.

In their study on the toxicity of chemicals with anaesthetic potency, Hermens *et al.*, 1985 calculated the 16 d-EC 50 (reproduction endpoint) from the relationship they could established between the hydrophobicity and the toxicity of 5 compounds.

The result (3.6 mg/L <16d-EC50< 6.2 mg/L) is lower than the experimental result from the subsequent chronic study performed in 1985 : 16d-EC50 = 59.9 mg/L. However the experimental NOEC from the same study is higher than the 21 days reproduction NOEC from the study by Kühn *et al.*, 1989. Both volatility and loss of substance were considered in the study by Kühn *et al.*, 1989 by using closed test vessels and performing analytical monitoring.

Therefore a **NOEC for Daphnia = 6.3 mg/L** can be retained.

### 3.2.1.3 Toxicity to algae

Several tests with algae have been carried out:

**Table 3-43 : Toxicity results towards algae**

| Species | Method | Endpoint (duration) | Relia-bility | Remarks | Reference |
|---|---|---|---|---|---|
| ***Haematococcus pluvialis*** | Warburg apparatus, 1983 | EC 10 (4 h) = 440 mg/L (reduction of $O_2$ production) | 4 | Static test.<br>No analytical monitoring.<br>No indication on volatility consideration | Knie *et al.*, 1983 |
| ***Skeletonema costatum*** | EPA | NOEC (5 d) = 216 mg/L<br>EC 50 (5 d) = 437-477 mg/L | 3 | No analytical monitoring<br>Closed bottles<br>Low growth in the controls | Cowgill *et al.*, 1989 |
| ***Skeletonema costatum*** | Erickson et al., 1970-1972 | EC 50 (7 d) > 32 mg/L (biomass measured by turbidity) | 3 | No analytical monitoring Volatility is not sufficiently taken into account | Erickson and Freeman, 1977 |
| ***Thalassiosira pseudonana*** | Erickson et al., 1970-1972 | EC 50 (7 d) > 32 mg/L (biomass measured by turbidity) | 3 | No analytical monitoring Volatility is not sufficiently taken into account | Erickson and Freeman, 1977 |
| ***Scenedesmus quadricauda:*** | Concentration of algal suspension is measured turbidimetrically | NOEC (8 d) = 1100 mg/L | 2 | No analytical monitoring<br>Closed system<br>Determination of the Toxicity Threshold | Bringmann & Kühn, 1977-1980 |
| ***Microcystis aeruginosa*** | Concentration of algal suspension is measured turbidimetrically | NOEC (8 d) = 185 mg/L | 2 | No analytical monitoring<br>Closed system<br>Determination of the Toxicity Threshold | Bringmann & Kühn, 1975-1978 |
| ***Scenedesmus subspicatus*** | DIN 38412, Part 9 Concentrations of algal suspension is measured turbidimetrically | Biomass :<br>EC 50 (48 h) = 560 mg/L<br>EC 10 (48 h) = 225 mg/L<br>Growth rate :<br>EC 50 (48h) = 950 mg/L<br>EC 10 (48h) = 360 mg/L | 2 | No analytical monitoring<br>Closed system Validity criteria are fulfilled | Kühn and Pattard, 1990 |
| ***Chlamydomonas reinhardii*** | Modified protocol to provide sufficient $CO_2$ concentration. Guideline validity criteria are fulfilled | EC 50 (72h) = 13.3 mg/L<br>EC 10 (72h) = 3.61 mg/L (biomass) | 1 | Analytical monitoring, closed system using bipartite vessels | Brack and Rottler, 1994 |

The studies from Knie *et al.*, 1983, Cowgill *et al.*, 1989 and Erickson and Freeman, 1977 are not considered. The main reason put forward is that volatility is not sufficiently taken into account. Bringman & Kühn (1975-1978) performed a toxicity test with the green algae *Scenedesmus quadricauda* and the blue-green algae *Microcystis aeruginosa*. Test cultures were kept under standardised conditions for a period of 8 days. The algal concentrations are determined with turbidity measurements. The culture tubes are closed with cotton-lined metal caps but there was no analytical monitoring of the test concentrations.

Results based on nominal concentrations are therefore considered as indicative ranges of toxicity for algae. The same comments could apply to the study from Kühn and Pattard, 1990 on *Scenedesmus subspicatus*.

The only test on algae with analytical monitoring has been performed by Brack and Rottler, 1994. The test method has been adjusted to prevent the substances from volatilising : closed flasks in which $KHCO_3$ / $K_2CO_3$ buffer is supplying the algae with $CO_2$ are employed. Bipartite culture flasks are used to separate the buffer from the test medium. The effective concentrations are determined using GC / ECD analysis. Measurements showed no significant losses of chloroform during the assay. Only percent inhibitions (related to biomass) for each concentration are provided. Therefore, it is not possible to calculate growth rate effect concentrations. Algal growth rate inhibition is normally the preferred observational endpoint because it is not dependant on the test design, whereas biomass depends both on growth rate of the test species as well as test duration and other elements of the test design. Nonetheless, as the validity criteria are fulfilled, as this is the only test on algae with an analytical monitoring and as the result is finally the lowest value compared to the other results based on nominal concentrations in closed systems it will be considered for the PNEC derivation.

A **NOEC value = 3.61 mg/L** can be retained for the risk assessment.

### 3.2.1.4 Determination of PNECaqua

**Fish :**
**NOEC-6/9 months : 1.463 mg/L (*Oryzias latipes*, Toussaint *et al.*, 2001)**

**Invertebrate :**
**NOEC-21d : 6.3 mg/L (*Daphnia magna*, Kühn *et al.*, 1989)**

**Algae:**
**72h-EC 10 : 3.61 mg/L (*Chlamydomonas reinhardii*, Brack and Rottler, 1994*)***

There are three long-term NOECs from species representing three trophic levels.
Therefore, the PNEC is derived using an assessment factor of 10 to the lowest NOEC.

**PNECaqua = 1.463 / 10 = 146 µg/L**

## 3.2.2. Effects assessment for micro-organisms

### 3.2.2.1 Toxicity to micro-organisms

**Table 3-44 : Toxicity results from tests towards micro-organisms**

| Species | Method | Endpoint (duration) | Relia-bility | Remarks | Reference |
|---|---|---|---|---|---|
| ***Aeromonas hydrophila***<br>**(bacteria)** | | LOEC = 815 mg/L | 4 | Static test.<br>Insufficient documentation.<br>Acetone is used to solubilize the substances | Schubert, 1979 |
| ***Bacillus subtilis***<br>**(bacteria)** | | LOEC = 4077 mg/L | 4 | Static test.<br>Insufficient documentation.<br>Acetone is used to solubilize the substances | Schubert, 1979 |
| ***Pseudomonas capacia***<br>**(bacteria)** | | LOEC = 4077 mg/L | 4 | Static test.<br>Insufficient documentation.<br>Acetone is used to solubilize the substances | Schubert, 1979 |
| **Polytox culture of bacteria** | Polytox respiration inhibition test | EC50 (20 min) = 1550 mg/L<br>EC50 (30 min) = 1360 mg/L<br>(Inhibition of oxygen uptake rate) | 4 | The test is not assignable<br>Lack of precision on the procedure and the mixture of bacteria<br>Volatility not taken into account | Elnabarawy *et al.*, 1988 |
| ***Photobacterium phosphoreum***<br>**(bacteria)** | Microtox | EC 50 (5 min) = 520 mg/L<br>EC50 (15 min) = 670 mg/L<br>EC50 (30 min) = 670 mg/L (concentration needed to reduce light produc-tion by 50 %) | 4 | Measurement of the inhibition of light production<br>Uncommon endpoint<br>Volatility not taken into account | Elnabarawy *et al.*, 1988 |
| ***Bacillus cereus***<br>**(bacteria)** | Liu et al., 1983-1986 | EC 3 (20 min) = 500 mg/L (Inhibition of bacterial growth) | 4 | Inhibition of dehydrogenase activity is measured with a dyes (resazurin)<br>Use of methanol<br>Irrelevant endpoint | Brouwer, 1991 |
| ***Glenodinium halli*** **(marine dinoflagellate)** | Erickson et al., 1970-1972 | EC50 > 32 mg/L<br>EC20 > 32 mg/L<br>(Inhibition of growth) | 3 | Closed vessel<br>Insufficient information<br>Results are not usable | Erickson and Freeman, 1977 |
| ***Isochrysis galbana*** **(marine microflagellate)** | Erickson et al., 1970-1972 | EC 50 (7 d) > 32 mg/L<br>EC 20 (7 d) > 32 mg/L<br>(Inhibition of growth) | 3 | Closed vessel<br>Insufficient information<br>Results are not usable | Erickson and Freeman, 1977 |

| Species | Method | Endpoint (duration) | Relia-bility | Remarks | Reference |
|---|---|---|---|---|---|
| **Activated sludge** | OECD guideline 209 | EC 50 (3 h) = 1,010 mg/L<br>EC50 (30 min) = 840 mg/L<br>(Inhibition of respiration rate) | 3 | Test system : unaclimated sample of activated sludge<br>Volatility is not sufficiently taken into account | Elnabarawy *et al.*, 1988 |
| **Anaerobic sludge** | ISO/DIS 13641-1 | NOEC (72 h)= 2.5 µg/L<br>EC 50 (72 h) = 76.6 µg/L<br>(Inhibition of respiration) | 3 | Measurement of the pressure in the incubation vessels to study the inhibition of gas production<br>Loss of test item in three tested concentrations | Dr. U. Noack laboratorium, 2004a |
| **Activated sludge** | DIN EN ISO 9509 | NOEC (4 h) = 5 µg/L<br>EC 50 (4 h) = 66 µg/L<br>(Inhibition of the nitrification) | 3 | Oxidized nitrogen and ammonia was measured by photometric determination<br>Closed system<br>Loss of test item in two tested concentrations | Dr. U. Noack laboratorium, 2004b |
| ***Pseudomonas putida***<br>**(bacteria)** | Bringmann, 1980 | NOEC (16 h) = 125 mg/L (Inhibition of bacteria multiplication) | 2 | No analytical monitoring<br>Closed system<br>Bacteria suspension are measured turbidimetrically | Bringmann and Kühn, 1976<br>Bringmann and Kühn, 1980 |
| ***Entosiphon sulcatum***<br>**(protozoa)** | Bringmann, 1980 | NOEC (72h) ≥ 6,560 mg/L<br>(Inhibition of cell multiplication) | 2 | No analytical monitoring<br>Closed system<br>Number of protozoa are determined with a cell counter | Bringmann and Kühn, 1980 |
| ***Chilomonas paramecium***<br>**(protozoa)** | Static cell multiplication | NOEC (48h) ≥ 3,200 mg/L<br>(Inhibition of cell multiplication) | 2 | No analytical monitoring<br>Determination of the biomass by cell counter Closed system | Bringmann and Kühn, 1980 |
| **activated sludge** | Non standard method (extended time period - 15 h) | EC 50 (15 h) = 640 mg/L (inhibition of oxygen uptake) | 2 | Sealed glass bottles.<br>The equilibrium concentration is calculated using the Henry's law constant to take into account volatilization. | Blum and Speece, 1991 |
| ***Nitrosomonas sp.***<br>**(bacteria)** | Blum & Speece, 1991 | EC 50 (24 h) = 0.48 mg/L (inhibition of ammonia consumption) | 2 | Sealed glass bottles.<br>The equilibrium concentration is calculated using the Henry's law constant to take into account volatilization | Blum and Speece, 1991 |
| **Methanogenic bacteria** | Owen et al., 1979 | EC 50 (48 h) = 0.9 mg/L (inhibition of gas production) | 2 | Sealed glass bottles.<br>The equilibrium concentration is calculated using the Henry's law constant to take into account volatilisation | Blum and Speece, 1991 |

Studies from Schubert, 1979, Elnabarawy *et al.*, 1988, Brouwer, 1991 and Erickson and Freeman, 1977 could not be considered because of irrelevant endpoints, unusable results and ignorance of volatility and use of saltwater species.

Two testings on micro-organisms have been made available recently after their request under a conclusion (i) program. Inhibition of nitrification by chloroform and its toxicity to anaerobic bacteria was investigated by Dr.U.Noack-laboratorium in 2004. Throughout these tests, severe losses of chloroform were observed. At the termination of both studies, no chloroform could be detected in many test vessels, actual concentrations being below the limit of quantification (LOQ = 0.002 mg/L). For those where chloroform could be detected, recovery rates were rather low (2 % and 30 % for the test on inhibition of methanogenic bacteria; 12 % 47 % and 75 % for the inhibition nitrification test). It is unknown whether chloroform leaked out of the system, was degraded, or if the analytical methods failed for some reason. Consequently, the exposure of sludge micro-organisms to chloroform cannot have been insured during these tests. During the tests, the headspace volume in test vessels was widely higher than the recommended one in OECD guidelines (80 % versus [10 % – 40 %]) and the test substance was tested after its expiry date. All these reasons lead to the invalidation of both tests that will not be used for the PNEC derivation.

In their studies, Bringman & Kühn (1976-1980) applied the cell multiplication test to the bacteria *Pseudomonas putida* and the protozoa *Entosiphon sulcatum*. The results are valid but the NOEC values are higher than the EC 50 determined in the well-documented study from Blum and Speece, 1991.

The lower EC 50 was found with Nitrosomonas bacteria, which convert ammonia nitrogen to nitrite as the first step of oxidation. The result to be considered for the toxicity to micro-organisms is therefore : **EC 50 = 0.48 mg.L$^{-1}$.** This value for aerobic bacteria is in accordance with the results from the study by van Vlaardingen and van Beelen, 1992 on inhibition of methanogenic activity with chloroform : EC 50-11 d = 6,9 mg/kg with a 3.2 % organic carbon sediment sampled in the estuary of the river Rhine (see 3.2.3.1).

#### 3.2.2.2 Determination of PNEC$_{\text{micro-organisms}}$

An assessment factor of 10 being applied to such results, the PNECmicro-organisms is therefore :

$$PNEC_{micro-organisms} = \frac{0.48\ mg/L}{10} = 48\ \mu g/L$$

## 3.2.3. Effects assessment for the sediment

### 3.2.3.1 Toxicity to sediment

**Table 3-45 : Toxicity results to sediment dwelling organisms**

| Species | Method | Endpoint (duration) | Relia-bility | Remarks | Reference |
|---|---|---|---|---|---|
| Methanogenic bacteria (sediment from the estuary of the river Rhine) | | EC 10 (11 d) = 5.5 mg/kg (dw)<br>EC 50 (11 d) = 6.9 mg/kg (dw)<br>(Inhibition of methane production) | 2 | Theoretical toxicant concentration<br>Sterile incubation closed bottles. No indication of the number of concentration and the final volume of methanol. | van Vlaardingen and van Beelen, 1992 |
| *Chironomus riparius* (Midge) | OECD<br>Guideline 218 | EC 50 (28 d) = 20.1 mg/kg (dw)<br>(Emergence)<br>NOEC (28 d) = 4.5 mg/kg (dw)<br>(Males development rate)<br>NOEC (28 d) = 10 mg/kg (dw)<br>(Emergence, development rate for females, and males + females pooled) | 1 | Five toxicant concentrations analytically monitored.<br>Flow-through system.<br>Sealed glass jars with minimal headspace.<br>NOEC refers to the emergence of midges, the development rate of males, females, females + males pooled. | Woodburn *et al.*, 2006a |
| *Lumbriculus variegatus* (Oligochaete) | Proposed OECD guideline (OECD, 2005)<br>(US-EPA, 2000) | NOEC (28d) = 19.2 mg/kg (dw)<br>(Survival/reproduction, growth) | 1 | Five toxicant concentrations analytically monitored.<br>Flow-through system.<br>Sealed glass jars with minimal headspace.<br>NOEC refers to the survival/reproduction and the growth (total dry biomass) of worms. | Woodburn *et al.*, 2006b |

van Vlaardingen and van Beelen, 1992 studied the toxicity of chloroform to the methanogenesis. Chloroform solution as a dilution in methanol was added to a sediment / water suspension. The sediment was primarily composed of methanogenic mud. Test bottles were incubated for 11 days at 20°C in a rotary shaker. Methane production in the contaminated bottles was measured at the end of the experiment and compared to the methane production of the blank bottles. Then EC 10 and EC 50 could be calculated. Although some details on experimental conditions are lacking, the EC 10 can be used as a long-term toxicity test result as methanogenesis is an important route of degradation of organic matter.

Two long-term testings on sediment organisms (*Chironomus riparius* and *Lumbriculus variegatus*) have been made available recently after their request under a conclusion (i) program. Woodburn *et al.*, 2006b and Woodburn *et al.*, 2006a performed these two 28-days toxicity tests using sealed glass jars and spiked sediment in a flow-through test system in order to maintain consistent sediment concentrations. Preliminary work indicated that this system would permit maintenance of relatively stable chloroform sediment concentrations and required dissolved oxygen levels in overlying water (OW).

For the study with the midge, *Chironomus riparius* Woodburn *et al.*, 2006a accurately followed the OECD guideline 218 with some particular precautions to avoid chloroform volatilisation during the test period (sealed glass jars, headspace set to minimum to ensure adults emergence…) and ensure required dissolved oxygen levels in OW (gentle aeration**)**.

The flow of pre-treated renewal water was initiated at the beginning of the seven days equilibration period, prior to organism addition. Twenty, two-to-three-day-old midge larvae (first-instar larvae) were introduced into each vessel and there were four replicates per control and treatment level. Each vessel was administered a suspension of ground fish food daily, at an elevated rate due to the unique flow-through conditions.

Water was monitored periodically for pH (7.4 ± 0.1), temperature (20.0 ± 0.4 °C), hardness (58 – 66 mg/L $CaCO_3$), dissolved oxygen (7.2 ± 0.3 mg/L), alkalinity, conductivity and total ammonia nitrogen.

Sediment samples in vessels were dosed at target concentrations of 0 (water control), 1.4, 2.8, 5.5, 11.0, and 22.0 mg/kg-dw sediment. Chloroform concentrations in sediment and OW were weekly measured in sacrificial replicates and renewal water was analysed daily to ensure that appropriate OW concentrations were maintained over the course of the study. Concentrations in the OW exhibited percent relative standard deviations (%RSD) of 7.0 to 24.2% over the 28-day exposure period and did not demonstrate any decline during the study. Sediment concentrations demonstrated good reproducibility over the 28-day exposure period (%RSD varied from 8.3% to 11.3%), with the exception of the lowest nominal dose level of 1.4 mg/kg-dw (%RSD of 66%).

Daily observations of organism activity and emergence of adult male and female midges were counted and collected. The endpoints of interest in this study were the proportion of larvae emerged (emergence ratio) and the development rate analysed separately by gender and pooled males and females. Results were evaluated using appropriate statistical procedures and are presented as time-weighted average concentrations of chloroform in sediment. The emergence ratio EC 50 value is 20.1 mg/kg-dw and the NOEC and LOEC values are 10.0 and 20.4 mg/kg-dw, respectively. The development rate NOEC and LOEC values for both the female midges and pooled male/female midges are 10.0 and 20.4 mg/kg-dw, respectively, while the NOEC and LOEC values for the male midges are 4.5 and 10.0 mg/kg-dw, respectively.

As this study is in accordance with the OECD guideline 218 requirements, the results are considered valid and will be used for the derivation of the PNECsed.

As no standard (finalized) guideline is currently available for ecotoxicity test with the oligochaete, *Lumbriculus variegatus*, the design of the study performed by Woodburn et al., 2006b was based on a proposed guideline (OECD, 2005).

An equilibration period was initiated nine days before addition of the worms. Ten artificially synchronized worms were added to each of four replicates per dose level. This uniform physiological state allows for natural fragmentation and morphallaxis (regeneration) to occur at the same rate across the population of organisms evaluated. The *Urtica* and peat moss present in the formulated sediment served as the food sources during this study, and no additional food was added during the test.

Water was monitored periodically for pH (7.6 ± 0.1), temperature (20.4 ± 0.2 °C), hardness (60 – 103 mg/L $CaCO_3$), dissolved oxygen (8.1 ± 0.3 mg/L), alkalinity, conductivity and total ammonia nitrogen.

Sediment samples in vessels were dosed at target concentrations of 0 (water control), 2.75, 5.5, 11.0, 22.0 and 44.0 mg/kg-dw sediment. Over the 28-day exposure period, a good

reproducibility in sediment concentrations (%RSDs from 10.3 to 17.3%) and OW concentrations (%RSD from 1.1 to 10.9%) could be observed.
The test vessels were observed approximately three times per week in order to assess any behavioural differences in the worms compared with the controls. The endpoints of interest in this study were the total number of live worms and worm biomass. Results were analysed using appropriate statistical procedures and are presented as time-weighted average concentrations of chloroform in sediment. The resulting survival, reproduction, and biomass endpoints calculated from these data produced NOEC and LOEC values of 19.2 and 36.9 mg/kg-dw, respectively.

As the study meets the validation requirements set out in the proposed OECD Guideline (OECD, 2005), the results will therefore be considered valid and will be used for the derivation of the PNECsed.

### 3.2.3.2 Determination of PNECsed

There are two methods of determination of PNECsed :

**1) Determination of the PNECsed using the sediment toxicity test**
As three long-term ecotoxicity tests with benthic species representing different living and feeding conditions are available, an assessment factor of 10 should be applied to the lowest NOEC, which is the one from the test on the midge *Chironomus riparius*:

PNECsed (1) = 4.5 mg/kg / 10 = 450 µg/kg (dw)

**2) Determination of the PNECsed using the Equilibrium partitioning method**

According to the TGD, $PNECsed(ww) = \frac{Ksusp - water}{RHOsusp} \cdot PNECaquatic * 1000$

Ksusp_water = suspended matter_water partition coefficient = 5.53 $m^3.m^{-3}$ (Table 3-15)

Therefore: PNECsed = 702 $\mu g.kg^{-1}$ (ww)
PNECsed = 3230 $\mu g.kg^{-1}$ (dw)

The result with the Equilibrium partitioning method is much higher than the result based on the toxicity to *Chironomus riparius*. The value based on experimental results will be preferred:

**PNECsed = 450 µg/kg (dw) and PNECsed = 97.8 µg/kg (ww)**

## 3.2.4. Atmosphere

### 3.2.4.1 Effects on plants

**Table 3-46 : Toxicity result to terrestrial organism through atmospheric exposure**

| Species | Method | Endpoint | Relia-bility | Remarks | Reference |
|---|---|---|---|---|---|
| *Lycopersicum esculentum*<br>*Helianthus annuus*<br>*Phaseolus vulgaris*<br>*Tropaeolum majus*<br>*Beta vulgaris*<br>*Glycine maxima*<br>*Triticium aestivum* | | Visible symptoms (on foliage) and effects on photosynthesis at 100 g/m$^3$ after 3 hours exposure | 2 | Effects on photosynthesis were measured by comparison of $CO_2$ content in inflowing and outflowing air. | Christ, 1996 |

The lowest test concentration at which effects were observed for visible symptoms and photosynthesis was 100 g/m$^3$. The test was however very short (3 hours) and this result could even not be used to assess an acute toxicity and derive a PNECair.

### 3.2.4.2 Abiotic effects

Global Warning Potential (GWP)

The impact of a substance on global warning depends on its IR absorption characteristics and its atmospheric lifetime. Using a lifetime of 1.7 years and an infrared absorption strength of 2,389/cm²/atm, the GWP is calculated to be 0.0326 for chloroform (Environment Canada and Health Canada, 2000). In comparison with the reference compound CFC-11, which has a GWP of 1, the global warning potential of chloroform is low and the substance is not classed as a greenhouse gas under the Kyoto protocol.

Stratospheric Ozone Depletion Potential (ODP)

With an atmospheric lifetime above one year (1.7 years), chloroform may have an effect on stratospheric ozone depletion.

Estimating the risks posed by chloroform to the stratospheric ozone layer requires realistic estimates of tropospheric half-lives, as well as information on the transport of chloroform and its breakdown products to and from the stratosphere. Assuming an atmospheric half-life of 193 days (which represents a worst case in comparison with the atmospheric half-life of 105 days (see section 3.1.1.5.1.3)), 1.7% of the chloroform in the trosposphere is expected to migrate to the stratosphere where its half-life would be 3.18 years (Environment Canada and Health Canada, 2000). In addition, with the estimation that 1 – 1.8% of the chlorine in chloroform molecules released at the earth's surface is transported into the stratosphere as reactive chlorine, a stratospheric Ozone Depletion Potential of 0.0083 is calculated for chloroform. In comparison with an ODP of 1 for the reference compound, CFC-11, chloroform is not expected to be an effective agent of stratospheric ozone depletion.

Photochemical Ozone Creation Potential (POCP)

Assuming a rate constant for the reaction of chloroform with OH radicals of $2.95 \times 10^{-13}$ $cm^3$/molecule.s, which is slightly higher than the rate considered in section 3.1.1.5.1.3), the POCP is estimated to be $8.14 \times 10^{-13}$. This result could be considered as negligible in comparison with the POCP of 100 calculated for the reference substance (Environment Canada and Health Canada, 2000).

Acidification

No information on the acidification of receiving soils or surface water due to chloroform releases to air could be found in the literature. However, chloroform degradation in the atmosphere is not expected to form the main acidifying components responsible for acidification.

In conclusion, the potential contribution of chloroform to climate change, stratospheric ozone depletion, ground-level ozone formation and acidification processes could be considered as negligible.

### 3.2.5. Terrestrial compartment

**Table 3-47 : Toxicity results to soil dwelling organisms**

| Species | Method | Endpoint (duration) | Reliability | Remarks | Reference |
|---|---|---|---|---|---|
| *Eisenia fetida* | | LC 50 (48 h) = 111 µg/cm² | 2 | Contact test method with filter paper | Neuhauser *et al.*, 1985 |

The only toxicity test on terrestrial organisms with chloroform is a contact filter paper test with the earthworm *Eisenia fetida* (Neuhauser *et al.*, 1985). In the definitive test, 5 concentrations were tested and 10 worms were individually exposed to chloroform impregnated filter papers (12 by 6.7 cm). The filter paper lined and completely covered the sides of the vial where the worm was introduced. The contact test was prepared as rapidly as possible to avoid volatilization from the vials. The authors classified chloroform as moderately toxic in comparison with the other results on organic chemicals (0.6 < LC50-48h < 5.9 µg/cm² for phenols). This result is however not used for the PNECsoil derivation as the test used filter paper and assessed only toxicity by contact.

A $PNEC_{soil}$ can be derived with the equilibrium partitioning method, using the PNECaqua as proposed by the TGD. However, additional information is available for other aquatic compartments showing that micro-organisms (for STP) and insects (for sediment) are more sensitive to chloroform. Micro-organisms are particularly sensitive to chloroform exposure and represent a relevant taxa for the soil compartment. Therefore, the $PNEC_{micro\text{-}organisms}$ will be used instead of the $PNEC_{aqua}$. As the $PNEC_{micro\text{-}organisms}$ is based on very short term tests relevant for the WWTP assessment but not for the soil compartment, an additional factor of 10 will be used to take into account the acute to chronic toxicity extrapolation. A higher assessment factor is not suitable here since a sensitive taxon has been identified.

$$PNECsoil(ww) = \frac{Ksoil-water}{RHOsoil} \cdot \frac{PNECmicro-organisms \cdot 1000}{10}$$

Ksoil_water = soil _water partition coefficient = 5.77 $m^3.m^{-3}$ (Table 3-15)

Therefore: **PNECsoil = 16.3 µg.kg$^{-1}$ (ww)**

**PNEC soil = 18.4 µg.kg$^{-1}$ (dw)**

### 3.2.6. Non compartment specific effects relevant to the food chain

Because of the low bioaccumulation potential of chloroform (BCF = 13), the potential for secondary poisoning can be considered to be negligible.

## 3.3. RISK CHARACTERISATION

### 3.3.1. Aquatic compartment

#### 3.3.1.1 Water

The PNEC $_{aquatic}$ has been estimated to be 146 µg/L (see section 3.2.1.4).
Using the $PEC_{regional\ aquatic}$ of 0.828 µg/L, (see section 3.1.2.2) a $PEC_{local\ aquatic}$ could be calculated: $PEClocal_{aquatic} = Clocal_{water} + PECregional_{water}$

The resulting PEC/PNEC ratios for the various scenarios considered in this assessment are presented below.

**Table 3-48 : Estimated PEC/PNEC ratios for surface water**

| Scenario | Step | PEC (µg/L) | PEC/PNEC |
|---|---|---|---|
| Production | Site A | 0.96 | 0.007 |
| | Site B | 1.52 | 0.010 |
| | Site C | 1.27 | 0.009 |
| | Site D | 0.89 | 0.006 |
| | Site E | 1.99 | 0.014 |
| | Site F[1] | 5.74 | 0.039 |
| | Site G | 0.88 | 0.006 |
| | Site H | 2.18 | 0.015 |
| | Site I | 0.85 | 0.006 |
| | Site J | 2.39 | 0.017 |
| Uses | HCFC Production | 3.4 | 0.023 |
| | Dyes and Pesticide Production | 13.4 | 0.092 |
| | Other applications | 12.8 | 0.088 |
| | **Uses as a solvent** | **2001.9** | **13.71** |
| Unintended releases | Losses as a by-product during chemical manufacturing | 7.48 | 0.051 |
| Regional scale | | 0.828 | 0.0057 |

[1] Site F had stopped manufacturing chloroform in 2004 and is being dismantled

The PEC/PNEC ratios obtained for surface water for chloroform are below 1.0 for all production sites. It can be concluded that there is no risk to aquatic organisms through production of chloroform (**conclusion ii**).

Only the **use of chloroform as a solvent** has a PEC/PNEC ratio above 1. The PEC value for this scenario is based on effluent monitoring in France (see section 3.1.1.2.2.2). In this monitoring study, chloroform concentrations might come from other releases than the releases due to the specific use of chloroform as a solvent. The highest release value of 38.9 kg/d after treatment was used assuming that on-site biological treatment was performed and using an elimination rate of 85.6 %.

Using the 90-percentile value of the monitoring study (10 kg/d after treatment) would give a PEC/PNEC ratio of 3.4, which is still above 1.

Therefore, it can be concluded that there is a need for limiting the risks for this application (**conclusion iii**).

#### 3.3.1.2 Sediment

A PNECsed for the sediment compartment of 450 µg/kg (dry weight) has been estimated using a test on *Chironomus riparius* (see section 3.2.3.2).
Using the PECregional $_{sed}$ of 5.35 µg.kg$^{-1}$ (dw) (see section 3.1.2.2), a PEClocal $_{sed}$ could be calculated: $PEClocal_{sed} = Clocal_{sed} + PECregional_{sed}$

The resulting PEC/PNEC ratios for chloroform risk characterization are presented below.

**Table 3-49 : Estimated PEC/PNEC ratios for sediments**

| Scenario | Step | PECsed (µg/kg) (dw) | PEC/PNEC |
|---|---|---|---|
| Production | Site A | 21.3 | 0.047 |
| | Site B | 33.7 | 0.075 |
| | Site C | 28 | 0.062 |
| | Site D | 19.7 | 0.044 |
| | Site E | 44.1 | 0.098 |
| | Site F[1] | 127 | 0.28 |
| | Site G | 19.5 | 0.043 |
| | Site H | 48.7 | 0.108 |
| | Site I | 18.9 | 0.042 |
| | Site J | 52.8 | 0.117 |
| Uses | HCFC Production | 73.9 | 0.164 |
| | Dyes and Pesticide Production | 297 | 0.660 |
| | Other applications | 282 | 0.628 |
| | **Uses as a solvent** | **44200** | **98.2** |
| Unintended releases | Losses as a by-product during chemical manufacturing | 165 | 0.368 |
| Regional scale | | 5.35 | 0.012 |

[1] Site F had stopped manufacturing chloroform in 2004 and is being dismantled

Additional toxicity testings on sediment organisms have been requested under article 10(2). Two long-term testings on sediment organisms (*Chironomus riparius* and *Lumbriculus variegatus*) have been performed under the conclusion (i) program and risks for the sediment compartment have been refined.

For all production sites, PEC/PNEC-ratios are below 1.

It can be concluded that there is no risk to sediment organisms through production of chloroform (**conclusion (ii)**).

For all uses **except the use of chloroform as a solvent,** PEC/PNEC ratios are below 1 and a **conclusion (ii)** can be derived.

Concerning the **use of chloroform as a solvent,** the outcome of both new sediment toxicity tests is not sufficient to cover the risk identified for this application and the PEC/PNEC ratio is far above 1. The PEC$_{sed}$ has been calculated based on the PEC$_{water}$, which is based on effluent monitoring in France. However, as explained in the risk charcaterisation part for the aquatic compartment, based on available information, this ratio cannot be reduced below 1.
Therefore, there is a need for limiting the risks for this application (**conclusion (iii)**).

### 3.3.1.3 Sewage treatment process

A PNEC micro-organisms of 48 µg/L has been estimated for sewage treatment plants. Assuming a homogeneous mixing in the aeration tank and continuous releases into the STP, the PECstp is equal to the effluent concentration (Clocal $_{eff}$). The resulting PEC/PNEC ratios are shown below:

**Table 3-50 : Estimated PEC/PNEC ratios for sewage treatment plants**

| Scenario | Step | C local $_{eff}$ (µg/L) | PEC/PNEC |
|---|---|---|---|
| Production | **Site A** | **124.8** | **2.60** |
| | Site B[1] | - | - |
| | **Site C** | **426.3** | **8.88** |
| | Site D | **25.6** | **0.42** |
| | **Site E** | **1162.3** | **24.21** |
| | Site F[1] | **-** | **-** |
| | Site G | 11.4 | 0.24 |
| | Site H | 28.5 | 0.59 |
| | Site I | 16.0 | 0.33 |
| | **Site J** | **62.2** | **1.30** |
| Uses | **HCFC Production** | **101** | **2.1** |
| | **Dyes and Pesticide Production** | **504** | **10.5** |
| | **Other applications** | **478** | **10** |
| | **Uses as a solvent** | **20,016** | **417** |
| Unintended releases | **Losses as a by-product during chemical manufacturing** | **266.4** | **5.6** |

[1] No Wastewater Treatment Plant

PEC/PNEC-ratios above 1 have been derived for four production sites, although specific information for these sites has been included.

For production site E, specific information has been requested in order to check whether dyes and pesticides were actually produced on this site. As no data was provided by the producer, a worst-case scenario has been anticipated leading to a PEC/PNEC-ratio above 1. However, it should be specified that if no dyes and pesticides are actually produced on this site, this ratio falls below 1 for site E.

PEC/PNEC-ratios above 1 have also been derived for uses where release estimates are based on effluent monitoring. Additional tests on micro-organisms have been performed in order to derive a NOEC and refine the PNEC. However, as explained in section 3.2.2.1, these studies have been invalidated and no improvement of the risk characterisation for STP processes has been possible.

Specific information on site sewage treatment plant has recently been provided by industry for site C and E. For site E, data confirm that no risk is expected from chloroform production only at this site, but from integrated production of chloroform, HCFC22 and dyes/pesticides. For site C, data were in line with these results showing that emissions have been realistically quantified.

Therefore, a **conclusion (iii)** has to be derived for production sites A, C, E and J, for all uses and for unintended releases.

### 3.3.2. Atmosphere

In the only experimental result available, the lowest test concentration at which effects were observed for visible symptoms and photosynthesis was 100 g/m$^3$ (see section 3.2.4). The test duration was too short to consider the result for a PNEC derivation. However, this concentration is much higher (more than 5 orders of magnitude) than local concentrations that were calculated at each production site and for every use (see section 3.1.3.1).

In addition the potential contribution of chloroform to climate change, stratospheric ozone depletion, ground-level ozone formation and acidification processes could be considered as negligible.

Therefore, although air is the main final receptive compartment for chloroform, no further work is recommended at present.

⇨ **Conclusion (ii)**

### 3.3.3. Terrestrial compartment

The PNEC $_{soil}$ has been estimated to be 16.3 µg/kg. (ww)

Using the PEC regional $_{natural\ soil}$ of 11.5 ng.kg$^{-1}$ (ww), a PEC $_{soil}$ could be calculated to be :

$$PEClocal_{soil} = Clocal_{soil} + PECregional_{natural\ \ soil}$$

The resulting PEC/PNEC ratios for the various scenarios considered in this assessment are presented below.

**Table 3-51 : Estimated PEC/PNEC ratios for agricultural soil**

| Scenario | Step | PEC (µg/kg) (ww) | PEC/PNEC |
|---|---|---|---|
| Production | Site A | 1.16 | 0.07 |
| | Site B | 0.01 | < 0.001 |
| | Site C | 0.11 | 0.007 |
| | Site D | 0.64 | 0.039 |
| | Site E | 0.85 | 0.052 |
| | Site F[1] | 0.31 | 0.019 |
| | Site G | 0.15 | 0.009 |
| | Site H | 0.13 | 0.008 |
| | Site I | 0.05 | 0.003 |
| | Site J | 0.89 | 0.055 |
| Uses | HCFC Production | 0.995 | 0.06 |
| | Dyes and Pesticide Production | 0.3 | 0.018 |
| | Other applications | 0.59 | 0.036 |
| | Uses as a solvent | 7.26 | 0.45 |
| Unintended releases | Losses as a by-product during chemical manufacturing | 3.08 | 0.19 |
| Regional scale | | 0.0115 | < 0.001 |

[1] Site F had stopped manufacturing chloroform in 2004 and is being dismantled

For the terrestrial compartment, the deposition of chloroform due to application of sludges from wastewater treatment plants was assumed to be negligible because sludges from chemical producing industries are not supposed to be applied on agricultural soils. The resulting PEC/PNEC ratios are below 1 for all production or uses scenarios. It could be concluded that there is at present no need for further information and/or testing and no need for risk reduction measures beyond those that are being already applied (**conclusion (ii**)).

### 3.3.4. Non compartment specific effects relevant to the food chain

Because of the low bioaccumulation potential of chloroform (BCF = 13), the potential for secondary poisoning can be considered to be negligible.

**=> Conclusion (ii)**

# 4. HUMAN HEALTH

The risk assessment for human health is currently being carried out by the Member State Rapporteur.

# 5. CONCLUSIONS / RESULTS

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account

Conclusion (iii) is applied to the use of chloroform as a solvent for all compartments.
Conclusion (iii) is also applied to production sites A, C, E and J, to all uses and to unintended releases for the sewage compartment.

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

Conclusion (ii) is applied to all levels of the life cycle of chloroform (except the use as a solvent) for the following compartments: aquatic, sediment, atmosphere, terrestrial (the assessment considers that sludge from chloroform and HCFC production sites are not applied on agricultural soils) and non-compartment specific effects relevant to the food chain.

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