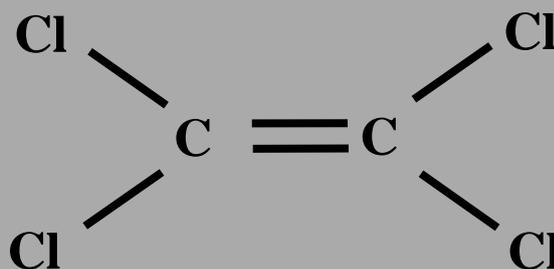


# European Union Risk Assessment Report

CAS No: 127-18-4

EINECS No: 204-825-9

## tetrachloroethylene Part I - environment





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## **TETRACHLOROETHYLENE**

### **Part I – Environment**

CAS No: 127-18-4

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### **RISK ASSESSMENT**

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# **TETRACHLOROETHYLENE**

## **Part I – Environment**

CAS No: 127-18-4

EINECS No: 204-825-9

## **RISK ASSESSMENT**

*Final Report, 2005*

United Kingdom

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

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<b>Final report:</b>	<b>2005</b>

## Foreword

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

The Risk Assessment was carried out in accordance with Council Regulation (EEC) 793/93<sup>1</sup> on the evaluation and control of the risks of “existing” substances. “Existing” substances are chemical substances in use within the European Community before September 1981 and listed in the European Inventory of Existing Commercial Chemical Substances. Regulation 793/93 provides a systematic framework for the evaluation of the risks to human health and the environment of these substances if they are produced or imported into the Community in volumes above 10 t/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<sup>2</sup>, which is supported by a technical guidance document<sup>3</sup>. Normally, the “Rapporteur” and individual companies producing, importing and/or using the chemicals work closely together to develop a draft Risk Assessment Report, which is then presented at a Meeting of Member State technical experts for endorsement. The Risk Assessment Report is then peer-reviewed by the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) which gives its opinion to the European Commission on the quality of the risk assessment.

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

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

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



**Roland Schenkel**  
Acting Director-General  
DG Joint Research Centre



**Catherine Day**  
Director-General  
DG Environment

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<sup>1</sup> O.J. No L 084, 05/04/1993 p.0001 – 0075

<sup>2</sup> O.J. No L 161, 29/06/1994 p. 0003 – 0011

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

## 0

## OVERALL RESULTS OF THE RISK ASSESSMENT

CAS No: 127-18-4  
EINECS No: 204-825-9  
IUPAC name: Tetrachloroethylene

### Environment

This assessment does not address risks arising from groundwater contamination.

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

This applies to the aquatic compartment (including sediment and waste water treatment plant), the terrestrial compartment and secondary poisoning for all life stages of tetrachloroethylene. It also applies to the air compartment for dry cleaning and metal cleaning for direct effects on plants. The conclusion also applies to the regional aquatic and terrestrial compartments for trichloroacetic acid (TCA) formed through the degradation of tetrachloroethylene in air.

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

This conclusion applies to the risk of harm to plants from air emissions of tetrachloroethylene from sites producing and processing tetrachloroethylene as an intermediate. Based on site specific data the conclusion relates to one site.

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

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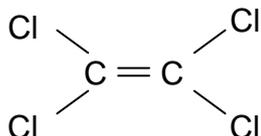
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# 1 GENERAL SUBSTANCE INFORMATION

## 1.1 IDENTIFICATION OF THE SUBSTANCE

CAS No:	127-18-4
EINECS No:	204-825-9
Annex 1 Entry:	602-028-00-4
IUPAC name:	Tetrachloroethylene
Synonyms:	Tetrachloroethylene is also known as tetrachloroethylene and perchloroethylene and is commonly abbreviated to PCE or Perc. A number of other synonyms and trade names are used, including: 1,1,2,2-tetrachloroethylene, Ethylene tetrachloride, 1,1,2,2-Tetrachloroethylene, Ethene, tetrachloro-, Ethylene, tetrachloro-, Perchloroethene, Per, Perstabil®, Ankilostin®, Didakene®, Perclene®, Dowper®, Perklone®
Molecular weight:	165.85
Molecular formula:	C <sub>2</sub> Cl <sub>4</sub>
Structural formula:	



In this risk assessment the name tetrachloroethylene will be used.

## 1.2 PURITY/IMPURITIES, ADDITIVES

### 1.2.1 Purity

The purities quoted in IUCLID where stated were all > 99-100% w/w.

The significant impurities (where stated) comprised some or all of the following:

• 1,1,1-Trichloroethane	< 100 mg/kg	(< 0.01% w/w)
• Carbon tetrachloride	< 50 mg/kg	(< 0.005% w/w)
• Dichloromethane	< 2 mg/kg	(< 0.0002% w/w)
• Other chlorinated solvents	< 150 mg/kg	(< 0.015% w/w)
• Trichloroethylene	< 50 mg/kg	(< 0.005% w/w)
• Water	< 50 mg/kg	(< 0.005% w/w)

Given the nature of the production and isolation methods, the purity is likely to be as high as stated. The impurities present vary according to the plant and production method.

### 1.2.2 Additives

The stated additives from suppliers included a selection of the following (% w/w unless otherwise stated):

- 2,3-epoxypropyl isopropylether 0.3
- 2,6-bis(1,1-dimethylethyl)-4-methylphenol < 0.01
- 2,4-di-tert-butylphenol < 0.005
- 4-methylmorpholine < 0.01
- Di-isopropylamine < 0.05
- Tert-amylphenol < 20 ppm
- Tert-butyl-glycidylether < 0.5

These compounds are added as stabilisers (see Section 1.3.15).

## 1.3 PHYSICO-CHEMICAL PROPERTIES

### 1.3.1 Physical state (at ntp)

Tetrachloroethylene is a colourless mobile liquid with an “ethereal” odour. The odour is detectable at around 27 ppm (183 mg/m<sup>3</sup>) (Amoore and Hauatala, 1983).

### 1.3.2 Melting point

The melting point of tetrachloroethylene has been quoted as -22.7°C (Kirk-Othmer, 1991), -2.4°C (Lange's Handbook, 1992), -22.3°C (CRC handbook, 1994) and -22°C (The Merck Index, 1989). The IUCLID data set gives a value of -22.7°C (Ullmans Encyclopaedia, 1975). The melting range is therefore -22 to -22.7°C, and a value of -22°C is used in this assessment.

### 1.3.3 Boiling point

The boiling point of tetrachloroethylene has been quoted as 121.2°C (The Merck Index, 1989; Kirk-Othmer, 1991), 121°C (Lange's Handbook, 1992), and 120°C (IUCLID data set). The original literature figure (Mumford et al., 1950) is 121.2°C. The method of determination is described in the paper (constant fractionation through a Young column) and this value can be accepted. This value has been used in this assessment. It is also quoted by the National Fire Protection Association, NFPA (1994) and is consistent with what would be expected from vapour pressure studies.

### 1.3.4 Density

The relative density ( $D_4^{20}$ ) of tetrachloroethylene has been quoted as 1.623 (Lange's Handbook, 1992; The Merck Index, 1989; CRC handbook, 1994, IUCLID data set (referenced to Ullmanns Encyclopaedia, 1975), and 1.6226 (Kirk-Othmer, 1991). The original literature figures for the density at 20°C (Mumford, 1950) are 1.6230 g/cm<sup>3</sup> and 1.6145 g/cm<sup>3</sup> at 25°C (water calibrated specific gravity bottles) and these can be accepted as valid.

### 1.3.5 Vapour pressure

The vapour pressure has been quoted as 0.1333 kPa at - 20.6°C, 1.333 kPa at 13.8°C, 5.466 kPa at 40°C, 13.87 kPa at 60°C, 30.13 kPa at 80°C, 58.46 kPa at 100°C and 101.3 kPa at 121.2°C (Kirk-Othmer, 1991). The IUCLID data set quotes Ullmans Encyclopaedia, (1988) as reporting vapour pressures of 1.9 kPa at 20°C, 5.47 kPa at 40°C, 13.9 kPa at 60°C, 30.1 kPa at 80°C, 58.5 kPa at 100°C and 100 kPa at 120°C. Polak et al. (1970) and Boublik et al. (1972) have compiled experimental and theoretical values for the vapour pressure of tetrachloroethylene. The experimental data are presented in Appendix A.

The data from the different sources are consistent and when plotted as a graph of  $1/T$  against  $\log$  (Vapour Pressure, kPa), where  $T$  is the temperature in K, gives an overlapping straight line, showing that the varying data sources concur. A vapour pressure of 1.9 kPa at 20°C is used in this assessment.

### 1.3.6 Solubility

Tetrachloroethylene can be considered as sparingly soluble in water, or “insoluble” (CRC Handbook, 1994). A value of 15 mg of tetrachloroethylene in 100 g of water has been quoted (Kirk-Othmer, 1991). The Merck Index (1989) quotes a value of 1 part in 10,000 parts of water ( $\sim 160$  mg/l assuming the density of tetrachloroethylene is  $1.6$  g/cm<sup>3</sup>) - this figure should be considered an indication of solubility rather than an accurate figure. The NFPA (1994) consider tetrachloroethylene as “insoluble” in water.

The IUCLID data set quotes 149 mg/l or 14.9 mg per 100 g water (assuming the density of water as 1) (Horvath, 1982). This value of 149 mg/l is used for the assessment.

Tetrachloroethylene is miscible with alcohol, ether, chloroform and benzene (The Merck Index, 1989; CRC Handbook, 1994). Tetrachloroethylene is considered to be an excellent non-aqueous solvent and this is entirely consistent with its uses.

### 1.3.7 N-octanol-water partition coefficient

The n-octanol-water partition coefficient of tetrachloroethylene has been measured at  $23 \pm 1.5^\circ\text{C}$  (Bannerjee et al., 1980) by the shake-flask method, giving a partition coefficient ( $K_{ow}$ ) of  $3.38 \cdot 10^2$ , i.e.  $\log K_{ow} = 2.53$ .

The IUCLID data set quotes a  $\log K_{ow}$  of 2.88 at 20°C (Neely et al., 1974) where the value is derived from experimental data for trichloroethylene ( $\log K_{ow} = 2.29$ ) by adjusting for the extra chlorine atom in tetrachloroethylene (the rapporteur obtained a value of 2.84 when repeating this adjustment). A further reference to a measurement ( $\log K_{ow} = 2.53$ ) by Veith et al. (1980) is given in the IUCLID data.

A value of 3.40 has been quoted in a paper by Connell et al. (1993) although the origin of the value is not clear (reference is made in the Connell article to a paper by Gargas et al. (1989) but on examination this does not give a  $\log K_{ow}$  for tetrachloroethylene). Mattie et al. (1994), quoting from Leo et al. (1971), give a partition coefficient ( $K_{ow}$ ) of 1,380.4, and hence a  $\log K_{ow}$  of 3.14. The cited paper by Leo et al., does not list a  $\log K_{ow}$  value for tetrachloroethylene. Another study (McCoy, 1990) quotes a calculated  $\log K_{ow}$  of 1.6647 based on theoretical calculations given generally in a previous paper (Klopman et al., 1985).

The value of 2.53 for log  $K_{ow}$  as obtained by Banerjee et al and Veith et al would seem to be the most acceptable value to use in the assessment.

### **1.3.8 Flash point**

Tetrachloroethylene is considered not to have a flash point under normal test conditions (NFPA, 1994). This is consistent with the structure.

### **1.3.9 Autoflammability**

There are no data to suggest that tetrachloroethylene undergoes autoignition (NFPA, 1994).

### **1.3.10 Explosivity**

Tetrachloroethylene is not explosive (NFPA, 1994). It has been reported that it can react explosively with butyl lithium in petroleum ether (Hurtley and Smiles, 1926) and also with metallic potassium (but not sodium) at its melting point (Rampino, 1958), but these are unusual and specific situations.

### **1.3.11 Oxidising properties**

Testing for this property is not applicable as the substance is a liquid. Tetrachloroethylene is not an oxidising agent and is stable at normal temperatures. This is entirely consistent with its structure and applications.

### **1.3.12 Granulometry**

Not applicable - the substance is a liquid.

### **1.3.13 Surface tension**

No value was reported in the IUCLID entry. Information on this property was available in the literature (Mumford and Phillips, 1950) which quotes a surface tension of 32.1 mN/m at 20°C for the pure liquid. This value was measured by Sugden's modification of the maximum bubble pressure method. The surface tension of tetrachloroethylene is low (e.g. compared to water which has a surface tension of 72.75 mN/m at 20°C).

No value could be found for surface tension of an aqueous solution of tetrachloroethylene. As the solubility is greater than 1 mg/l strictly this is part of the base set requirement.

### **1.3.14 Other physico-chemical properties**

Tetrachloroethylene has a vapour density of 5.8 (Kirk-Othmer, 1991 and NFPA, 1994) relative to air (= 1) and will therefore tend to accumulate at ground level. A saturated vapour concentration of 25,000 ppm (169,500 mg/m<sup>3</sup>) at 20°C has been calculated.

Pure tetrachloroethylene has a viscosity of  $0.891 \text{ N}\cdot\text{m}^{-2}\cdot\text{s}$  at  $20^\circ\text{C}$  and  $0.842 \text{ N}\cdot\text{m}^{-2}\cdot\text{s}$  at  $25^\circ\text{C}$  (Mumford and Phillips, 1950).

The Henry's Law constant has been calculated at  $2,114 \text{ Pa m}^3/\text{mole}$  at  $20^\circ\text{C}$  using the molecular weight of 165.85, a vapour pressure of 1.9 kPa and water solubility of 149 mg/l.

A factor of 1 ppm to  $6.78 \text{ mg/m}^3$  (at  $25^\circ\text{C}$ , 101.325 kPa) has been used to convert between the two units of concentration in air.

### **1.3.15 Hazardous reactions (especially with water)**

When exposed to light and air (oxygen), tetrachloroethylene will slowly oxidise to trichloroacetyl chloride and phosgene at ambient temperatures. This auto-oxidation is suppressed by the addition of stabilisers (usually amines or phenols). With such stabilisers tetrachloroethylene is stable in the presence of light, air, water and common materials up to about  $140^\circ\text{C}$ .

Above  $150^\circ\text{C}$  and in the presence of air, tetrachloroethylene begins to decompose into chlorine, carbon monoxide and carbon dioxide. In addition, hexachloroethane, hexachlorobutadiene, carbon tetrachloride and phosgene may also be formed, and possibly hydrogen chloride (Margossian et al., 1971). This may be of some concern if the evolution of phosgene occurs where welding of metal degreased with tetrachloroethylene takes place (Rinzema, 1971).

### **1.3.16 Summary**

The basic physico-chemical parameters of tetrachloroethylene are well documented, have been checked back to the literature sources and can be accepted as valid. The vapour pressure data have been shown to be reliable and the low water solubility (149 mg /l) can be accepted as valid. Tetrachloroethylene is denser than air (vapour density = 5.8) and would therefore tend to accumulate at ground level. Tetrachloroethylene is not flammable nor is it an oxidising agent. It does not undergo auto-ignition and does not have explosive properties. Decomposition can occur at elevated temperatures (above  $150^\circ\text{C}$ ) as previously indicated.

The physico-chemical properties of tetrachloroethylene are summarised in **Table 1.1**.

**Table 1.1** Physical and chemical properties of tetrachloroethylene

Property	Value
Molecular weight	165.85
Melting point	-22.0 to -22.7°C
Boiling point	121.2°C
Relative density	1.623 at 20°C
Vapour pressure	1.9 kPa at 20°C
Octanol-water partition coefficient (log $K_{ow}$ )	2.53
Water solubility	~149 mg/l at 20°C
Solubility in other solvents	Miscible with alcohol, ether, chloroform and benzene
Viscosity	0.891 N.m <sup>2</sup> .s at 20°C
Henry's Law constant	2,114 Pa m <sup>3</sup> /mole at 20°C
Flammability	Flash point: None under test conditions
Autoflammability	n/a
Explosive properties	Not explosive
Oxidising properties	Not considered as an oxidising agent but can oxidise in presence of air and light
Vapour density	5.8 (Air=1)
Surface tension of aqueous solution	No information
Saturated vapour concentration	25,000 ppm (169,500 mg/m <sup>3</sup> ) at 20°C
Odour recognition	~180 mg/m <sup>3</sup>
Conversion factors	1 mg/m <sup>3</sup> = 0.147 ppm at 25°C 1 ppm = 6.78 mg/m <sup>3</sup> at 25°C

## 1.4 CLASSIFICATION

### Current classification

The current classification and labelling according to Directive 67/548/EEC, 22<sup>nd</sup> ATP (Annex I, index-no 602-028-00-4) is:

### Classification

Carc. Cat. 3; R40

N; R51-53

### Labelling

Xn; N

R: 40-51/53

S: (2-)23-36/37-61

Concentration Limits

C ≥ 1%: Xn; R40

Explanations:

Xn; R40	Limited evidence of a carcinogenic effect.
N	Dangerous for the Environment.
R51	Toxic to aquatic organisms.
R53	May cause long-term adverse effects in the aquatic environment.
S23	Do not breathe dust.
S36/37	Wear suitable protective clothing and gloves.
S61	Avoid release to the environment. Refer to special instructions/safety data sheet.

Carcinogen category 3 indicates a substance which causes concern for humans owing to possible carcinogenic effects but in respect of which the available information is not adequate for making a satisfactory assessment. There is some evidence from appropriate animal studies, but this is insufficient to place the substance in category 2. This classification applies to both the pure compound and products containing ≥1% of tetrachloroethylene.

## **2 GENERAL INFORMATION ON EXPOSURE**

Information in this section on quantities produced and used in the EU relates to 1994 unless otherwise noted. Some changes from these figures may have occurred in subsequent years, but these are not expected to affect the outcome of the assessment significantly (some details are provided in footnotes).

### **2.1 PRODUCTION**

#### **2.1.1 Production volume and capacity**

In the European Union (EU), tetrachloroethylene is produced by six manufacturers located in Belgium, France, Germany, Italy, Spain and the United Kingdom (UK)<sup>4</sup>. The largest manufacturers are those in Germany and the UK. Tetrachloroethylene produced by companies in the EU may be used internally by the company, sold onto the EU market, or exported from the EU. Tetrachloroethylene is also imported into the EU from the USA, though the amounts are thought to be negligible. The manufacturers supply directly to the end-user or via distributors.

Total production capacity in the EU is in the range 100,000-200,000<sup>5</sup> tonnes per annum, with actual production reported as 164,000 tonnes per annum in 1994<sup>6</sup> (Personal Communication from the European Chlorinated Solvent Association (ECSA), 1995). Plant capacities vary and are typically in the range of 10,000-50,000 tonnes per annum (a large scale plant would have a capacity in the range of 50,000-100,000 tonnes<sup>7</sup> per annum). Sales of tetrachloroethylene in 1994 were reported as 78,000 tonnes (Personal Communication (ECSA), 1995) and exports as 56,000 tonnes (Personal Communication (ECSA), 1996), the remainder being used by the chemical industry as an intermediate<sup>8</sup>.

There are a number of companies in the UK who re-cycle small quantities of used tetrachloroethylene from a variety of industries. This is usually re-sold to the engineering industry for use in metal degreasing.

#### **2.1.2 Production methods**

Tetrachloroethylene may be produced by oxychlorination, chlorination and/or dehydrochlorination reactions of hydrocarbons or chlorinated hydrocarbons. The most common methods of production reported are the chlorination of propylene and the oxychlorination of 1,2-dichloroethane (Brooke et al., 1993). Carbon tetrachloride is also produced via the chlorination of propylene route, and the amounts produced are dependent upon the reaction conditions employed. Due to controls on the production and use of carbon tetrachloride, the current reaction conditions are likely to favour the production of

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<sup>4</sup> There are now five producers in the enlarged EU (in the Czech Republic, France, Germany, Spain and UK) (Personal communication (ECSA), 2005). No calculations have been performed for the production site located in the Czech Republic, because this part of the assessment was completed before the accession took place.

<sup>5</sup> Range in 2003 is 100,000 - 500,000 tonnes (Personal communication (ECSA), 2005).

<sup>6</sup> 2003 production 127,000 tonnes (Personal communication (ECSA), 2005).

<sup>7</sup> 50,000 tonnes in 2003 (Personal communication (ECSA), 2005).

<sup>8</sup> 2003 sales were 53,000 tonnes, with exports of 46,000 tonnes (Personal communication (ECSA), 2005).

tetrachloroethylene. Trichloroethylene and tetrachloroethylene are both produced by the oxychlorination of 1,2-dichloroethane route, and by varying the reaction conditions the amounts produced of either compound can be varied. Production is carried out in closed systems limiting human and environmental exposure under normal operating conditions.

In the UK, tetrachloroethylene is produced by the oxychlorination of 1,2-dichloroethane. There are two sites in Italy which manufacture tetrachloroethylene. At one site, manufacture is by the oxychlorination of 1,2-dichloroethane as in the UK. At the other site, it is by the thermal chlorination of various feedstocks. The manufacturing methods for sites in EU Member States other than the UK and Italy have not been established.

## 2.2 USE

The major uses of tetrachloroethylene are as a chemical intermediate and a dry cleaning solvent. Other uses include in metal cleaning and extraction processes. Some minor uses have been reported and these include use as a textile scouring solvent, fumigant, stain remover, paint remover and heat transfer media ingredient. **Table 2.1** gives an estimation of the amount used in each application, based upon a survey by ECSA of their members. It should be noted that use of tetrachloroethylene will vary in different European countries.

Table 2.1 Breakdown of tetrachloroethylene use (1994)

Application	Percentage of production volume	Percentage of Sales	Tonnes per annum
Dry cleaning agent	38	80	62,400
Metal cleaning agent	9	18	14,000
Chemical intermediate	18		30,000
Exports	34		56,000
Other	1	2	1,600
Total	100	100	164,000

(Personal Communications (ECSA), 1995 and 1996)

The estimates of emissions from the use of tetrachloroethylene in this assessment are based on the figures in the table for 1994. More recent information for 1998 (ECSA, 2001) indicates that the sales of tetrachloroethylene in the EU may have decreased slightly from the 1994 figures<sup>9</sup> (sales cover the dry cleaning, metal cleaning and other uses above). As a result, the overall total emissions may be over-estimated to a small extent. Further information is also given in Appendix D.

### 2.2.1 Dry cleaning

A report to the Commission of European Communities in 1991 indicated that there were close to 60,000 dry cleaning establishments in the EU (Final Report to the CEC, DG XI, 1991). According to this report there were 20,000 dry cleaning units in Italy, 9,000 in France, 6,400 to 6,950 in the UK, 6,600 in Spain, 6,600 in West Germany, 3,500 in Greece, 1,000 in

<sup>9</sup> Sales further reduced in 2003 (see footnote 8), in particular in dry cleaning (Personal communication (ECSA), 2005).

Denmark, 1,000 in Portugal, 840 in the Netherlands, 800 in Ireland, 450 in Belgium and 50 in Luxembourg. More than 90% of European units use tetrachloroethylene as the dry-cleaning agent, although the southern European countries use more white spirit for dry-cleaning than those in the north (see Section 4, which will be added later).

In 1994 tetrachloroethylene accounted for approximately 90% of the total solvent used by the dry cleaning industry within the EU. Small quantities of other solvents such as 1,1,2-trichloro-1,2,2-trifluoroethane (R113), 1,1,1-trichloroethane, trichloroethylene and white spirit were also used. However, the production of the first two of these alternative solvents is now prohibited under the Montreal Protocol (see Section 2.4).

In the UK, tetrachloroethylene use was approximately 10,000 to 12,000 tonnes per annum in 1994. Tetrachloroethylene accounted for over 80% of the total solvent used, the remaining 20% being accounted for by R113 and a small quantity of 1,1,1-trichloroethane. The latter solvents were used on leather or more delicate fabrics but are subject to the requirements of the Montreal Protocol.

The UK dry cleaning industry is split between factory dry cleaning and unit shops. There are an estimated 200 to 250 public coin operated machines available through high street launderettes; 6,000 to 6,500 unit shops and between 100 and 200 industrial factory cleaning units. Coin operated machines may be more prevalent in other European countries (e.g. France) although no detailed information was available. Factory cleaning units usually carry out aqueous cleaning with perhaps one dry cleaning machine for non-aqueous cleaning. Aqueous washing requires less attention to detail and is therefore cheaper and more competitive. Dry cleaning is used where aqueous cleaning would damage the fabric or cannot remove the dirt. The factory units are usually co-located with textile rental or commercial laundry plants.

In the UK, unit shops are split between the major dry cleaning groups and the independent operators. Approximately 1,200 unit shops are in the control of the two major groups. The 'independent sector' comprises a number of medium sized companies and a further 4,500 independently operated unit shops in the control of companies with 10 units or less. This situation, however, may not be typical of other European countries. It is reported (Aggazzotti et al., 1994) that in Italy dry-cleaners tend to be smaller and run by the owners. No information was available for other member states.

### **2.2.2 Chemical feedstock**

In the EU, tetrachloroethylene is used by the chemical industry as a feedstock in the production of other chemicals. In the past, products included R113 (1,1,2-trichloro-1,2,2-trifluoroethane), R114 (1,2-dichloro-1,1,2,2-tetrafluoroethane) and R115 (chloropentafluoroethane). Although production of these chemicals has declined, tetrachloroethylene continues to be used in the production of the following chemicals: H(C)FCs 113 (also an intermediate), 115, 116, 121, 122, 123, 124, 125, and 134a.

### **2.2.3 Metal degreasing**

Tetrachloroethylene, along with trichloroethylene, 1,1,1-trichloroethane, dichloromethane and R113 can be used in the vapour, boiling liquid, or ultrasonic cleaning of metalwork in the

engineering industry. Because of its higher boiling point tetrachloroethylene can be more effective in removing persistent deposits than other solvents. This is the second major industrial use of tetrachloroethylene in the EU and UK, with approximately 14,000 tonnes per annum been sold to companies in the EU. Tetrachloroethylene is the major degreasing solvent used in Germany.

#### **2.2.4 Other uses**

It has been estimated that UK industries other than dry cleaning and chemical manufacture consume between 500 to 1,000 tonnes of tetrachloroethylene per annum.

During the production of textile fabrics from synthetic and natural sources, lubricants are added to facilitate the knitting or weaving of yarns. A water/detergent cleaner is usually used to remove the lubricants. However, they can also be removed in continuous open width solvent scouring machines, which use tetrachloroethylene. Textiles can also be scoured in washing machines utilising tetrachloroethylene, in a process similar to dry cleaning.

Tetrachloroethylene also has a number of other minor uses. These include use as a biocide for the treatment of textiles against insects in museums and buildings of cultural, artistic and historical interest; in some spot stain removers; in paint removers; in heat transfer media; in a mixture with n-butanol to wash away the developer in the preparation of photo-polymer plates; in oil refineries for regeneration of catalysts; as a solvent in paints; to degrease electrical components during refurbishment, this process being very similar to metal degreasing; and on a small scale to degrease chamois leathers. These uses are thought to be in decline (Personal Communication (ECSA), 2001). These minor uses are not considered to be significant on a local scale for the environment. The regional and continental emissions estimated in Section 3.1 cover the whole tonnage of tetrachloroethylene used in the EU and can be considered to include the contribution from these minor uses.

### **2.3 TRENDS**

According to information made available by ECSA, there was a decline in the production of tetrachloroethylene in Western Europe between 1986 and 1994 (Solvents Digest No.9, 1991; Personal Communication (ECSA), 1994). Production fell from 340,800 to 164,000 tonnes and total sales (Western Europe) fell from 161,600 to 78,000 tonnes during this period. Information on the ECSA web-site (ECSA 2001) indicates that the sales tonnage in 1998 was slightly lower than this. The latest data from ECSA suggest that the 2001 sales were 63,500 tonnes, and 2003 showed a further fall to 54,000 tonnes (ECSA, personal communication). These reductions are reportedly due to the use of more efficient dry cleaning machines, an increased emphasis on re-cycling, improved housekeeping and the use of enclosed systems. The difference between the production and sales figures is due to a combination of exports to countries outside the EU and chemical intermediate use by the manufacturers, both of which are not recorded in ECSA's figures.

#### **2.3.1 Dry cleaning**

With the exception of Spain, there has been a decline in the amount of dry cleaning being carried out in the EU as water-washable textiles have become more common.

A number of changes occurred in the UK dry cleaning industry during the late 1980s and early 1990s. In particular, there has been a move away from the factory cleaning of domestic items. This has resulted in a corresponding increase in the number of unit shops carrying out cleaning on the premises, rather than acting as receiving shops. However, this trend may be reversed in the future because of technical, environmental and economic reasons, resulting in an increase in the number of receiving shops serving dry cleaning factory units.

With the phasing out of the ozone depleting solvents under the Montreal Protocol (see Section 2.4), it is likely that most companies in the industry would have turned to tetrachloroethylene. This would have meant buying new machines in most cases. Any increase in tetrachloroethylene usage is likely to be balanced by the use of modern, more efficient, machines.

However, after the phase-out, there will still be a need to clean fabrics and garments which can be damaged by tetrachloroethylene. Current developments include the use of hydrocarbon solvents; a kit to modify R113 machines to use a related but different solvent (hydrochlorofluorocarbon-141b) and the formulation of a 'drop-in' replacement based on other hydrocarbon solvents which could be used with the minimum of machine modification.

The design and use of dry cleaning machines is influenced by a number of factors, which assist solvent economy and reduce emissions to atmosphere. These include the cost of the solvent, increasing environmental awareness and the pressures exerted by existing and proposed environmental, health and safety legislation. These have led to a move away from open-circuit to closed-circuit machines, which recover a very high proportion of the solvent during the cleaning cycle. Design features such as carbon recovery units and enclosed still rake-out facilities are also becoming increasingly common. These trends will be reinforced by the Solvent Emissions Directive (1999/13/EC), which requires that emissions of solvent from dry cleaning are limited to a maximum of 20 g/kg of product cleaned and dried.

Standards and regulatory pressures will be exerted by the draft CEN/ISO CD 8230 'Dry cleaning Machinery - Building and Safety Rules' which will require existing machines to comply with the standards for new machines within ten years (the average life span of a machine).

The major dry cleaning groups normally replace their machines at the end of the average life span. This is achieved through a rolling programme of replacement, which ensures that new generation machines are brought into use relatively quickly. However, the small independent users need to extend the life span to between fifteen and seventeen years in order to remain economically viable. This means that new innovations in machine design are taken up more slowly in this sector. More machines are therefore refurbished, which can maintain them in a condition close to their original specification but they may not be as effective at controlling worker exposure as more modern machines.

### **2.3.2 Chemical feedstock**

Tetrachloroethylene is used as a feedstock in the manufacture of the replacement solvents for those prohibited under the Montreal Protocol. It has been assumed in the exposure assessment that the level of use of tetrachloroethylene as a feedstock has remained the same as that in 1994, although recent information (ECSA in 2001) indicates that this area of use has declined.

### 2.3.3 Metal degreasing

In the UK, the phasing out of the ozone depleting solvents is unlikely to have resulted in a significant increase in the use of tetrachloroethylene in the metal degreasing area. The existing equipment used for 1,1,1-trichloroethane could be more readily converted for use with trichloroethylene than tetrachloroethylene. However, a limited number of enclosed units similar to dry cleaning machines, which use tetrachloroethylene, have been imported into the UK. These machines are only suitable for the cleaning of small items. Emissions from metal cleaning will be controlled under the Solvent Emissions Directive (1999/13/EC) to a fraction of the solvent tonnage used, depending on the total amount used per year.

## 2.4 CONTROLS ON TETRACHLOROETHYLENE

Directive 1999/13/EC (the Solvent Emissions Directive) requires Member States of the EU to implement controls on the emissions of volatile organic compounds, which includes tetrachloroethylene. The two major dispersed use areas for tetrachloroethylene, dry cleaning and metal cleaning, are both identified in the Directive. For dry cleaning, equipment is required to meet an emission rate of 20 g of tetrachloroethylene for every kilogram of product cleaned and dried. For surface cleaning, there are emission limit values for the concentration in waste gas (for all emitted compounds together) and limits to the fugitive emissions as a percentage of the solvent input. These vary with the quantity of solvent used on site each year. In each area, new equipment is to meet this standard on installation, while existing equipment has to be brought up to the standard by 2007.

Earlier regulations and controls have already had an impact on the emissions of tetrachloroethylene. The Montreal Protocol requires that production of substances that deplete the Ozone Layer cease by certain prescribed dates. This has affected the use of R113 and 1,1,1-trichloroethane, production of which ceased in 1994 and 1995 respectively. Consumption is still allowed provided that it is from existing stocks or recovered solvent, but use of these substances will reduce as stocks are used up. Countries differ in their interpretation of the Montreal Protocol with restrictions on both production and use.

The European Chlorinated Solvent Association began a programme of voluntary activity in 1992 aimed at developing 'Charters of Co-operation' with end user and distributor associations throughout Europe. These Charters have four key aims (ECSA, 1995a):

- I. 'To identify the routes towards maximising the practical reduction of emissions within the relevant industry'.
- II. 'To encourage recovery, recycling and re-use schemes and to ensure that proper waste disposal practices are followed'.
- III. 'To set up a voluntary auditing scheme which allows progress to be assessed'.
- IV. 'The establishment of Best Available Techniques; that is approaches which are technically feasible in practical industry use (not just in principle) and which are economically feasible'.

Since the programme was begun fourteen Charters have been signed in six countries. Charters are in place in the UK and French metal finishing, surface cleaning and engineering industries. There is a Charter with the European Federation of Dry Cleaning Trade Associations and agreements with local associations in the UK and Italy. Charters are in place

with the distributor associations in France, Italy, Germany, Belgium and Holland. The latest of these was signed in April 1995 with the Dutch national trade association of chemical distributors, the *Verbond van Handelaren in Chemische Producten*. The benefits of these Charters are already being seen. The French *Fédération des Industries Mécaniques* has noted an annual reduction in solvent use of around 10%. The UK Metal Finishing Association has surveyed its 35 members and found some significant reduction in solvent use. The *Comité International de la Teinture et du Nettoyage* has confirmed the trend towards closed cycle dry cleaning machines which has led to a reduction in the use of tetrachloroethylene.

These, and other, environmental initiatives are aimed at reducing the emissions of chlorinated solvents, including tetrachloroethylene, to the environment. The subsequent improvements in solvent management and control techniques have resulted in the decline in the demand for chlorinated solvent, which has been noted over the past ten years.

Tetrachloroethylene was one of the 36 substances in Annex 1A of the Hague Declaration (ECSA, 1995a) which are cited for a 50% reduction in both air and water emissions in the period 1985 to 1995. The Hague Declaration focuses on chlorinated solvents as they are more likely to persist in the environment than hydrocarbon and oxygenated solvents, due to their density and relative insolubility in water. Emissions to air of trichloroethylene, tetrachloroethylene and 1,1,1-trichloroethane in Western Europe had reduced by 55% between 1985 and 1995, exceeding the target set by the Hague Declaration. This reduction has principally been a result of better solvent management and the use of closed cycle processes.

In addition to the Hague Declaration, the United Nations Economic Commission for Europe called for a 30% reduction in the emissions to air of chlorinated solvents, including tetrachloroethylene, over the period 1988 to 1999 (ECSA, 1995a).

Tetrachloroethylene is one of the chemicals identified by the Commission of the European communities as being a List I compound under the Dangerous Substances Directive (76/464/EEC). A daughter directive, 86/280/EEC, has set limit values for the emission of tetrachloroethylene from industrial plants.

An average monthly emission limit value of 10 g/tonne tetrachloroethylene produced was set for tetrachloroethylene production plants to be achieved by the end of 1992; this limit value was then reduced to 2.5 g/tonne to be achieved by the end of 1994. An average monthly limit value of 0.1 mg/l was set for the release of tetrachloroethylene from plants using the compound for metal degreasing, again to be achieved by the end of 1992. This limit value only applies to plants with a yearly discharge of tetrachloroethylene in excess of 30 kg. This directive also sets an Environmental Quality Objective (EQO) (known as Environmental Quality Standards (EQS) in the UK) of 10 µg/l (and an indicative value of 2.5 µg/l) for tetrachloroethylene in surface waters to be achieved by the end of 1992.

Tetrachloroethylene is included by the Danish Environment Protection Agency on its "List of Undesirable Substances" due to its classification for carcinogenicity: Carc. Cat 3. The list - which identifies industrial chemicals of very high concern - has no legal status but is a signal to industry to, as far as possible, avoid these chemicals when choosing chemicals for their production.

As an organohalogen compound, tetrachloroethylene is a List I substance under the Groundwater Directive (80/68/EEC) and as such must be prevented from reaching groundwater.

In 2003 a statutory order for dry cleaning establishments came into force in Denmark. According to this order establishment of new dry cleaning facilities in residential housing is not allowed. For existing dry cleaning facilities in residential housing the concentration of tetrachloroethylene in neighbouring flats and flats above must not exceed  $0.1 \text{ mg/m}^3$  measured over 14 days. Furthermore there are several technical demands for the dry cleaning machines and for the arrangement of the rooms of the establishment (e.g. ventilation and vapour impermeable membranes) to avoid fugitive emissions of tetrachloroethylene. These measures are considered to result in an update of technology at the establishments and in significant reductions of the amount of tetrachloroethylene used in the dry cleaning establishments.

Other legislative controls relating to human exposure are detailed in Section 4 (which will be added later).

## **3 ENVIRONMENT**

### **3.1 ENVIRONMENTAL EXPOSURE**

#### **3.1.1 General discussion on environmental exposure**

The level of exposure of the environment to a chemical is dependent upon the quantities and compartments of release and subsequent degradation, distribution and accumulation in the environment. This section discusses the releases of tetrachloroethylene to the environment and its subsequent behaviour in the environment. Detailed information on the resulting levels in the different environmental compartments is given in Sections 3.1.6 to 3.1.8.

#### **3.1.2 Environmental releases**

In estimating releases to the environment three scales are considered; local, regional and continental. On the local scale, emissions are calculated for point sources and concentrations estimated close to the source. For this assessment these include production of tetrachloroethylene and processing as an intermediate, dry cleaning and metal cleaning.

The regional scenario is defined in the Technical Guidance Document. It is assumed that the regional environment contains one large scale production plant and one site using tetrachloroethylene as a chemical intermediate, together with 10% of the total EU activity for other uses of the substance. The regional scenario also includes 10% of the estimated fugitive emissions due to disposal in landfill sites.

The continental region includes the remaining releases from production sites, uses and fugitive emissions from landfill sites.

In calculating the releases on a daily basis it is assumed that emissions occur for 300 days per year in the local scenario and 365 days a year in the regional and continental scenarios.

Further details on the assumptions made and the area of effect of the different releases are given in the sections below.

##### **3.1.2.1 Releases during production and use as an intermediate**

Figures for releases of tetrachloroethylene from production and processing plants have been reported by industry and these are detailed in **Table 3.1**. In 1994 there were thought to be six production plants and four chemical intermediate plants operating in the EU. Of these sites one site contained both production and processing operations. Production finished in 1995 at one plant and use as an intermediate finished at two plants in 1994. Another company which included data on IUCLID ceased production and use in the early 1990s. The total number of sites considered in this report is therefore one production and processing site, 4 production only sites and one processing only site.

Table 3.1 Releases to air and water during production \*

Site	Production capacity (tonnes/year)	Use as intermediate (tonnes/year)	Release to air	Release to water	Comments
A	See text	Yes	220 tonnes/year (00)	244 kg/year to on-site treatment	Monitoring data show concentration in effluent after treatment to be below detection limit (0.1 µg/l)
B	70,000 (93) 65,000 (94)	No	6,000 kg/year (93) 5,400 kg/year (94) 3,000 kg/year (Fugitive)	110 kg/year (93) 60 kg/year (94)	
C	4,064 (93)	No	450 kg/year	30 kg/year	Measured concentration (GC analysis) of tetrachloroethylene in wastewater after treatment on site. Discharge to sea
D	22,246 (93)	No	0.7 kg/year	5 kg/year	
E	15,729 (93) 21,803 (94) 21,255 (95)		3.5 tonnes/year (93) 4.1 tonnes/year (94) 3.6 tonnes/year (95)	<0.00025 %	Emissions to air include fugitive emissions
F	See text	Yes	<0.004%	<0.00025 %	
G	40,000 (94)	No		1 kg/day	Production finished in 1995
H		5,348 (94)		0.18 tonnes/year	Use as an intermediate finished in 1994
I		4,799 (94)		0.73 tonnes/year	Use as an intermediate finished in 1994

Notes The year to which the values apply is given in parentheses.

\* No calculations have been performed for the production site in the Czech Republic (see Section 2.1.1). Two of the sites listed in this table no longer produce tetrachloroethylene as of 2005.

In 1994 the total tonnage of tetrachloroethylene produced was reported as 164,000 tonnes. The total tonnage of tetrachloroethylene produced by sites reporting data for 1994 was 126,803 tonnes (3 sites); the total tonnage produced at the remaining three sites must therefore be in the region of 37,000 tonnes. If the production volumes for sites C and D for 1993 are taken as representative for these sites in 1994 the production volume at site A is assumed to be in the region of 11,000 tonnes. The total amount of tetrachloroethylene used as a chemical intermediate was estimated as 30,000 tonnes in 1994. Based upon the total amount processed at sites H and I the amount processed at sites A and F is approximately 20,000 tonnes. As no other information is available it will be assumed that this tonnage is split equally between the two sites.

In calculating releases from production and processing plants site-specific data are available for all sites, and will be used in the assessment. The default values for emissions derived from Chapter 3 Appendix 1 of the TGD are shown in **Table 3.2** for reference.

Table 3.2 Default values for production and use as an intermediate

Step	Main category	Tables used	Fraction released to		Number of days
			Air	Water	
Production	1c	A1.2, B1.6	0.01	0.003	300
Intermediate	1b	A3.3, B3.2	0.0001	0.007	300
	1c	A3.3, B3.2	0.001	0.007	300

#### Site-specific releases to water

For site A the monitored emissions to water from production and processing combined are 244 kg/year. These are released to on-site treatment.

For sites B, C, D and E the releases to water are 110 kg/year (0.37 kg/day), 30 kg/year (0.1 kg/day), 5 kg/year (0.02 kg/day) and 53 kg/year (0.2 kg/day) respectively. For sites G, H and I daily releases to water in 1994 were 1 kg/day, 0.0006 kg/day and 0.002 kg/day respectively. As these three sites have now stopped producing and using tetrachloroethylene they will not be considered further.

For processing site F use as an intermediate is estimated as 10,000 tonnes. The emission factor for release to water from the site is reported as <0.00025% which gives a total emission of 25 kg/year (0.08 kg/day).

#### Site-specific releases to air

The reported air emissions from site A are 220 tonnes/year; these are combined emissions from production and processing. For a working year of 300 days the daily emission rate is 733 kg/day.

For site B the emissions to air are reported as 5,400 kg/year from production and 3,000 kg/year due to fugitive emissions, this gives a total emission of 8,400 kg/year (28 kg/day).

For sites C, D and E the emissions to air are reported as 450 kg/year (1.5 kg/day), 0.7 kg/year (0.002 kg/day) and 3.6 tonnes/year (12 kg/day) respectively.

For site F emissions to air are reported as <0.004% of volume used. Based upon a tonnage of 10,000 tonnes used as a chemical intermediate this gives an emission to air of 0.4 tonnes/year (1.3 kg/day).

### Summary of specific releases

The emissions from production and processing plants are summarised as follows:

Site A	Air	733 kg/day	Water	0.81 kg/day
Site B	Air	28 kg/day	Water	0.37 kg/day
Site C	Air	1.5 kg/day	Water	0.1 kg/day
Site D	Air	0.002 kg/day	Water	0.02 kg/day
Site E	Air	12 kg/day	Water	0.2 kg/day
Site F	Air	1.3 kg/day	Water	0.08 kg/day
Total	Air	776 kg/day	Water	1.6 kg/day

Later in the risk assessment these emission estimates will be used to calculate local concentrations for production and processing. For the regional emissions, the highest emission to air and to water will be used. For the continental scenario the total emissions less those for the region are used. (Note that the emissions above are based on 300 working days; for the regional and continental emissions these are averaged over a year and so appear as lower values later in the risk assessment.)

#### **3.1.2.2 Releases during dry cleaning**

Releases of tetrachloroethylene during dry cleaning will vary depending on the type of system in use. This section considers the releases from the different systems and tries to quantify the releases for modelling purposes. Information in this section is based upon the final report by Organisation and Environment (1991) for the European Commission on the 'Technical and economic aspects of water pollution abatement measures for discharges from dry cleaning firms'.

#### The dry cleaning industry

The common practices and machines used in the dry cleaning industry in the EU vary widely from country to country. In 1991 it was estimated that there were approximately 60,000 dry cleaning units in operation in the EU. There are two main types of dry cleaning machines in current operation. In the past the most common type of machine has been the open-circuit machine in which the drying air is vented to atmosphere in the final drying stage. In recent years closed circuit machines where solvent vapours are recovered in the drying cycle have become more common. Open circuit machines may be fitted with carbon filters to adsorb the solvent prior to release to the atmosphere.

Emissions of solvents from different dry cleaning machine types have been estimated (Organisation & Environment, 1991). For open machines, the losses are 15.5 kg per 100 kg of clothes cleaned; for open machines with carbon filters and for closed circuit machines, 2.03 kg per 100 kg of clothes. These values are respectively 90% and 53.5% of the total solvent losses from these machines (17.3 kg/100 kg for open, and 3.8 kg/100 kg for the others; other losses are to water and to solid waste).

In 1991, of the 60,000 dry cleaning units, 5,000 units were thought to be open circuit machines with activated carbon filters fitted (8% of total). The percentage of closed circuit machines in operation varies between 20-80% depending upon the country; based upon a survey of 6 countries the average appears to be 50%. The percentage of open circuit machines in operation varies between 20-80% depending upon the country, the average being 50% including open circuit machines fitted with activated carbon filters. If open circuit machines with activated carbon filters fitted are taken as 8% of the total the percentage of open circuit machines is about 42% in the EU.

The capacity of dry-cleaning machines ranges from 8 kg to 50 kg clothes per load. The average capacity of machines is 10-12 kg in dry cleaning shops operating 1 to 2 machines. The large capacity machines are open circuit type machines and typically located in larger firms in outer town areas. The daily cleaning capacity of a usual dry cleaning machine (10-12 kg clothes per load) is about 80 kg/day (range 65 to 100 kg/day).

In recent years the amount of tetrachloroethylene used in the dry cleaning industry has decreased. The main reason for this is thought to be the switch from older open circuit machines to modern closed circuit machines, which are capable of recycling the solvent. The number of dry cleaning outlets is also thought to have decreased since 1991 when this survey was carried out. In 1994 the amount of tetrachloroethylene sold for use in the dry cleaning industry was reported as 62,400 tonnes.

#### Releases to air during dry cleaning

Local releases to air will depend upon the type of machine being used. As a realistic worst case local emissions will be based upon an open circuit machine cleaning 100 kg clothes per day. This gives a daily emission of 15.5 kg to air or 4.65 tonnes/year based upon 300 days operation per year. For comparison, emissions from a closed circuit machine or open circuit machine fitted with carbon filters cleaning 100 kg clothes per day are estimated as 2.03 kg/day or 0.6 tonnes/year based upon 300 days operation.

In order to calculate the emissions on the regional and continental scales, the relative use of tetrachloroethylene in the different types of machine has to be estimated. For this estimate, open machines with carbon filters and closed circuit machines are treated together as they have similar emissions. It is also assumed that all types of machine clean the same amount of clothes on average. From the discussion above, the ratio of open to closed machines is 25,000:35,000, or 1:1.4. The ratio of emissions from individual machines, open:closed, is 17.3:3.8, or 1:0.22. Assuming that emissions relate to the amounts used, the ratio between the amounts used in open and closed machines is the product of these two ratios, or 1:0.31. The quantity of tetrachloroethylene used in this area is taken as 62,400 tonnes. So the calculated amounts used in the two types of machine are 47,726 tonnes in open machines, and 14,678 tonnes in closed machines.

It is assumed that the quantity of tetrachloroethylene used in dry cleaning each year goes to replace that lost, so the total losses are 62,400 tonnes. The percentages of the losses which are to air were given above. Hence the total air emissions from dry cleaning are:

Open machines	90% of 47,726	= 42,953 tonnes
Closed machines	53.5% of 14,678	= 7,852 tonnes
Overall total		= 50,805 tonnes.

As a worst case, it is assumed that 10% of the total machines (i.e. 6,000) are in the region and that they are all open machines. This gives an emission of 10,309 tonnes/year, or 28,244 kg/day to air. The continental emission is 40,496 tonnes/year, 110,948 kg/day.

### Releases to water during dry cleaning

There are two types of water effluents produced during dry cleaning; cooling water, which does not come into contact with the solvent, and contact water. Water may enter the dry cleaning cycle for several reasons. A small amount of water is sometimes added to the solvent to remove water soluble impurities. Water may be contained in the clothes; the amount contained varies depending upon the fabrics. Water is also added at the end of the distillation stage in order to dry the sludge. With open-circuit equipment the waste air stream in the final drying stage may be passed through an activated carbon bed and water may be used to regenerate the activated carbon. The water and solvent in the contact water are separated in a separator where the heavy solvent forms a bottom layer and water rises to the top and may be run off. The separated water may contain tetrachloroethylene up to its solubility limit in water (approximately 150 mg/l).

The total amount of contact water varies considerably depending upon the type of machine and fabrics being processed. The amount of contact water produced is estimated at between 0.2 litres to 9 litres per 100 kg clothes processed. For open circuit machines equipped with activated carbon air filters up to 14 litres of water may be used for regeneration of the carbon filter. The average amount of contact water produced is thought to be between 2 to 5 litres per 100 kg of clothes cleaned. Based upon a water solubility of 149 mg/l this gives the amount of tetrachloroethylene in contact water as between 0.3 g to 0.75 g per 100 kg of clothes processed for open circuit machines and closed circuit machines. For open circuit machines fitted with activated carbon filters the average amount of contact water is estimated as 20 litres per 100 kg of clothes cleaned, this gives a release of 3 g tetrachloroethylene for each 100 kg of clothes cleaned. **Table 3.3** calculates the daily releases of tetrachloroethylene in contact water for different use scenarios. The daily releases are estimated at between  $3 \cdot 10^{-4}$  kg/day and  $3.75 \cdot 10^{-3}$  kg/day depending upon the type of machine used and quantity processed. The release for open circuit machines with activated carbon filters ( $3 \cdot 10^{-3}$  kg/day) will be used in the assessment.

**Table 3.3** Daily releases of tetrachloroethylene from different dry cleaning operations

Scenario	1	2	3	4	5
Machine Type	Open circuit	Open circuit	Open circuit	Open circuit with activated carbon filters	Closed circuit
Typical machine load	10-12 kg	10-12 kg	50 kg	10-12 kg	10-12 kg
Typical daily through put	100 kg	100 kg	500 kg	100 kg	100 kg
Contact water produced	2 litres/100 kg clothes	5 litres/100 kg clothes	5 litres/100 kg clothes	20 litres/100 kg clothes	5 litres/100 kg clothes
Daily emission of tetrachloroethylene	$3 \cdot 10^{-4}$ kg/day	$7.5 \cdot 10^{-4}$ kg/day	$3.75 \cdot 10^{-3}$ kg/day	$3 \cdot 10^{-3}$ kg/day	$7.5 \cdot 10^{-4}$ kg/day

The continental and regional releases can be estimated from the number of dry cleaning units in 1991. For dry cleaning units operating open circuit machines with activated carbon filters the continental release of tetrachloroethylene to water is 5.5 tonnes/year (15 kg/day) - this is based

upon 5,000 units operating for 365 days a year and a daily emission in contact water of  $3 \cdot 10^{-3}$  kg tetrachloroethylene. For open circuit machines and closed circuit machines the continental release of tetrachloroethylene to water is 15.1 tonnes/year (41 kg/day) - this is based upon 55,000 units operating for 365 days a year and a daily emission in contact water of  $7.5 \cdot 10^{-4}$  kg tetrachloroethylene. This gives total releases of 20.6 tonnes/year (56 kg/day). The regional release is taken as 10% of the total or 2.1 tonnes/year (5.6 kg/day); the rest is taken as the continental release, 18.5 tonnes/year (51 kg/day).

### Releases to residues during dry cleaning

Solid residues may be produced during dry cleaning due to collection of fabric dust, distillation sludges and use of cartridge filters. Of these, distillation sludges are likely to contain the largest amounts of solvent. Distillation sludges consist of water, solvent, fat, conditioners, and powder if powder filters are used. The consistency of the sludge produced can vary greatly depending upon the exact system in use. Similarly the amount of solvent in the sludge can vary considerably from 80% of sludge weight to 10% of sludge weight with the average being 35% of sludge weight. Organisation & Environment (1991) estimated losses of solvent to solid waste as 1.76 kg/100 kg clothes for all machine types; this is 10% of open machine losses and 46.5% of closed (and open with filter) losses. These figures give a total loss to solid residues of 4,773 tonnes/year from open machines, and 6,825 tonnes/year from closed machines, an overall total of 11,598 tonnes/year. These amounts are not released directly to the environment, if at all.

Waste disposal practices for the residues produced vary depending upon the country. In most countries legislation exists such that the residues should be treated as special wastes. In some countries disposal with household waste does occur. Emissions from residues after disposal to landfill are discussed in Section 3.1.5.1.4.

### Summary of releases during dry cleaning

**Table 3.4** summarises the releases of tetrachloroethylene from dry cleaning units within the EU.

Table 3.4 Summary of releases from dry cleaning units

	Release to air	Release to water	Release in solid residue
Continental	40,496 tonnes/year 110,948 kg/day	18.5 tonnes/year 51 kg/day	10,438 tonnes/year 28,598 kg/day
Regional	10,309 tonnes/year 28,244 kg/day	2.1 tonnes/year 5.6 kg/day	1,159 tonnes/year 3,175 kg/day
Local	4.7 tonnes/year 15.5 kg/day	0.0009 tonnes/year 0.003 kg/day	0.53 tonnes/year 1.76 kg/day

### **3.1.2.3 Releases from metal cleaning operations**

Tetrachloroethylene is used within the metal industry as a cleaning agent. The exact pattern of use in the EU and environmental releases is not known. In conversations with experts in the metal finishing industry the following data have been derived as being representative of the industry for the purposes of calculating a PEC. It should be noted that these data have been derived from experience of the UK metal finishing industry. In the UK tetrachloroethylene and trichloroethylene are the main solvents used in the metal finishing industry for metal cleaning. Of these, trichloroethylene is thought to have had the widest application in the past.

Tetrachloroethylene is thought to be used mainly by small to medium scale processors, while large scale processors are thought to use trichloroethylene. The tonnage chosen for the local scenario is thought to be most representative of the local situation in the UK.

For the local scenario a small to medium scale processor using 10 tonnes tetrachloroethylene per year and operating for 210 days per year (EUSES) is assumed. The tonnage supplied to the metal cleaning industry is estimated to be 14,000 tonnes based on 1994 figures. Regional releases are taken as 10% of the total releases. The release pattern of tetrachloroethylene to the environment is taken as 90% to air, 1% to water and 9% in solid wastes. The solid wastes will typically be disposed of as special wastes though they may be co-disposed of to landfill. Using this information the release estimates in **Table 3.5** are made:

**Table 3.5** Releases from metal cleaning operations

	Release to air	Release to water
Continental	11,340 tonnes/year 31,068 kg/day	126 tonnes/year 346 kg/day
Regional	1,260 tonnes/year 3,452 kg/day	14 tonnes/year 38 kg/day
Local	9 tonnes/year 42 kg/day	0.1 tonnes/year 0.48 kg/day

Note that the same emissions could apply for a site using more than 10 tonnes per year, but requiring 10 tonnes per year to replace losses.

#### **3.1.2.4 Releases during disposal**

Incineration is the preferred disposal option for tetrachloroethylene-containing wastes, such as the solid residues from dry cleaning, and is recommended by ECSA to its members. Landfilling of tetrachloroethylene-containing wastes is still permitted in the EU. The hazardous waste directive (91/689/EEC) considers wastes containing less than 25% tetrachloroethylene to be non-hazardous and suitable for disposal by landfill. Landfilling of tetrachloroethylene-containing wastes may potentially lead to groundwater contamination via leachate, though no information on this potential exposure has been found to allow quantification of these releases.

Emissions to air of tetrachloroethylene from landfill sites are estimated at 300 tonnes per annum in the United Kingdom (private communication (AEA Technology), 1996). No other information on releases from landfill sites has been reported, and so this value will be taken as an estimate of regional releases. This is probably a realistic worst case scenario because disposal by landfill accounts for a high percentage of United Kingdom waste disposal practice. Continental releases are taken as nine times the regional releases, i.e. 3,000 tonnes a year to the atmosphere.

#### **3.1.2.5 Other releases**

Water pollution by tetrachloroethylene leaching from vinyl liners in asbestos-cement water pipelines for water distribution has been reported, though no indication is given as to the amount released (Aschengrau et al., 1993; see Section 4, which will be added later).

Other reported uses of tetrachloroethylene include use in oil refineries for regeneration of catalysts and as a solvent in paints for the printing industry. The amounts used in these industries are thought to be small compared to the uses in other applications, and the nature of their releases is thought to be similar to releases from dry cleaning and metal cleaning, i.e. the majority goes to air.

Abrahamsson et al. (1994) suggest that certain marine algae are capable of producing tetrachloroethylene. The amounts produced may be large enough to add to the global emissions of tetrachloroethylene, though they were unable to quantify the amounts. Due to lack of further information this route of exposure is not considered further.

### 3.1.2.6 Summary of environmental releases

**Table 3.6** summarises the amounts of tetrachloroethylene released to the environment from various sources. These figures will be used later in the assessment as the basis for calculation of the PECs. The regional and continental releases to water will be split in the ratio 70:30 between release to a wastewater treatment plant (WWTP) and direct release to surface water.

Table 3.6 Summary of environmental releases of tetrachloroethylene (kg/day)

Scenario	Continental		Regional		Local	
	Air	Water	Air	Water	Air	Water
Production and use as a chemical intermediate*	35	0.66	602	0.67	733	0.81
Dry cleaning	110,948	51	28,244	5.6	15.5	0.003
Metal cleaning	31,068	346	3,452	38	42	0.48
Landfill	7,397		822			
Total	149,448	398	33,120	44		

\* Regional and continental releases adjusted to 365 days per year

### 3.1.3 Degradation in the environment

On release to the environment tetrachloroethylene may undergo a number of degradation and removal processes. The processes that can occur are dependent upon the systems into which the release occurs.

#### 3.1.3.1 Atmospheric degradation

The data in this Section are largely based on the ECETOC Joint Assessment of Commodity Chemicals report on tetrachloroethylene (ECETOC 1999). References to other papers are quoted where appropriate.

#### Photodegradation reactions

The lifetime for removal of tetrachloroethylene by gas phase photolysis has been calculated to be about 3 years in the troposphere. Direct photolysis is therefore thought to be of negligible importance compared to other tropospheric removal mechanisms.

Tetrachloroethylene will react in the atmosphere with a number of photochemically produced species. The major reaction that occurs is with hydroxyl radicals, and this is the major removal process for tetrachloroethylene from the atmosphere. Atkinson (1985) reviewed the available data for this process and recommended the following value for the second order reaction rate constant:

$$k_{\text{OH}} = 9.64 \cdot 10^{-12} \exp(-1209/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This gives a value for  $k_{\text{OH}}$  of  $1.23 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $T = 277 \text{ K}$ .

The atmospheric lifetime of tetrachloroethylene due to reaction with hydroxyl radicals has been estimated to be around 0.43 years (World Meteorological Organisation, 1991). The Technical Guidance Document recommends a value for the atmospheric hydroxyl radical concentration of  $5 \cdot 10^5 \text{ molecules cm}^{-3}$ . Using this concentration, a half-life of around 3.2 months (lifetime = 4.6 months) is estimated for the reaction. The estimated half-life is long enough to allow transport of tetrachloroethylene from the point of emission.

The reaction with atmospheric chlorine atoms is thought to be the next most important atmospheric degradation mechanism for tetrachloroethylene. The second order rate constant for the reaction has been quoted as (Nicovich et al., 1996):

$$k_{\text{Cl}} = 4.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The actual concentration of chlorine radicals in the atmosphere is unknown. Concentrations of around  $1000 \text{ molecules cm}^{-3}$  have been suggested, but a recent study by Sidebottom and Franklin (1996) suggests that the actual concentration in the troposphere is generally close to zero and is at most  $500 \text{ molecules cm}^{-3}$ . The half-life for the reaction is estimated (for  $[\text{Cl}] = 1,000$  or  $500 \text{ molecules cm}^{-3}$ ) as 6-12 months (lifetime 9-17 months).

The overall lifetime for the two processes combined is thought to be around 3 months (ECETOC, 1999), although the exact contribution of the reaction with chlorine atoms to the overall degradation of tetrachloroethylene is uncertain.

Class and Ballschmiter (1987) measured the concentration of tetrachloroethylene in the atmosphere at sites remote from any anthropogenic sources in the Northern and Southern hemispheres. The lifetime in the Northern hemisphere was estimated as 0.46 years (5-6 months) and in the Southern hemisphere as 0.18 years (2 months). These lifetimes have been calculated based on estimated release rates and measured levels.

Reactions of tetrachloroethylene with other atmospheric species such as ozone ( $k < 3 \cdot 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson and Carter, 1984);  $k < 2 \cdot 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Franklin, 1994)), oxygen atoms ( $k(\text{O}^3\text{P}) = 1.6 \cdot 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k(\text{O}^1\text{D}) < 5 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Franklin, 1994)), nitrate radicals ( $k < 1 \cdot 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson et al., 1992);  $< 5.2 \cdot 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Franklin, 1994) and hydroperoxy radicals ( $k < 1 \cdot 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Franklin, 1994) have been reported but are thought to be insignificant atmospheric degradation processes (estimated atmospheric lifetimes for these processes range from  $>5$  years to  $>1,500$  years) for tetrachloroethylene (Franklin, 1994).

For the risk assessment, the reactions rates with OH and with Cl are combined to give an overall half life of 96 days. This is used in the EUSES calculations (entered as the reaction rate with OH radicals which would give a half life of 96 days).

### Contribution to photochemical ozone production

The reactivity of tetrachloroethylene in the troposphere has been reported as being low enough so as not to contribute significantly to tropospheric ozone formation and the related 'photochemical smog'. The photochemical ozone creation potential (POCP) of tetrachloroethylene in the troposphere is estimated as 1, expressed relative to ethene (a substance thought to be important in photochemical ozone creation), with a POCP of 100 (Derwent and Jenkin, 1990).

### Reaction products

Several studies have been carried out on the products formed during the photochemical degradation of tetrachloroethylene in air under laboratory conditions. The main products identified are phosgene, trichloroacetyl chloride, hydrogen chloride, carbon dioxide and carbon monoxide, but other products such as carbon tetrachloride, dichloroacetyl chloride and chloroform have also been detected (ECETOC, 1999).

Gay Jr. et al. (1976) irradiated mixtures of tetrachloroethylene (5 ppm) using a smog chamber with air containing NO<sub>2</sub> for 140 minutes. Over this time, around 7% of the tetrachloroethylene reacted forming carbon monoxide (0.27 ppm), ozone (0.07 ppm), hydrogen chloride (0.42 ppm) and phosgene (0.12 ppm). Trichloroacetyl chloride was also identified.

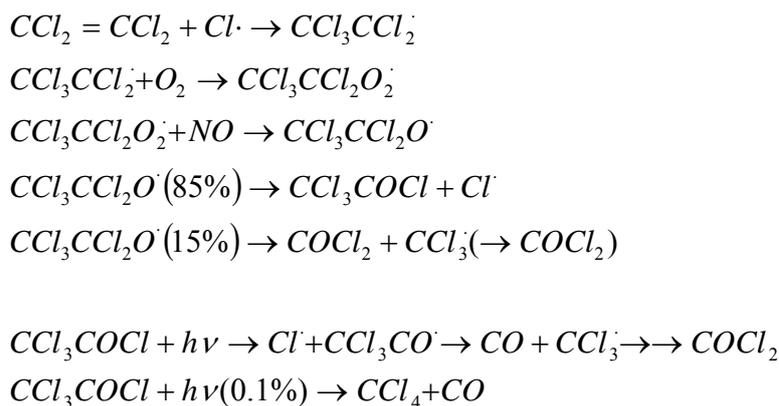
Singh et al. (1975) studied the degradation of various concentrations of tetrachloroethylene in ultrazero air illuminated with simulated sunlight. After 7 days illumination, the product yields were around 70-85% phosgene and 8% carbon tetrachloride. The concentration of carbon tetrachloride continued to increase long after the tetrachloroethylene had disappeared, indicating that it was formed from an intermediate substance, probably trichloroacetyl chloride.

Tuazon et al. (1988) looked at the products formed during the reaction of tetrachloroethylene with hydroxyl radicals. During the 2 hour experiment only around 10% of the tetrachloroethylene reacted. The main products formed were phosgene (product yield 0.47-0.52) and trichloroacetyl chloride (product yield 0.39-0.41). When the experiment was repeated in the presence of a chlorine atom scavenger (ethane), a marked decrease in the amount of trichloroacetyl chloride formed (product yield <0.15) was seen, indicating that trichloroacetyl chloride is formed by chlorine atom attack on the tetrachloroethylene.

Itoh et al. (1994) has studied the products from the hydroxyl radical initiated reactions of tetrachloroethylene in detail. In the system used, tetrachloroethylene (26.3 ppm) was irradiated for 12 hours in air (20% relative humidity) using hydrogen peroxide as a source of hydroxyl radicals. Under the conditions used all the tetrachloroethylene reacted and the products formed were 19.7 ppb of carbon tetrachloride (0.07% yield), 6.1 ppm of trichloroacetyl chloride (23.2% yield), 1.9 ppm of phosgene (7% yield), 4.8 ppm of carbon monoxide (18% yield) and 5.3 ppm of carbon dioxide (20% yield). The shapes of the degradation curves were consistent with two competing reactions, i.e. addition of hydroxyl radical to form phosgene and addition of chlorine atoms to form trichloroacetyl chloride, the latter becoming more prevalent with time as the chlorine atom concentration in the reaction chamber increased. Further experiments were carried out to investigate the source of carbon tetrachloride in the experiments. Photolysis experiments with trichloroacetyl chloride showed that carbon tetrachloride was formed from this species rather than directly from tetrachloroethylene. The conversion of trichloroacetyl chloride to carbon tetrachloride was estimated to be around 0.1% based on 24 hours illumination.

From the product studies described above, it is clear that there are two competing reactions occurring in the closed laboratory studies. The main products formed of relevance to the environment are phosgene, trichloroacetyl chloride and carbon tetrachloride. It is clear from the available data that phosgene is derived from hydroxyl radical addition to tetrachloroethylene. Trichloroacetyl chloride is derived from chlorine atom addition to tetrachloroethylene and carbon tetrachloride is formed as a result of further degradation of trichloroacetyl chloride. The main reaction pathways for the chlorine atom addition are shown below (based on Sidebottom and Franklin (1996) and Itoh et al. (1994)).

#### Chlorine atom addition



Some authors have suggested that trichloroacetyl chloride is a major atmospheric degradation product of tetrachloroethylene. As described by Reimann et al. (1996), chloroacetyl chlorides can react further (hydrolysis) to form chloroacetic acids, which can be washed out of the atmosphere. They are toxic to many plants and some have been used as herbicides.

In many experiments, seemingly large yields of trichloroacetyl chloride and carbon tetrachloride are formed but in the environment this behaviour is likely to be modified. This is because chlorine atoms are formed during the hydroxyl radical-initiated degradation of tetrachloroethylene. In laboratory studies, these can build up in the test system and so the chlorine addition pathway can effectively compete with hydroxyl radical addition, resulting in high yields of trichloroacetyl chloride (and subsequently carbon tetrachloride). In the environment however, there are many other chemical species (e.g. hydrocarbons) that are capable of reacting with (scavenging) the reactive chlorine atoms and so the proportion of tetrachloroethylene reacting via this pathway will be much diminished in the environment. This has been demonstrated in laboratory studies when a chlorine atom scavenger was added.

The potential formation of trichloroacetic acid from tetrachloroethylene is discussed in more detail in Appendix B. Information on the levels of trichloroacetic acid found in the environment and their possible effect is presented in the appendix, and a risk assessment for this degradation product is conducted. The conclusions are also included in Section 3.3 of the main report.

#### Reactions in the stratosphere and ozone depletion

The lifetime of tetrachloroethylene in the troposphere is such that the fraction of emitted tetrachloroethylene that enters the stratosphere is low, estimated at around 1% of total emissions to the atmosphere. In the stratosphere, tetrachloroethylene will be degraded by reaction with hydroxyl radicals. It may also undergo photolysis, the products of which may lead to ozone depletion. While the potential for ozone depletion by tetrachloroethylene exists, the actual

impact is likely to be negligible, when compared to other ozone depleting chemicals such as chlorofluorocarbons and methyl chloroform. The estimated stratospheric chlorine loading potential of tetrachloroethylene is less than 0.01. Some of the degradation products of tetrachloroethylene formed in the troposphere may enter the stratosphere and contribute to ozone depletion. The contribution these products make to ozone depletion has not been quantitatively assessed (ECETOC, 1999).

### 3.1.3.2 Aquatic degradation

#### Abiotic degradation

Degradation of tetrachloroethylene in water by hydrolysis is very slow, with half lives in the order of years reported (ECETOC, 1999).

Tetrachloroethylene may be removed from aquatic systems by photochemical reactions, involving free radicals or electronically excited molecular species. These reactions are only likely to compete with volatilisation in still, sunlit waters where volatilisation is limited by the available surface area for evaporation (ECETOC, 1999).

Reductive pathways involving transition metals or their organic complexes may be significant in the presence of soils or sediments (ECETOC, 1999). No further information on this process has been found.

#### Biodegradation

##### *Aerobic biodegradation*

The data reported indicate that tetrachloroethylene is persistent under aerobic conditions, although there are some reports of degradation under aerobic conditions. The authors attribute this to anaerobic biodegradation occurring within micro-niches. The anaerobic biodegradation products of tetrachloroethylene may undergo aerobic biodegradation.

Fogel et al. (1986) studied the aerobic biodegradation of chlorinated ethenes using a mixed culture of methane-utilising bacteria, obtained by methane enrichment of a sediment sample. No degradation of tetrachloroethylene was observed after incubation for 190 hours.

Vannelli et al. (1990) studied the aerobic degradation of chlorinated ethenes using a pure culture of the ammonium-oxidising bacterium *Nitrosomonas europaea* under ammonia-stimulated aerobic conditions. No degradation of tetrachloroethylene was observed.

No degradation was observed in either a modified shake flask closed bottle biodegradation test or a river die-away study (Mudder, 1982). A 21-day acclimation period was used with adaptive transfers after 48 or 72 hours, with lactose and without a co-metabolite in the closed bottle test. In the river die-away study a 21-day acclimation period without co-metabolite was used.

No degradation was observed in aerobic degradation experiments conducted by Bouwer et al. (1981). A bacterial inoculum obtained from primary sewage effluent was used. The cultures were incubated in the dark for 25 weeks at 20°C. Three concentrations of tetrachloroethylene were used (9, 33 and 74 µg/l) and analysis of the test solution was undertaken by gas chromatography every 2-4 weeks.

A sterile salt solution containing a mixture of chlorinated compounds, including tetrachloroethylene, at concentrations of between 10-30 µg/l each, was applied continuously to an up-flow glass column. The column contained inert material and was seeded with primary sewage. It was operated at 22-23°C under aerobic conditions for two years. No degradation of tetrachloroethylene was observed (Bouwer and McCarty, 1982).

No degradation of tetrachloroethylene was observed during the infiltration of river water to groundwater. Samples were taken from groundwater sites near a contaminated river. During the monitoring period of one year the conditions were predominately aerobic (Schwarzenbach et al., 1983).

Phelps et al. (1991) reported a 60% decrease in concentrations of tetrachloroethylene within 21 days in an aerobic packed-column. Similar results were obtained by Enzien et al. (1994) who reported a 90% removal of tetrachloroethylene from a soil column held under bulk aerobic conditions. In both cases it was speculated that the decrease may have been due to the presence of anaerobic niches within the column bed, though no specific evidence of anaerobic biodegradation was found.

Gradual biodegradation with adaptation was observed in tests conducted by Tabak et al. (1981). A static-culture, flask screening procedure method based upon BOD was used. The inoculum used was settled domestic sewage sludge. The cultures were incubated for seven days in the dark at 25°C. A subculture of the inoculum was taken after 7 days and incubated for a further 7 days. A total of three subcultures were taken, i.e. at the end of the incubation period of the third subculture the inoculum had been adapted for 28 days. Samples of the cultures were analysed for tetrachloroethylene by gas chromatography after each seven day period; volatilisation losses were monitored by measuring total organic carbon in non-biological volatility controls. At a concentration of 5 mg/l, tetrachloroethylene losses were 45% after the initial incubation period, 54% after the first subculture, 69% after the second subculture and 87% after the third subculture; losses due to volatilisation were 23%. At a concentration of 10 mg/l tetrachloroethylene losses were 30% after the initial incubation period, 41% after the first subculture, 67% after the second subculture and 84% after the third subculture; losses due to volatilisation were 16%. The tests show that tetrachloroethylene may undergo primary degradation, the rate of degradation increasing with adaptation of the micro-organisms.

#### *Anaerobic biodegradation*

Tetrachloroethylene undergoes anaerobic degradation. The process by which the degradation occurs is reductive dechlorination, the degradation products reported are trichloroethylene, dichloroethylene, vinyl chloride, ethene and ethane. The degradation products found vary and are dependent upon the experimental conditions used.

The inocula used in the majority of experiments were adapted and degradation of tetrachloroethylene was usually observed at elevated temperatures and in the presence of nutrients. Several methanogenic organisms were found to be capable of dechlorinating tetrachloroethylene. The redox potential is important in determining the level of dechlorination. Anaerobic dechlorination takes place under methane and sulphate reducing conditions. For dechlorination to occur an electron donor is usually required, for example acetate and lactate.

De Bruin et al. (1992) studied the reductive dechlorination of tetrachloroethylene in a fixed bed column. The column was filled with a mixture (3:1) of anaerobic sediment from the Rhine river and anaerobic granular sludge. The column was continuously percolated with an anaerobic

mineral medium. Reducing conditions were maintained in the column by the presence of  $\text{Na}_2\text{S}$  (10 mg/l) and lactate was used as an electron donor (1 mM). The flow rate through the column was 15 ml/hour (column retention time 24 hours) at 20°C in the dark. After adaptation of the micro-organisms in the column, tetrachloroethylene was found to be dechlorinated stepwise via trichloroethylene, cis-1,2-dichloroethene, and vinyl chloride to ethene. Ethene was then reduced to ethane within 24 hours. The conversion of tetrachloroethylene to ethane was 95-98% during a 24-hour period at an initial tetrachloroethylene concentration of 1.5 mg/l. Increasing the flow rate appeared to have little effect on the degradation products. Lowering the temperature of the column to 10°C caused an initial decrease in the conversion to ethane, but after two week's operation at the lower temperature, only ethane and ethene were detected in the column effluent.

DiStefano et al. (1991) studied the reductive dechlorination of tetrachloroethylene using a methanol-tetrachloroethylene methanogenic culture. The methanogenic culture was incubated in sealed serum bottles at 35°C. Every two days samples were taken for analysis and fresh medium containing tetrachloroethylene was added to maintain the sample volume. Methanol was added to serve as co-metabolite. Reducing conditions were maintained by the presence of sulphide. After 115 days adaptation the tetrachloroethylene concentration was increased in the medium from 0.6 mg/l to 91 mg/l over a 42-day period. From day 115 to day 135, each addition of tetrachloroethylene was degraded giving about two-thirds vinyl chloride and one third ethene within the 2-day period between additions. Traces of trichloroethylene and dichloroethene were also observed. After 170 days, tetrachloroethylene was degraded to ethene (80%) and vinyl chloride (20%) within 2 days, even though methanogenic activity (as measured by methane production) had declined. Occasionally longer periods were allowed between additions of tetrachloroethylene and it was found that the amount of vinyl chloride remaining after four days was <1% of the total products. The authors reported that methanogenic conditions seem to promote dechlorination activity, though methane production is not necessary for dechlorination to occur under all conditions. They also found that methanogenesis is inhibited by high concentrations of tetrachloroethylene.

In a further study using a similar tetrachloroethylene enrichment culture DiStefano et al. (1992) studied the difference in methanol- and hydrogen-fed mixed anaerobic cultures amended with selective inhibitors. The culture and tetrachloroethylene concentrations used were as described previously (DiStefano et al., 1991). Hydrogen was added to two cultures, and methanol to two other cultures, in identical doses. The report states that hydrogen acted as the electron donor in the dechlorination of tetrachloroethylene to ethene (80%), vinyl chloride (20%) and traces of trichloroethylene and dichloroethylene. Hydrogen was able to sustain tetrachloroethylene reduction over short periods (30 days), but not over longer periods. This was thought to be due to the nutritional dependency of the hydrogen-utilising dechlorinators on the activities of other organisms which were not supported in the hydrogen cultures, but were in the methanol cultures.

Fathepure et al. (1987) identified and prepared several pure cultures of anaerobic bacteria capable of degrading tetrachloroethylene (1 mg/l) to trichloroethylene. The bacteria tested were 4 strains of acetate-utilising methanogens (*Methanosarcina* sp., *Methanosarcina mazei*, *Methanosarcina acetivorans* and *Methanotherix* sp.), *Desulfovibrio desulfuricans*, *Clostridium pasteurianum*, *Clostridium butyricum* and a pure-culture dehalogenator (DCB-1) isolated from a methanogenic consortium which utilised 3-chlorobenzoic acid as its sole carbon and energy source. *Methanosarcina* sp. and *Methanosarcina mazei* cultures were shown to degrade tetrachloroethylene to trichloroethylene. The maximum yields of trichloroethylene were obtained with methanol rather than acetate as growth substrate. The highest rate of dechlorination was obtained with DCB-1 with pyruvate as growth substrate. None of the other species tested were

capable of degrading tetrachloroethylene. The process by which methanogens dechlorinate tetrachloroethylene is a co-metabolic process and appears to be dependent on the formation of methane from the carbon source (Fathepure and Boyd, 1988).

Fathepure and Tiedje (1994) studied the reductive dechlorination of tetrachloroethylene in a chlorobenzoate enriched biofilm reactor. A continuously-fed, up-flow biofilm reactor, inoculated with an enrichment culture capable of mineralising 3-chlorobenzoate was used. The enrichment culture contained *Desulfomonile tiedjei* DCB-1, an anaerobic organism. The column was incubated at 35°C with 3-chlorobenzoate as the primary carbon source. After steady state conditions had been achieved (4 months) tetrachloroethylene was added to the mineral medium. The column was then left to acclimatise for 3-4 weeks. Degradation rates of between 78-86% were measured for tetrachloroethylene concentrations of 0.26-1.0 mg/l and trichloroethylene and dichloroethylene were observed as degradation products. The hydraulic retention time of the column was 37.5 hours. At higher flow rates, tetrachloroethylene dechlorination decreased when the hydraulic retention time of the column became less than 4 hours. High concentrations of tetrachloroethylene were found to damage the bed. When substrates other than 3-chlorobenzoate were used, negligible dechlorination of tetrachloroethylene was observed.

Freedman and Gosset (1989) studied the anaerobic degradation of tetrachloroethylene with micro-organisms from a wastewater treatment plant. The organisms were adapted prior to use by incubation at 35°C under anaerobic conditions with a solution of tetrachloroethylene. When the addition of tetrachloroethylene had been degraded, a sample of the culture was removed from each bottle and replaced by fresh medium and a new dose of tetrachloroethylene. Some of the removed samples were used to start new cultures. Operating in this semi-continuous way, sixth generation cultures were obtained. The minimum retention time for the cultures was 50 days. Methanol and glucose were used as co-metabolites and redox conditions were maintained by the presence of  $\text{Fe}^{2+}$  ions. Ethene was reported as the main degradation product formed, with traces of trichloroethylene and dichloroethene detected. Reductive dechlorination was only found to occur when methanol was used a co-metabolite. The addition of hydrogen to dechlorinating microcosms increased the dechlorination rate by about 500 times after 200 days.

Holliger et al. (1993) isolated a bacterium capable of growing on tetrachloroethylene from an inoculum derived from anaerobic sediment and anaerobic granular sludge. Hydrogen or formate was necessary as electron donor for growth to occur. Tetrachloroethylene was degraded in the anaerobic packed-bed column from which the bacterium was derived. The main degradation product was ethane with traces of cis-1,2,-dichloroethane, trichloroethylene, vinyl chloride and ethene detected.

Kästner (1991) found that reductive dechlorination of tetrachloroethylene to cis-1,2-dichloroethene occurred upon the transfer from aerobic to anaerobic conditions. The cultures used contained aerobic isolates in a co-culture with a *Bacillus* sp. and a *Desulfotomaculum* sp. under conditions of limited oxygen supply. Degradation of tetrachloroethylene only occurred in cultures that were initially aerobic but became anaerobic after a few days incubation. No degradation was observed in cultures that were anaerobic from the start. Transformation of tetrachloroethylene required a decrease in redox potential of the system caused by sulphide formation from degradation of sulphur compounds present in the system.

Liang et al. (1993) studied the degradation of tetrachloroethylene under methanogenic conditions using aquifer material obtained from contaminated sites. They incubated microcosms containing inocula and anaerobic mineral medium at 35°C. Reducing conditions were maintained by the

presence of  $\text{Fe}^{2+}$  ions. Tetrachloroethylene was added to the microcosms on its own or in the presence of either toluene, ethylbenzene or benzoate. Trichloroethylene, trans-1,2-dichloroethene and vinyl chloride were detected as the degradation products. The addition of benzoate caused a decrease in the rate of dechlorination but toluene and ethylbenzene did not appear to affect the rate of tetrachloroethylene degradation.

Pavolstathis and Zhuang (1993) studied reductive dechlorination of tetrachloroethylene (11.5 mg/kg) using static microcosms packed with contaminated soil. After incubation at 20°C, trichloroethylene and cis-1,2-dichloroethylene were observed as the degradation products under both sulphate reducing and methanogenic conditions. They found that electron donors such as ethanol, acetate and lactate were necessary for reductive dechlorination to occur. The redox potential was found to have a considerable influence on the rate of dechlorination.

In a further study, Zhuang and Pavlostathis (1995) studied the effect of temperature, pH and electron donor concentration on the reductive dechlorination of tetrachloroethylene. A methanogenic culture derived from contaminated soils was used. The culture was maintained as a semicontinuously fed batch reactor with a hydraulic retention time of 50 days, the pH of the culture was adjusted to 7, and acetate was used as the electron donor. The tetrachloroethylene concentration of the liquid phase was 1 mg/l. Two series of cultures, a methanogenic culture and a contaminated soil-based culture, were developed and incubated at a range of temperatures. Dechlorination was found to increase up to 35°C and then decrease as the temperature rose above 45°C. The effect of pH was studied in a methanogenic culture at five different pHs. The maximum level of dechlorination was observed at pH 7. The effect of varying the electron donor concentration on dechlorination was studied using the methanogenic culture amended with different amounts of acetate. The rate of dechlorination increased rapidly with initial increases in acetate concentration and then slowed with subsequent increases in the acetate concentration.

Ninomiya et al. (1994) studied the biotransformation of tetrachloroethylene to trichloroethylene and cis-1,2-dichloroethylene under anaerobic conditions. Microcosms were prepared from aquifer solids and distilled water spiked with 3  $\mu\text{mol}$  tetrachloroethylene. The microcosms were then incubated in the dark for 10 days. Analysis of the microcosms was by GC/MS. Complete dehalogenation of tetrachloroethylene was observed after seven days.

Vogel and McCarty (1985) studied the degradation of tetrachloroethylene under anaerobic conditions using a continuous-flow fixed-film methanogenic column. In a column with a 2-day retention time, tetrachloroethylene concentrations were reduced from 20.5 mg/l to 4.4  $\mu\text{g/l}$  (99.98% reduction). Trichloroethylene, dichloroethylene and mainly vinyl chloride were identified as the degradation products. Mineralisation to  $\text{CO}_2$  was detected by tracer studies.

Bouwer and McCarty (1983) conducted batch experiments with deoxygenated anaerobic medium. The medium was seeded with a methanogenic mixed culture, and tetrachloroethylene (200  $\mu\text{g/l}$ ) was added and then incubated at 35°C in the dark. Tetrachloroethylene was degraded after an eight-week incubation period. The degradation product was thought to be mainly trichloroethylene. Continuous fixed-film studies were conducted with two up-flow glass columns in series. Primary sewage effluent was used to seed the first column, the effluent of which was used in the second column. A methanogenic bacterial inoculum was used as seed for the second column. A chemical mixture containing tetrachloroethylene was added, with acetate as a primary substrate, to the influent of the second column (tetrachloroethylene concentration 18  $\mu\text{g/l}$ ). The columns were operated in the dark at 22-23°C for 19 months. Steady state removal of tetrachloroethylene was 86% after a 10 week acclimation period.

Suflita et al. (1988) compared biodegradation under methanogenic and sulphate reducing conditions. In both instances tetrachloroethylene was dechlorinated by sequential reduction reactions to form mainly trichloroethylene and dichloroethylene and vinyl chloride. Degradation was found to occur faster in the methanogenic cultures.

Gibson and Sewell (1992) showed that dehalogenation activity occurs in the presence of a suitable electron donor, such as lactate and acetate. Trichloroethylene and dichloroethene were detected as degradation products.

#### Summary of aquatic degradation data

A number of studies have been reported on the biodegradation of tetrachloroethylene. Based upon the data reported tetrachloroethylene undergoes anaerobic biodegradation by a process of reductive dechlorination. The conditions and inocula used appear to be important. Tetrachloroethylene does not appear to undergo aerobic biodegradation. Therefore, in modelling the behaviour of tetrachloroethylene in a wastewater treatment plant the rate constant for biodegradation is taken as 0 ( $k_{\text{bio}_{\text{water}}} = 0$ ). The half-life for hydrolysis of tetrachloroethylene in surface water is in the order of years. The first order rate constant for hydrolysis in surface waters is therefore taken as 0 ( $k_{\text{hydr}_{\text{water}}} = 0$ ). Removal by photolysis may be important in some water systems where volatilisation is limited, the rate constant for photolysis being dependent upon the specific conditions. As a worst case the half-life for photolysis in surface waters will be taken as 0 ( $k_{\text{photo}_{\text{water}}} = 0$ ). This gives a total first order rate constant for degradation in surface waters of zero.

#### Environmental concerns over the breakdown products of tetrachloroethylene in the aquatic environment

Concern has been expressed over the contamination of groundwater by vinyl chloride. The studies presented in this section show that vinyl chloride could be formed from tetrachloroethylene, under anaerobic conditions, by a process of reductive dechlorination. Hence it is possible that vinyl chloride detected in groundwater may have come from the degradation of tetrachloroethylene. However several studies also show that the process of dechlorination can continue under anaerobic conditions with the end products being ethene and ethane. Several other chlorinated solvents such as trichloroethylene are also likely to break down in the environment to vinyl chloride. Therefore while vinyl chloride may be formed from tetrachloroethylene in groundwater it is not possible to quantify the extent to which this process contributes to the levels of vinyl chloride found. Possible risks from this are not assessed in this risk assessment.

Some countries have expressed concern over the possible production of trichloroacetic acid in surface waters from the breakdown of tetrachloroethylene. From the studies presented here tetrachloroethylene appears to be relatively stable to degradation in surface waters with volatilisation being the main removal process. In anaerobic environments reductive dechlorination producing trichloroethylene, vinyl chloride and ultimately ethene and ethane appears to be the most likely degradation path. No evidence for the formation of trichloroacetic acid from tetrachloroethylene in water could be found in the available literature. Formation of trichloroacetic acid in air from the photodegradation of tetrachloroethylene has been discussed in Section 3.1.3.1.

### 3.1.4 Environmental distribution

Tetrachloroethylene is distributed between environmental compartments by volatilisation, precipitation and adsorption. Tetrachloroethylene is predominantly released and transported to the atmosphere. Based upon its environmental chemistry, computer models predict that the atmosphere will be the major sink for tetrachloroethylene. In this section the major distribution processes in the environment are reviewed and the results of computer modelling reported.

#### 3.1.4.1 Adsorption

Test results indicate that tetrachloroethylene can be adsorbed onto soils of varying organic carbon contents. The amounts adsorbed though are negligible, hence tetrachloroethylene is relatively mobile in groundwater in the absence of any removal processes.

Tetrachloroethylene can leach rapidly (retardation 2.5 times that of water, Wilson et al., 1981) through sandy soil (0.0087% organic matter) into groundwater. In a bank-filtration system tetrachloroethylene was rapidly transported to groundwater. It was estimated that only 0.01% was adsorbed to particulate matter (Schwarzenbach et al., 1983; Wilson et al., 1981; Zoeteman et al., 1980).

It has been reported that the sorption of non-ionic compounds such as tetrachloroethylene depends not only on the organic carbon content of the soils and sediments, but also on the nature of the organic matter. Grathwohl (1990) measured the sorption coefficient of tetrachloroethylene and different soil types. The highest level of adsorption was noted with anthracite (organic carbon 80.1%) and the lowest level with lignite (organic carbon 18.5%). The results indicated a decrease in sorption with increasing proportions of oxygen containing functional groups in natural organic substances (this effect has not been incorporated into the estimates of sorption in the risk assessment).

Biswas et al. (1992) measured the equilibrium constants for four types of granular media; sandy loam soil, organic top soil, peat moss and granular activated carbon. The level of adsorption increased as the carbon content increased, the least adsorption occurring with the sandy loam soil (1% organic carbon) and the greatest adsorption occurring with the granular activated carbon (74% organic carbon).

Doust and Huang (1992) found similar results. They measured the adsorption and desorption of tetrachloroethylene on a range of soils and clays. Sorption was found to be rapid in all cases. The highest degree of adsorption was noted in soils with high organic carbon content.

Soil/water partition coefficients for tetrachloroethylene of 6.5 over 24 hours and 7.3 over 72 hours have been reported for fine sand loam soil with aqueous solutions of 4.18-68.2 µg/l tetrachloroethylene (Pignatello, 1990).

Dilling et al. (1975) found that 22% of a solution containing 1 mg/l tetrachloroethylene was absorbed by bentonite clay (750 mg/kg) after 30 minutes. No further sorption was noted after this time. They also found that peat moss (500 mg/kg) absorbed 40% of 1 mg/l tetrachloroethylene solution in 10 minutes.

Partition coefficients for soil organic carbon/water adsorption have been reported at 20°C and these are presented in **Table 3.7**. Based upon the coefficients reported a log K<sub>oc</sub> of 2.40 (251 l/kg) is taken as representative for tetrachloroethylene.

Table 3.7 Soil organic carbon/water adsorption partition coefficients

Partition coefficient (log K <sub>oc</sub> )	Reference
2.14 (c)	Technical Guidance Document Method
2.42 (c)	Abdul et al.(1987)
2.13 (m)	Friesel et al. (1984)
2.32 (m) 2.36 (c)	Giger et al. (1983)
2.38 (c)	Kenaga (1980)
1.64-1.71 (m)	Lee et al. (1989)
2.56 (c)	Mabey et al. (1982)
2.34 (m) 2.31 (m) 2.54 (m)	Seip et al. (1986)
2.08 (m) 2.72 (m) 2.57 (c)	Zytner et al. (1989)

m measured value  
c calculated

Using a log K<sub>oc</sub> value of 2.40 the following partition coefficients have been calculated for tetrachloroethylene using the Technical Guidance Document method:

Partition coefficient solid-water in suspended matter	$K_{p_{susp}}$	25.1 l/kg
Partition coefficient solid-water in sediment	$K_{p_{sed}}$	12.6 l/kg
Partition coefficient solid-water in soil	$K_{p_{soil}}$	5.0 l/kg
Soil-water partitioning coefficient	$K_{soil-water}$	7.91 m <sup>3</sup> /m <sup>3</sup>
Suspended matter-water partitioning coefficient	$K_{susp-water}$	7.18 m <sup>3</sup> /m <sup>3</sup>
Sediment-water partitioning coefficient	$K_{sed-water}$	7.08 m <sup>3</sup> /m <sup>3</sup>

### 3.1.4.2 Volatilisation

Tetrachloroethylene released to surface waters is rapidly lost through volatilisation to the atmosphere. The volatilisation rate is dependent upon the degree of mixing in the water system and so removal will therefore be quicker in water systems with a high degree of mixing. The degree of mixing is dependent upon water movements and wind speed and this may lead to considerable differences between evaporation rates measured in the laboratory and evaporation rates measured in the environment. The evaporation half-life of tetrachloroethylene from field measurements and theoretical considerations is of the order of 1-10 days in rivers and 10 days to one month in lakes and ponds (ECETOC, 1999).

Using representative oxygen aeration rates for various bodies of water, the half-lives for evaporation of tetrachloroethylene have been calculated as: pond 5-12 days; river 3 hours - 7 days; lake 3.6-14 days (Lyman et al., 1981).

Dilling et al. (1975) measured the evaporation of tetrachloroethylene (1 mg/l) from solution at ambient temperatures. The half life was between 24-28 minutes with constant stirring at 200 rpm

and was around 90 minutes with stirring for 15 seconds every five minutes. In later experiments (Dilling, 1977), using the same technique, the measured half-life for evaporation was 20-27 minutes.

Volatilisation from water is reported as  $0.18 \mu\text{g}/\text{cm}^2/\text{hr}$  by Wilson et al. (1981). The half-life for evaporation from water is reported as 3.2 min under stirring conditions by Chiou et al. (1980).

Volatilisation of tetrachloroethylene was measured in a model mesocosm containing  $13 \text{ m}^3$  sea water plus associated planktonic and microbial communities. The tank was mixed for 2 hours, four times a day. The measured volatilisation half-lives were 11 days in winter, 25 days in spring and 14 days in summer (Wakeham et al., 1983).

Volatilisation of tetrachloroethylene from dry soil is likely to be rapid due to its high vapour pressure and low adsorption to soil. Volatilisation from a sandy soil is reported as  $0.103 \mu\text{g}/\text{cm}^2/\text{hour}$ . (Wilson et al., 1981)

The Henry's Law constant for tetrachloroethylene and the air-water partitioning coefficient are calculated as  $2,110 \text{ Pa}\cdot\text{m}^3/\text{mol}$  and  $0.893 \text{ m}^3/\text{m}^3$  respectively using EUSES with a vapour pressure of 1,900 Pa and a water solubility of 149 mg/l.

### 3.1.4.3 Precipitation

Tetrachloroethylene has the potential to dissolve in atmospheric water droplets and be deposited by rainout. This is supported by the fact that tetrachloroethylene has been detected in rainwater (Section 3.1.6.2, **Table 3.10**). Trichloroacetic acid formed by the photodegradation of tetrachloroethylene may be rained out, together with the hydrogen chloride formed. Trichloroacetic acid has been found in rainwater samples, soil samples and in spruce needles (see Appendix B).

### 3.1.4.4 Modelling

Using FUGMOD (OECD workshop) a Mackay Level I model the distribution of tetrachloroethylene in the environment was calculated as:

Air	99.69%
Water	0.23%
Soil	0.07%
Sediment	<0.01%
Biota	<0.01%

Using FUGMOD (OECD workshop) a Mackay Level III model the distribution of tetrachloroethylene in the environment was calculated as:

Air	76.39%
Water	23.32%
Soil	0.06%
Sediment	0.23%

A release rate of 1,000 kg/hour was used in the level III model. It was assumed that 90% of releases were to air and 10% to water.

The fate of tetrachloroethylene in a wastewater treatment plant, as estimated with EUSES, is: 91.2% to air; 6.54% to water; 2.2% to sludge; zero degradation.

### 3.1.4.5 Accumulation

Bioconcentration factors (BCFs) of approximately 40-50 have been reported for aquatic species with tetrachloroethylene. For Bluegill *Lepomis macrochirus* exposed to 3.43 µg/l tetrachloroethylene for 21 days at 16°C, a BCF of 49 is reported (Barrows et al., 1980). For Rainbow trout *Oncorhynchus mykiss* a BCF of 40 is reported (Neely et al., 1974). Based on these data, no significant bioaccumulation of tetrachloroethylene in fish is expected. The BCF of tetrachloroethylene in marine algae has been calculated by Wang et al. (1996) as 312 for *Heterosigma akashiwo* and 101 for *Skeletonema costatum*.

The log  $K_{ow}$  value for tetrachloroethylene is below 3, indicating a low potential for bioaccumulation. The BCF for fish is calculated as 28.2 by the Technical Guidance Document method, and this value is used in the risk assessment.

## 3.1.5 Aquatic compartment (incl. sediment)

### 3.1.5.1 Predicted environmental concentrations in water

The predicted environmental concentrations (PECs) of tetrachloroethylene in water have been calculated using the Technical Guidance Document and appropriate computer modelling programs.

#### 3.1.5.1.1 Calculation of $PEC_{local_{water}}$

Full details on how to calculate a  $PEC_{local_{water}}$  may be found in the Technical Guidance Document (Chapter 3 Sections 2.3.7. and 2.3.8.3.).

The  $PEC_{regional}$  is calculated in Section 3.1.5.1.2. as 0.011 µg/l, and is added to the local concentration estimates to give the  $PEC_{local}$ . Calculations for  $PEC_{stp}$  and  $PEC_{local_{sediment}}$  are described in Sections 3.1.5.1.3 and 3.1.5.1.4 respectively.

#### $PEC_{local_{water}}$ from tetrachloroethylene production and processing plants

The  $PEC_{local_{water}}$  has been calculated for each production and processing site detailed in Section 3.1.2.1. The results are presented in **Table 3.8**, together with the PECs for sediment and sewage treatment plant (stp).

**Table 3.8** PEClocal values for tetrachloroethylene production and processing sites

Site	PEC <sub>STP</sub> (µg/l)	PEC <sub>local</sub> <sub>water</sub> (µg/l)	PEC <sub>local</sub> <sub>sed</sub> (µg/kg)	Notes
A		0.02	0.12	Direct discharge after on-site treatment; not detected in effluent (detection limit 0.1 µg/l); 10 · dilution in receiving water assumed.
B	6.5 (on-site)	0.011	0.07	Monitored concentration in inflow to on-site STP; specific dilution factor in receiving water.
C	50 (on-site)	5	31	Monitored concentration in site effluent. Direct discharge, dilution · 10 assumed.
D	8.5 (on-site) 0.55 (off-site)	0.85 (d) 0.07 (STP)	5.3 (d) 0.4 (STP)	No information on whether site discharge goes to STP or surface water, so PECs calculated for both scenarios. For STP, default size and dilution factor used.
E	91 (on-site) 6 (off-site)	9.1 (d) 0.6 (STP)	57 (d) 3.7 (STP)	No information on whether site discharge goes to STP or surface water, so PECs calculated for both scenarios. For STP, default size and dilution factor used.
F	42 (on-site) 2.7 (off-site)	4.2 (d) 0.28 (STP)	26 (d) 1.8 (STP)	No information on whether site discharge goes to STP or surface water, so PECs calculated for both scenarios. For STP, default size and dilution factor used.

On-site The PEC applies to an on-site STP (if present)

Off-site The PEC applies to an STP away from the production/processing site.

(D) Values apply assuming a direct discharge of plant effluent to surface water.

(STP) Values apply assuming discharge of plant effluent to off-site STP.

#### PEC<sub>local</sub><sub>water</sub> from tetrachloroethylene use in dry cleaning operations

In calculating the PEC<sub>local</sub><sub>water</sub> for dry cleaning the emissions are based upon one dry cleaning unit using an open circuit machine fitted with activated carbon filters. This type of machine gives the highest release to water. The daily load of clothes cleaned is taken as 100 kg and the number of days operation per year as 300. For more details on the assumptions made see Section 3.1.5.1.2.

$$\text{Clocal}_{\text{eff}} = 0.12 \text{ µg/l (PEC}_{\text{STP}})$$

$$\text{PEC}_{\text{local}}_{\text{water}} = 0.02 \text{ µg/l}$$

$$\text{PEC}_{\text{local}}_{\text{sed}} = 0.13 \text{ µg/kg}$$

#### PEC<sub>local</sub><sub>water</sub> from tetrachloroethylene use in metal cleaning operations

In calculating the PEC<sub>local</sub><sub>water</sub> for metal cleaning the emissions are based on one small to medium metal processing factory using 10 tonnes tetrachloroethylene per year. For more details on the assumptions made see Section 3.1.5.1.3.

$$\text{Clocal}_{\text{eff}} = 16 \text{ µg/l}$$

$$\text{PEC}_{\text{local}}_{\text{water}} = 1.6 \text{ µg/l}$$

$$\text{PEC}_{\text{local}}_{\text{sed}} = 9.9 \text{ µg/l}$$

### 3.1.5.1.2 Calculation of $PEC_{\text{regional}}$ and $PEC_{\text{continental}}$

The regional and continental PECs for tetrachloroethylene have been calculated using the EUSES model. The input to the model for the continental and regional scenarios is detailed in Section 3.1.2.6. The following regional and continental PECs are calculated for tetrachloroethylene:

$PEC_{\text{regional}}(\text{surface water})$	0.011 $\mu\text{g/l}$
$PEC_{\text{continental}}(\text{surface water})$	0.0015 $\mu\text{g/l}$

### 3.1.5.1.3 Calculation of $PEC_{\text{stp}}$

The PEC for sewage treatment plant ( $PEC_{\text{stp}}$ ) is taken as being equivalent to the  $C_{\text{local,eff}}$ . For tetrachloroethylene the following  $C_{\text{local,eff}}$  are calculated:

Production and processing plants:	91 $\mu\text{g/l}$ (Site E as highest calculated value)
Dry cleaning:	0.12 $\mu\text{g/l}$
Metal cleaning:	16 $\mu\text{g/l}$

Note that the production site value above relates to an on-site treatment plant. The risk characterisation only considers off-site treatment plants, and so the highest concentration for production is 6  $\mu\text{g/l}$  (see **Table 3.8**).

### 3.1.5.1.4 Calculation of $PEC_{\text{sediment}}$

The  $PEC_{\text{local, sediment}}$  can be derived from the  $PEC_{\text{local, water}}$  assuming a thermodynamic partition equilibrium. The following equation is used to derive the  $PEC_{\text{local, sediment}}$ :

$$PEC_{\text{local, sed}} = \frac{K_{\text{susp-water}}}{RHO_{\text{susp}}} \times PEC_{\text{local, water}} \times 1000 \quad (\text{TGD 35})$$

Explanation of symbols:

$K_{\text{susp-water}}$  Suspended matter-water partition coefficient [7.18  $\text{m}^3/\text{m}^3$  Section 3.1.4.1]

$PEC_{\text{local, sed}}$  [mg/kg]

$PEC_{\text{local, water}}$  [Section 3.1.6.1.]

$RHO_{\text{susp}}$  Bulk density of suspended matter [1,150  $\text{kg}/\text{m}^3$  ]

The following  $PEC_{\text{local, sed}}$  are calculated for tetrachloroethylene:

$PEC_{\text{local, sed}}$  57  $\mu\text{g}/\text{kg}$  Production and use as a chemical intermediate  
(Site E. Direct discharge. Highest calculated value)

$PEC_{\text{local, sed}}$  0.13  $\mu\text{g}/\text{kg}$  Use in dry cleaning

$PEC_{\text{local, sed}}$  9.9  $\mu\text{g}/\text{kg}$  Use in metal cleaning

The calculated values for the assessment are given in **Table 3.8**.

### 3.1.5.1.5 Summary of PECs for tetrachloroethylene

**Table 3.9** summarises the calculated PECs for tetrachloroethylene. In the table direct releases to surface water are indicated. Where no information is available as to waste treatment both direct releases and releases via a wastewater treatment plant are considered.

Table 3.9 Summary of PECs for tetrachloroethylene

	PEC <sub>water</sub> (µg/l)	PEC <sub>stp</sub> (µg/l)	PEC <sub>sediment</sub> (µg/kg)
<b>Production and processing sites</b>			
Site A	0.02 (Direct, based on detection limit)		0.12 (Direct, based on detection limit)
Site B	0.01 (via WWTP)	8	0.07 (via WWTP)
Site C	5 (Direct)		31 (Direct)
Site D	0.85 (Direct) 0.07 (via WWTP)	0.55	5.3 (Direct) 0.4 (via WWTP)
Site E	9.1 (Direct) 0.6 (via WWTP)	6	57 (Direct) 3.7 (via WWTP)
Site F	4.2 (Direct) 0.28 (via WWTP)	2.7	26 (Direct) 1.8 (via WWTP)
Dry cleaning	0.02	0.12	0.13
Metal cleaning	1.6	16	9.9
Regional	0.011		0.07
Continental	0.0015		0.01

Note Only the PEC<sub>stp</sub> which refer to external treatment plants are taken forward in the risk assessment.

### 3.1.5.2 Measured levels in water

Tetrachloroethylene levels have been measured in a number of water systems; these levels are detailed in **Tables 3.10-3.15** (groundwater levels are reported in Section 3.1.7.2). In surface (river) waters the measured concentrations range from 0.01 µg/l to 168 µg/l, with typical concentrations below 5 µg/l. Measured concentrations in coastal and estuarine waters are below 3 µg/l and the majority of drinking water concentrations are below 0.5 µg/l. Rainwater concentrations are also low, with a high value of 0.15 µg/l reported for an industrial area.

**Table 3.14** details concentrations of tetrachloroethylene in municipal wastewaters. The data suggest that tetrachloroethylene is removed by a significant amount during the wastewater treatment process, probably by volatilisation.

**Table 3.10** Concentration of tetrachloroethylene in surface (river) water

Country	Concentration	Reference
Germany, Elbe	0.14-0.87 µg/l Mean 0.34 µg/l	Malle (1990)
Germany, Rhine	<0.1 µg/l	
Germany, Rhine	0.22-0.97 µg/l	Hellmann (1984)
Germany, Elbe	0.2-9.9 µg/l	
Germany, Mosel	0.8-1.3 µg/l	
Germany, Neckar	0.3-1.0 µg/l	
Germany, Wesser	<0.01-0.15 µg/l Mean 0.05 µg/l	Bohlen et al. (1989)
Finland, Aura	<0.1 µg/l	Kroneld (1986)
Finland, Aurajoki	0.01 µg/l	Reunanen and Kroneld (1982)
Netherlands, Rhine	0.3 µg/l	Van der Graff (1988)
Netherlands, Rhine	0.5 µg/l	Van de Meent D et al. (1986)
Netherlands, Rhine	0.05 µg/l	RIVM (1993)
Netherlands, Meuse	0.3 µg/l	
Italy (Industrial)	48-168 µg/l Mean 136 µg/l	Aggazzotti and Predieri (1986)
France, Rhone	0.15-0.25 µg/l	Marchand et al. (1988)
Switzerland, Glatt	0.22-1.3 µg/l Mean 0.59 µg/l	Ahel et al. (1984)
Switzerland, Chimlibach	0.01-0.18 µg/l Mean 0.06 µg/l	
Switzerland, Chriesbach	0.25-4.5 µg/l Mean 0.88 µg/l	
USA	0.1 µg/l	Staples et al. (1985)
United Kingdom, Severn Trent	(1992) 28 sampling sites, 971 samples, 74 detections. Mean 0.09 µg/l. Range 0.05-3.90 µg/l.  (1993) 47 sampling sites, 319 samples, 89 detections. Mean 0.08 µg/l. Range 0.05-1.1 µg/l.  (1994) 48 sampling sites, 493 samples, 152 detections. Mean 0.20 µg/l. Range 0.05-5.13 µg/l.  (1995(6 months)) 37 sampling sites, 193 samples, 69 detections. Mean 0.57 µg/l. Range <0.1-69.1 µg/l.	Personal Communication (NRA) (1995)
United Kingdom, Wales	40 sampling sites.  (1992) 804 samples. Mean 0.06 µg/l. Range <0.02-0.84 µg/l.  (1993) 507 samples. Mean 0.06 µg/l. Range <0.02-1.04 µg/l.  (1994) 483 samples. Mean 0.06 µg/l. Range <0.05-1.12 µg/l.	

Table 3.10 continued overleaf

**Table 3.10 continued** Concentration of tetrachloroethylene in surface (river) water

Country	Concentration	Reference
United Kingdom, Thames Water	43 sampling sites. (1992) 503 samples 64 detections Mean 0.45 µg/l Range <0.2-20 µg/l. (1993) 529 samples 22 detections Mean 0.57 µg/l Range <0.1-8.2 µg/l. (1994) 517 samples 164 detections Mean 0.25 µg/l Range <0.05-24.3 µg/l.	Personal Communication (NRA) (1995)
United Kingdom, Southern Water	86 sampling sites. (1992) 314 samples, 29 detections. Mean 0.10 µg/l. Range 0.02-7.1 µg/l. (1993) 339 samples, 18 detections. Mean 0.10 µg/l. Range 0.05-9.5 µg/l. (1994) 342 samples, 13 detections. Mean 0.21 µg/l. Range 0.05-4.0 µg/l.	
United Kingdom, Northumbria and Yorkshire	(1992-1995) 13 sampling sites, 1905 samples, 367 detections. Mean 0.14 µg/l. Range 0.05-5.3 µg/l	
United Kingdom, Northwest water	(1992-1995) 127 sampling sites, 1557 samples. 1 sample 146 µg/l, 12 samples >10<100 µg/l, 1544 samples nd-0.56 µg/l	
United Kingdom, Anglian water	(1992-1995) 60 sampling sites, 159 samples, 82 detections. Range nd-13 µg/l	

**Table 3.11** Tetrachloroethylene concentrations in coastal and estuarine water

Country	Concentration	Reference
Germany, Ostsee	<10-600 ng/l	Hellmann (1984)
Germany, North Sea	160-430 ng/l	
United Kingdom, North Sea	<2-19 ng/l Mean 3.8 ng/l 110-160 ng/l (Industrial)	Hurford et al. (1989)
North Sea	<90 ng/l Mean 9 ng/l	Van de Meent et al. (1986)
United Kingdom, Humber estuary	51.1-274 ng/l	Dawes and Waldock (1994)
United Kingdom, Tees estuary	<10-175 ng/l	
United Kingdom, Tyne estuary	<25-42.5 ng/l	
United Kingdom, Wear estuary	<25-72 ng/l	
United Kingdom, Mersey estuary	<25-52 ng/l	
United Kingdom, Poole harbour	< 25 ng/l	
United Kingdom, 10 sample points	< 10 ng/l	
United Kingdom, East Anglia -Estuary waters	36 sampling sites, 446 samples, 95 detections. Max conc 2.4 µg/l	Personal Communication (NRA) (1995)

Table 3.11 continued overleaf

**Table 3.11 continued** Tetrachloroethylene concentrations in coastal and estuarine water

Country	Concentration	Reference
Sweden, Stenungsand	2.0-3.6 ng/l	Abrahamsson et al. (1989)
France, Rhone delta	150-250 ng/l	Marchand et al. (1988)
France, Lyon gulf	<0.5-0.8 ng/l	
France, Provence	1.1 ng/l	
France, Corsica	0.6 ng/l	
France, Var estuary	6.3 ng/l	
France, Gulf of Fos	6.2 ng/l	
Mediterranean, Open sea	0.5-0.7 ng/l	
France, Loire estuary	4-60 ng/l	Marchand et al.(1986)
Greece, Gulf of Thermaikos	0.27-2.10 µg/l	Fytianos et al. (1985)
Greece, Gulf of Kavala	0.39-3.00 µg/l	

**Table 3.12** Tetrachloroethylene concentrations in drinking water

Country	Concentration	Reference
Germany	< 0.001 µg/l (51% of drinking water supplies) 0.001-0.5 µg/l (40% of drinking water supplies) > 0.5 µg/l (9% of drinking water supplies)	Bauer (1991)
Germany	1.3 µg/l	Lahl et al. (1981)
United Kingdom	29 water companies. 2682 samples, 454 detections (dl 0.1-1.0 µg/l) Max Conc. 12.2 µg/l	Personal Communication (DWI) (1995)
Finland	0.02 µg/l (Water disinfected with Cl <sub>2</sub> )	Reunanen and Kroneld (1982)
Finland	≤0.05 µg/l	Kroneld (1986)

**Table 3.13** Concentration of tetrachloroethylene in rainwater

Country	Concentration	Reference
Germany	24 ng/l	Kubin et al. (1989)
Germany	80 ng/l (As mist)	
Germany	2-20 ng/l	Renner et al. (1990)
Switzerland	<10-115 ng/l	Czuczwa et al. (1988)
United Kingdom (Industrial)	150 ng/l	Atri (1985)
Netherlands	< 5 ng/l	Van de Meent et al. (1986)
USA	21 ng/l	Kawamura and Kaplan (1983)

**Table 3.14** Concentrations of tetrachloroethylene in municipal wastewaters

Country	Concentration		Reference
	Influent	Effluent	
Germany, Seehausen		0.23-3.1 µg/l	Bohlen et al. (1989)
Germany, Delmenhorst		0.010-3.1 µg/l	
Germany, Osterholz		Max 0.220 µg/l	
Germany Farge, Unterweser		0.03-0.080 µg/l	
Germany, Bremerhaven		0.02-5.9 µg/l	
Germany, Klockner-Werke		Max 0.09 µg/l	
United Kingdom		Typical n.d.- 2 µg/l Max 144 µg/l	Brown (1978)
France, Toulon	19.8 µg/l	8.5 µg/l	Marchand et al. (1989)
France, Mortaix	1.96 µg/l	0.41 µg/l	
France, Nantes (north)	7.8-18.1 µg/l	Not detected	
France, Nantes (south)	1.05-22.96 µg/l	0.01-0.39 µg/l	
France, Marseille	13.3 µg/l		
France, Cortiou		0.07-0.79 µg/l	Marchand et al. (1988)
France, Nice		0.31 µg/l	
Switzerland		0.03-6.4 µg/l Mean 0.16-1.0 µg/l	Ahel et al. (1984)
Switzerland	15 µg/l	1 µg/l	Fahrni (1984)
USA		Median 5 µg/l	Staples et al. (1985)

**Table 3.15** Concentration of tetrachloroethylene from industrial activities

Country	Industrial activity	Concentration	Reference
France	Manufacture of ceiling coating material	4 µg/l (effluent)	DRIRE Franche Comté (1996)  Tetrachloroethylene detected in 14 out of 46 effluents from industrial sites
	Metal working	2-75 µg/l (effluent)	
	Packaging of chemical products	10 µg/l (effluent)	
	Treatment of industrial effluents	4 µg/l (effluent)	
	Chemical industry	508 µg/l (effluent)	
	Surface treatment	4-5 µg/l (effluent)	
	Wood preservation	6-8 µg/l (effluent)	
	Car equipment manufacture	7-29 µg/l (effluent)	
	Paint manufacture	4 µg/l (effluent)	

Table 3.15 continued overleaf

Table 3.15 continued Concentration of tetrachloroethylene from industrial activities

Country	Industrial activity	Concentration	Reference
Finland	Dry cleaning	2.5 to 580,000 µg/l (Contact water) Arithmetic mean 88 µg/l Geometric mean 2.5 µg/l	Finnish Environment Agency (personal communication) (1996)

### 3.1.5.3 Measured levels in sediment

Tetrachloroethylene has been measured in sediment samples in Germany at 1-50 µg/kg (wet weight) by Alberti (1989) and in the USA at < 5 µg/kg (wet weight) by Staples et al. (1985).

### 3.1.5.4 Comparison of PECs and measured levels of tetrachloroethylene in the aquatic compartment

PECs have been calculated for all the major uses of tetrachloroethylene and these are summarised in **Table 3.9**. The highest  $PEC_{local,water}$  is 9.1 µg/l; this is calculated for production site E assuming no on-site treatment of waste effluent. Measured levels of tetrachloroethylene in surface waters are summarised in **Table 3.10**; the majority of these measurements are very low with concentrations generally below 5 µg/l and with the majority below 1 µg/l. The highest measured results are reported by Aggazzotti and Predieri (1986), and come from samples taken from a canal which collects wastewater from the City of Modena in Italy. This situation is not considered to be representative of surface waters within the EU. A value of 5 µg/l will be taken as a realistic worst case in the risk characterisation section.

The  $PEC_{stp}$  values range from 0.12 to 91 µg/l. The higher values are calculated for industrial wastewater treatment plants. Measured levels of tetrachloroethylene in the influent of municipal wastewaters are reported in **Table 3.14** and range from 1-23 µg/l. The  $PEC_{stp}$  values would appear to be in reasonable agreement with the measured levels. The  $PEC_{stp}$  values for off-site treatment plants are taken forward to the risk characterisation.

The highest  $PEC_{sediment}$  is 57 µg/kg (wet weight) for a production site. Only a few measured levels of tetrachloroethylene in sediment are reported; the highest measured level is 50 µg/kg (wet weight). The  $PEC_{sediment}$  is close to the measured level and appears to be acceptable.

## 3.1.6 Terrestrial compartment

### 3.1.6.1 Calculation of PECs for soil

Three routes by which a substance can reach the terrestrial compartment are considered in this assessment: direct application, deposition from air and sewage sludge application. Direct releases of trichloroethylene to the terrestrial compartment are expected to be small; concentrations resulting from the other two routes have been calculated using EUSES (Appendix C). The inputs from air and from sludge are derived from the emissions to air and water respectively, described in Section 3.1.2. The estimated concentrations in the different soil types are given in **Table 3.16**.

Concentrations in groundwater under agricultural soil are also given. The percentage of steady state reached after ten years is 100%.

**Table 3.16** Local PECs for soil and groundwater

Process	PEC <sub>local,soil</sub> (µg/kg)			PEC <sub>local,grw</sub> (µg/l)
	Agricultural soil (30 day average)	Agricultural soil (180 day average)	Grassland soil (180 day average)	
Production	3.9	2.3	2.0	0.5
Dry cleaning	0.06	0.05	0.05	0.01
Metal cleaning	2.5	0.5	0.17	0.1

\* Production estimate is based on combination of largest individual release to air and to water from actual sites (not necessarily From the same site)

The EUSES model and parameters described earlier have been used to calculate the regional and continental concentrations in **Table 3.17**.

**Table 3.17** PEC<sub>regional</sub> and PEC<sub>continental</sub> for soil

	PEC <sub>regional,soil</sub> (µg/kg)	PEC <sub>continental,soil</sub> (µg/kg)
Natural soil	$4.6 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$
Agricultural soil	$5.3 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$
Industrial soil	$4.6 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$
Pore water (µg/l)	$1.1 \cdot 10^{-3}$	$4 \cdot 10^{-4}$

### 3.1.6.2 Measured levels of tetrachloroethylene in soil and groundwater

The concentration of tetrachloroethylene in soil air has been reported by Frank et al. (1989) as between 2.1–4.5 µg/m<sup>3</sup>. The samples were taken in Germany. No other measured soil levels are reported. Measured levels in groundwater are given in **Table 3.18**.

**Table 3.18** Concentration of tetrachloroethylene in groundwater

Country	Concentration	Reference
Germany, Düsseldorf	Mean 0.9 µg/l Contaminated land 370 µg/l	Sagunski et al. (1987)
Germany	10% samples > 1 µg/l 4% samples > 10 µg/l	Bauer et al. (1991)
Germany (Contaminated land)	0.2-1.3 µg/l	Heil et al. (1989)
Germany (Contaminated land)	<1-1,300 µg/l	Leschber et al. (1990)
Italy	4-10 µg/l Mean 7.8 µg/l	Aggazzotti and Predieri (1986)

Table 3.18 continued overleaf

Table 3.18 continued Concentration of tetrachloroethylene in groundwater

Country	Concentration	Reference
Netherlands	168 sites <0.01 µg/l 52 sites 0.01-0.1 µg/l 8 sites 0.1-1.0 µg/l 2 sites 1.0-10 µg/l 2 sites >10 µg/l	Trowborst (1981)
United Kingdom, East Anglia	43 sampling sites, 159 samples, 82 detections. Max conc 13 µg/l	Personal Communication (NRA) (1995)
United Kingdom	Chalk groundwater: 19 samples 15 detections Max 3.5 µg/l Mean 1.0 µg/l Sandstone groundwater: 3 samples 1 detection 0.26 µg/l	Fielding et al. (1981)
Switzerland	Max 17.5 µg/l Mean 0.8 µg/l	Fahrni (1984)
USA	Private wells (1.5 miles from waste disposal site): 63 samples, 3 detections (detection limit 0.2 µg/l), median 2.5 µg/l, maximum 4.7 µg/l. Community wells: 97 samples, 2 detections (detection limit 0.2 µg/l), median 1.8 µg/l, maximum 3.0 µg/l.	Goodenkauf and Atkinson (1986)

In 1999 tetrachloroethylene was found in approximately 2% of samples taken in the general groundwater monitoring part of the general Danish Monitoring Programme NOVA ( $n \approx 1,000$ ), whereas the detection frequency in drinking water wells was 5% ( $n \approx 1,700$ ) (Personal Communication, 2001).

Groundwater concentrations of tetrachloroethylene vary widely, but generally they appear to be higher than surface water concentrations. This could be due to the fact that measurements in groundwater are often taken where a problem (e.g. spill) is thought to exist. The majority of groundwater levels are below 10 µg/l, though concentrations as high as 1,300 µg/l have been reported for a contaminated site.

### 3.1.6.3 Comparison of PECs and measured levels of tetrachloroethylene in the terrestrial compartment

The  $PEC_{\text{groundwater}}$  is calculated as 0.01-0.5 µg/l. The maximum measured levels of tetrachloroethylene in groundwater are 17.5 µg/l and 1,300 µg/l for contaminated soil. The majority of measurements are below the detection limit of 0.01-0.2 µg/l. The  $PEC_{\text{groundwater}}$  values are within the range of the majority of measured levels reported. The measured levels from contaminated sites are not taken as representative for the purposes of this risk assessment, and so are not considered in the risk characterisation.

### 3.1.7 Atmospheric compartment

The majority of releases of tetrachloroethylene will be to the atmosphere. The atmospheric reactions of tetrachloroethylene are of great importance in assessing the environmental impact of tetrachloroethylene and these are reviewed in Section 3.1.8.

### 3.1.7.1 Calculation of PEC<sub>local,air</sub>

The PEC<sub>local,air</sub> is calculated using a gaussian plume model with standard parameters. The method used is described in more detail in the TGD Chapter 3 Section 2.3.8.2. In calculating the PEC<sub>local,air</sub> the emissions from point sources and sewage treatment plants need to be taken into consideration. The concentration on the regional scale (PEC<sub>regional</sub>) is taken to represent the background concentration and is therefore added to the local concentration. The sewage treatment plant is assumed to be a point source and the concentration of the chemical is calculated at a 100 m distance from it. The maximum from the two concentrations (direct release and via sewage treatment plant) is used as the PEC<sub>local,air</sub>.

The indirect emission of tetrachloroethylene from a sewage treatment plant to air is calculated from the fraction of emission to water directed to air by the sewage treatment plant (EUSES Fstp<sub>air</sub> 0.91). For tetrachloroethylene the largest local release to a sewage treatment plant is 0.3 kg/day (metal cleaning); this gives an indirect emission to air from the sewage treatment plant of 0.25 kg/day. This value is significantly less than direct emissions to air, therefore direct emissions will be used to calculate the PEC<sub>local,air</sub>.

The direct emission to air is multiplied by the concentration in air at a source strength of 1 kg/day (Cstd<sub>air</sub> 2.78 · 10<sup>-4</sup> mg/m<sup>3</sup>) to give the local air concentration. The local concentration can be converted to an annual concentration if the number of days emission per year are known.

$$C_{local,air} = \max(E_{local,air}, E_{stp,air}) \times C_{std,air} \quad (\text{TGD 25})$$

$$C_{local,air,ann} = C_{local,air} \times \frac{T_{emission}}{365} \quad (\text{TGD 26})$$

Direct releases to air have been estimated for six production and processing sites, and for use in dry cleaning and metal cleaning. The PEC<sub>air</sub> for the regional and continental scenarios are calculated using EUSES. The regional PEC is taken as a background concentration and added to the local concentrations to give the values for PEC<sub>local</sub>. **Table 3.19** summarises the PEC<sub>air</sub> calculated for each production/chemical intermediate processing site, for dry cleaning, metal cleaning and for the regional and continental scales.

Table 3.19 PEC<sub>air</sub>

	C <sub>local,air</sub> (µg/m <sup>3</sup> )	C <sub>local,air,ann</sub> (µg/m <sup>3</sup> )	PEC <sub>air,ann</sub> (µg/m <sup>3</sup> )
Site A*	204	167	168 (36)
Site B	7.8	6.4	7.3
Site C	0.42	0.35	1.2

Table 3.19 continued overleaf

Table 3.19 continued PEC<sub>air</sub>

	Clocal <sub>air</sub> (µg/m <sup>3</sup> )	Clocal <sub>air,ann</sub> (µg/m <sup>3</sup> )	PEC <sub>air,ann</sub> (µg/m <sup>3</sup> )
Site D	0.00056	0.00046	0.88
Site E	3.3	2.7	3.6
Site F	0.36	0.29	1.2
Dry cleaning	4.3	3.5	4.4
Metal cleaning	12	6.9	7.7
PEC <sub>continental</sub>			0.32

\* Value for PEC in brackets is measured, see Section 3.1.8.2.

### 3.1.7.2 Measured levels

**Table 3.20** gives details of measured atmospheric concentrations of tetrachloroethylene. The majority of measured levels are below 10 µg/m<sup>3</sup>, with most below 1 µg/m<sup>3</sup>.

Bruckmann et al. (1989) sampled air from 12 sites in Hamburg, between April 1986 and April 1987. The activities near to the sites were characterised. Three locations were found to have significantly higher concentrations than the others. These were located near to a chemical laundry (dry cleaning), a rubber factory, and an industrial area with metal working industry and small chemical factories. The highest yearly average concentration was 71 µg/m<sup>3</sup>. The overall average concentration was 3.5 µg/m<sup>3</sup>.

Monitoring of air concentrations at the site boundary for site A (production and processing) was carried out over a four week period when both areas of activity were operating. Samples were taken over 24-hour periods for 28 consecutive days. The average daily mean concentration was 36 µg/m<sup>3</sup>.

Table 3.20 Atmospheric concentrations of tetrachloroethylene

Country	Concentration (all as µg/m <sup>3</sup> )	Reference
Germany	Individual means 1.8-70.8; overall mean 13 Excluding sites near to point sources, mean 3.5 (see text)	Bruckmann et al. (1989)
	1.2-2.6	Kubin et al. (1989)
	Mauzenberg 0.89; Bernstein 0.78; Sulzbach 0.63; Schönbuch 0.69. All mean values, Aug-Sept 1986	Frank and Frank (1988)
	Mauzenberg 1.9; Bernstein 2.5; Schönbuch 0.9. All mean values, Sept 1987.	Frank et al. (1989)
	Southwest Germany (four sites): mean 0.9, range 0.2-20, 1986- 1988.	Frank and Frank (1990)
	Centre of Tübingen: mean 2, range 1-120 Rastatt, Black Forest: mean 1, range 0.2-9	Frank et al. (1991)

Table 3.20 continued overleaf

Table 3.20 continued Atmospheric concentrations of tetrachloroethylene

Country	Concentration (all as $\mu\text{g}/\text{m}^3$ )	Reference
Germany	4.2-5.1 (contaminated site)	König (1989)
	0.2-1.8; mean 0.77 (rural) 0.74-23; mean 9.02 (urban)	Güthner et al. (1990)
	Breman 1.12; Bochum 6.1; Munich 4.8; urban 1.8; rural 0.79-3.0	Lahl et al. (1981)
Madeira	< 0.3	Frank et al. (1991)
Portugal	0.2-1.0	Frank et al. (1991)
Netherlands	0.18-0.42 (Background) 0.45-0.53 (City) 0.78 (Street side)	RIVM (1993)
	Mean 0.61-2.4 Max 3.6-38.6	Guicherit and Schulting (1985)
Italy	Samples from 'urban canyon' in Turin, 1988. 1.0-71.2 Mean 13.6 Cold weather 1.3-13.1 Mean 4.8 Warm weather	Gilli et al. (1990)
Switzerland	0.14	Fahrni (1984)
Japan	4.2 (Industrial site - yearly average) 4.5 (Commercial site - yearly average) 2.7 (Residential site -yearly average)	Urano et al. (1988)

BUA (1993) reviewed the measured levels of tetrachloroethylene in Germany in 1988; concentrations in rural areas ranged between 0.5 and 2  $\mu\text{g}/\text{m}^3$ , and concentrations in urban areas ranged between 2 and 15  $\mu\text{g}/\text{m}^3$ .

More recent monitoring in the Rhine valley in 1996 showed a maximum value from one site (Freiburg) of 2.9  $\mu\text{g}/\text{m}^3$ ; the highest 98<sup>th</sup> percentile value for a sampling site was 1.8  $\mu\text{g}/\text{m}^3$  at Karlsruhe (UMEG, 1996). Data from 1998 for the Nordrhein-Westfalen region, including the industrialised area between Dortmund and Cologne, showed a peak value of 2.4  $\mu\text{g}/\text{m}^3$ , with average values generally below 0.5  $\mu\text{g}/\text{m}^3$  (LUA, 1999).

Global background concentrations were measured by Koppman et al. (1993) in 1989, as 13±6 pptv (0.09  $\mu\text{g}/\text{m}^3$ ) for the Northern hemisphere and 2.7±0.4 pptv (0.02  $\mu\text{g}/\text{m}^3$ ) for the Southern hemisphere.

Indoor air levels have been measured at dry cleaners in order to quantify occupational exposure (see Section 4, which will be added later), and in buildings adjacent or close to dry cleaning premises. In all the surveys, levels were found to be higher in or near dry cleaners which used open systems. Section 4 (which will be added later) gives further details of fugitive emissions of tetrachloroethylene from dry cleaners to neighbouring buildings, and discusses the level of tetrachloroethylene to be used in the assessment of indirect exposure through this route.

### 3.1.7.3 Comparison of PECs and measured levels

The calculated  $\text{PEC}_{\text{air}}$  are summarised in **Table 3.19**. For production and processing sites the calculated values vary from 0.88  $\mu\text{g}/\text{m}^3$  to 168  $\mu\text{g}/\text{m}^3$ . For use of tetrachloroethylene in dry

cleaning and metal cleaning the resulting concentrations are calculated as 4.4 and 7.7  $\mu\text{g}/\text{m}^3$  respectively. The regional concentration is calculated as 0.88  $\mu\text{g}/\text{m}^3$ .

**Table 3.20** summarises the measured levels of tetrachloroethylene reported. The majority of measurements are below 10  $\mu\text{g}/\text{m}^3$  with most below 1  $\mu\text{g}/\text{m}^3$ . Those measurements that are higher than 10  $\mu\text{g}/\text{m}^3$  appear to have been taken from industrial sites, and the highest value reported among these is 71  $\mu\text{g}/\text{m}^3$ . As noted, these are not directly comparable with the calculated levels. The measured level of 36  $\mu\text{g}/\text{m}^3$  at the site boundary for site A is somewhat lower than the calculated concentration, which is itself derived from monitored emissions. The difference probably relates to actual site characteristics in comparison to the assumptions in the calculation. The monitoring data are considered to be valid, and so are preferred to the calculated value. The measured value is higher than the concentration calculated for any of the other production or processing sites, and so will be used as being representative of a realistic worst case.

The measured levels and PECs would appear to be in reasonable agreement with each other, with the majority of measured levels agreeing with the  $\text{PEC}_{\text{regional}}$ . The recent measured levels from urban areas appear to be in reasonable agreement with the PECs calculated for industrial uses (including dry cleaning); some older measurements indicate higher levels in the past. As there are no comprehensive data sets of measurements of tetrachloroethylene in urban air from the recent past, the calculated values will be taken forward for the risk characterisation together with the measured level for site A.

Production/processing site (measured):	36 $\mu\text{g}/\text{m}^3$
Dry cleaning calculated value:	4.4 $\mu\text{g}/\text{m}^3$
Metal cleaning calculated value:	7.7 $\mu\text{g}/\text{m}^3$
Regional calculated value:	0.88 $\mu\text{g}/\text{m}^3$

### 3.1.8 Secondary poisoning

Tetrachloroethylene has a  $\log K_{\text{ow}}$  less than 3 and aquatic studies confirm that it has a low potential for bioaccumulation. The indications are that tetrachloroethylene will not accumulate in the food chain and therefore an assessment of non-specific exposure will not be carried out.

Tetrachloroethylene has been measured in a range of biota and food products (see Section 3.1.8.1). This is particularly important when considering the effects on human health. The levels observed in aquatic species are likely to arise due to exposure of the organism to tetrachloroethylene in water. For plants the concentrations observed may be due to atmospheric deposition and water adsorption. The levels observed in food products are likely to arise due to exposure to atmospheric tetrachloroethylene. A number of studies have been conducted measuring tetrachloroethylene levels in food products near possible sources of contamination, in particular dry cleaners. It should be noted that the observed levels are thought to be due to exposure to tetrachloroethylene not due to accumulation in the food chain.

### 3.1.8.1 Predicted environmental levels in biota and indirect exposure of humans via the environment

**Table 3.21** details the predicted levels of tetrachloroethylene in biota and food products calculated using EUSES. In the calculations the concentrations resulting from production and processing, dry cleaning and metal cleaning are calculated separately. The calculation for production and processing is based on the largest emissions to air and to water as described in Section 3.1.5.1.1; however, the highest estimated concentration in water from the site-specific calculations is used to estimate uptake from drinking water and in fish, and the air concentration used is the measured value for site A. This is therefore a composite scenario and a worst case combination.

The daily human intake of tetrachloroethylene is estimated by EUSES. The estimation is based upon typical human consumption and inhalation rates. The total human dose of tetrachloroethylene is calculated as 0.01 mg/kg/day for the local environment (production and processing) and  $2.5 \cdot 10^{-4}$  mg/kg/day for the regional environment.

The calculations performed by EUSES are in agreement with the procedure described in the Technical Guidance Document for assessing the indirect exposure of humans via the environment.

### 3.1.8.2 Measured levels in biota

**Table 3.22** details levels of tetrachloroethylene measured in biota.

### 3.1.8.3 Measured levels in food

**Table 3.23** details tetrachloroethylene levels measured in food. Note that measured levels in drinking water were given in **Table 3.12**.

Table 3.21 Calculated levels of tetrachloroethylene in human intake media (from EUSES, but assuming 100% availability from air)

Compartment	Process	Concentration	Uptake (mg/kg/d)
Local			
Air (mg/m <sup>3</sup> )	Production	0.036	0.01
	Dry cleaning	$4.4 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$
	Metal cleaning	$7.8 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$
Drinking water (mg/l)	Production	$3.8 \cdot 10^{-3}$	$1.1 \cdot 10^{-4}$
	Dry cleaning	$1.1 \cdot 10^{-5}$	$3.0 \cdot 10^{-7}$
	Metal cleaning	$4.6 \cdot 10^{-4}$	$1.3 \cdot 10^{-5}$
Fish (mg/kg)	Production	0.212	$3.5 \cdot 10^{-4}$
	Dry cleaning	$5.4 \cdot 10^{-4}$	$8.9 \cdot 10^{-7}$
	Metal cleaning	0.026	$4.2 \cdot 10^{-5}$

Table 3.21 continued overleaf

Table 3.21 continued Calculated levels of tetrachloroethylene in human intake media (from EUSES, but assuming 100% availability from air)

Compartment	Process	Concentration	Uptake (mg/kg/d)
<b>Local</b>			
Plant (leaves) (mg/kg)	Production	$2.0 \cdot 10^{-4}$	$3.4 \cdot 10^{-6}$
	Dry cleaning	$2.4 \cdot 10^{-5}$	$4.2 \cdot 10^{-7}$
	Metal cleaning	$4.3 \cdot 10^{-5}$	$7.3 \cdot 10^{-7}$
Plants (roots) (mg/kg)	Production	$2.2 \cdot 10^{-3}$	$1.2 \cdot 10^{-5}$
	Dry cleaning	$4.8 \cdot 10^{-5}$	$2.6 \cdot 10^{-7}$
	Metal cleaning	$4.8 \cdot 10^{-4}$	$2.7 \cdot 10^{-6}$
Meat (mg/kg)	Production	$3.9 \cdot 10^{-5}$	$1.7 \cdot 10^{-7}$
	Dry cleaning	$4.6 \cdot 10^{-6}$	$2.0 \cdot 10^{-8}$
	Metal cleaning	$8.3 \cdot 10^{-6}$	$3.6 \cdot 10^{-8}$
Milk (mg/kg)	Production	$3.7 \cdot 10^{-5}$	$2.9 \cdot 10^{-7}$
	Dry cleaning	$4.3 \cdot 10^{-6}$	$3.4 \cdot 10^{-8}$
	Metal cleaning	$7.7 \cdot 10^{-6}$	$6.2 \cdot 10^{-8}$
Total human dose	Production		0.01
	Dry cleaning		$1.3 \cdot 10^{-3}$
	Metal cleaning		$1.7 \cdot 10^{-3}$
<b>Regional</b>			
Air		$8.8 \cdot 10^{-4}$ mg/m <sup>3</sup>	$2.5 \cdot 10^{-4}$
Drinking water		$5.6 \cdot 10^{-6}$ mg/l	$1.6 \cdot 10^{-7}$
Fish		$3.2 \cdot 10^{-4}$ mg/kg	$5.2 \cdot 10^{-7}$
Plant (leaves)		$4.9 \cdot 10^{-6}$ mg/kg	$8.3 \cdot 10^{-8}$
Plants (roots)		$5.2 \cdot 10^{-6}$ mg/kg	$2.81 \cdot 10^{-8}$
Meat		$9.2 \cdot 10^{-7}$ mg/kg	$4 \cdot 10^{-9}$
Milk		$8.5 \cdot 10^{-7}$ mg/kg	$6.8 \cdot 10^{-9}$
Total			$2.5 \cdot 10^{-4}$

Table 3.22 Measured levels of tetrachloroethylene in biota

Species	Concentration	Comments	Reference
Algae	13-20 µg/kg	Wet tissue concentration. Water concentration 0.12 µg/l.	Pearson and McConnell (1975)
Invertebrates	0.05-15 µg/kg		

Table 3.22 continued overleaf

Table 3.22 continued Measured levels of tetrachloroethylene in biota

Species	Concentration	Comments	Reference
Crab	8-9 µg/kg	Wet tissue concentration. Water concentration 0.12 µg/l.	Pearson and McConnell (1975)
Fish	0.3-41 µg/kg		
Mollusc bodies and organs	0-176 µg/kg	Dry body weight. Irish Sea.	Dickson and Riley (1976)
Fish organs	≤ 43 µg/kg	Body weight Irish Sea	
Fish	0.3 µg/kg	Body weight Finland	Kroneld (1989)
Fish	31% ≤ 1 µg/kg 25% 1-10 µg/kg 26% 10-25 µg/kg 13% 25-100 µg/kg 4% >100 µg/kg	Germany	Binnemann et al. (1983)
Fish	Sprat 140-2400 µg/kg Eel 170-190 µg/kg Whiting 120-220 µg/kg Perch 15 µg/kg Roach 25 µg/kg Cod 65 µg/kg Freshwater herring 50 µg/kg Trout 15 µg/kg	Norway Wet weight	Ofstad et al. (1981)
Biota	< 50 µg/kg	USA Wet weight	Staples et al. (1985)
Plants (spruce needles)	15-26 µg/kg (1 km from industry) 12-16 µg/kg (10 km from industry) not detected (Rural)	United Kingdom	Brown et al. (1993)
Spruce needles	≤ 3.5 µg/kg	Germany	Frank and Frank (1989)

Table 3.23 Tetrachloroethylene levels in food

Sample	Concentration (µg/kg) (nd - not detected)	Reference
Dairy products	0.3-13	McConnell et al. (1975)
	nd (detection limit 2.3)	Entz and Hollifield (1982)
Milk	0.2	Kroneld (1989)
Fresh milk	0.3	McConnell et al. (1975)

Table 3.23 continued overleaf

Table 3.23 continued Tetrachloroethylene levels in food

Sample	Concentration ( $\mu\text{g}/\text{kg}$ ) (nd - not detected)	Reference
Cheshire cheese	2	McConnell et al. (1975)
English butter	13	
Eggs	nd	
Margarine	7	
Butter (Supermarket near dry cleaners)	21	Vieths et al. (1988)
Butter (Private house near dry cleaners)	120	
Cheese (Supermarket near dry cleaners)	36	
Ice-cream (Supermarket near dry cleaners)	340-18,000	
Margarine (Supermarket near dry cleaners)	110	
Margarine (Private house near dry cleaners)	30-5,070	
Margarine (Private house near dry cleaners)	33,000	Vieths et al. (1987)
Milk (Private house near dry cleaners)	790	
Eggs(Private house near dry cleaners)	440	
Parmesan cheese (Private house near dry cleaners)	2,670	
Butter	1.4-38	Heikes (1987)
Margarine	1.3-37	
Cheese	0.94-9.4	
Butter	300-600	Gulyas et al. (1988)
Milk	10	Zimmerli et al. (1982)
Butter and cheese	120-500	
Eggs	380	
Meat	0.9-5	McConnell et al. (1975)
	1.1	Kroneld (1989)
	nd (detection limit 4.6)	Entz and Hollifield (1982)
	3-3,490	Zimmerli et al. (1982)
Oils and fats	0.01-7	McConnell et al. (1975)
	nd (detection limit 13)	Entz and Hollifield (1982)
Beverages	nd-3	McConnell et al. (1975)
	0.01-0.3	Kroneld (1989)
	nd (detection limit 0.5)	Entz and Hollifield (1982)
Biscuits	3.5-3.8	Heikes (1987)
Granola (Cereal)	3.3-25	
Corn chips	2.7-9.7	

Table 3.23 continued overleaf

Table 3.23 continued Tetrachloroethylene levels in food

Sample	Concentration ( $\mu\text{g}/\text{kg}$ ) (nd - not detected)	Reference
Cereal	nd-3.1	Heikes (1987)
Peanut butter	0.77-3.5	
Drinking water	nd-0.084	
Fruit and vegetables	nd-2	McConnell et al. (1975)
Fresh bread	1	McConnell et al. (1975)

### 3.1.8.4 Indirect exposure of humans via the environment

The indirect exposure of humans via the environment has been calculated using a combination of the measured levels reported in Sections 3.1.8.2-3, 3.1.8, and 3.1.6.1 and the predicted levels reported in Section 3.1.8.1. Exposure through air in dwellings close to dry cleaning establishments is based on the levels selected in Section 4 (which will be added later). The results are summarised in **Table 3.24** and repeated in Section 4 in the human health section.

In **Table 3.24** the parameters for daily intake are taken from Chapter 2 Appendix 2 of the TGD. The daily dose is calculated by multiplying the concentration in medium by daily intake of medium and then dividing by the body weight (standard body weight 70 kg). Bioavailability is taken as 1 for oral intake and for inhalation. The total daily intake is used in Section 4 (which will be added later) to consider the effects of indirect exposure of humans via the environment to tetrachloroethylene. N.B. Section 4 contains further details of measured levels in premises above dry cleaning establishments.

Table 3.24 Daily human intake via indirect exposure to tetrachloroethylene in the environment.

Medium	Concentration	Daily intake	Dose ( $\mu\text{g}/\text{kg}_{\text{bw}}/\text{d}$ )	Reference
Air: Background	0.88 $\mu\text{g}/\text{m}^3$	20 $\text{m}^3/\text{day}$	0.25	PEC <sub>regional,air</sub> EUSES
Air: Fugitive emissions from dry cleaners	5,000 $\mu\text{g}/\text{m}^3$	20 $\text{m}^3/\text{day}$	1,429	Reinhard et al. (1989) Altmann et al. (1995)
Air: production plants	36 $\mu\text{g}/\text{m}^3$	20 $\text{m}^3/\text{day}$	10	PEC Site A (Section 3.1.8.)
Drinking water (reasonable worst case)	12.2 $\mu\text{g}/\text{l}$	0.002 $\text{m}^3/\text{day}$	0.35	Highest measured level in drinking water (Section 3.1.6.2. <b>Table 3.9</b> )
Drinking water (background)	0.5 $\mu\text{g}/\text{l}$	0.002 $\text{m}^3/\text{day}$	0.14	Typical measured level in drinking water (Section 3.1.6.2. <b>Table 3.9</b> )
Fish (reasonable worst case)	200 $\mu\text{g}/\text{kg}$	0.115 $\text{kg}_{\text{ww}}/\text{day}$	0.33	Ofsted et al. (1981)
Fish (background)	0.315 $\mu\text{g}/\text{kg}$	0.115 $\text{kg}_{\text{ww}}/\text{day}$	$5.2 \cdot 10^{-4}$	Regional model EUSES
Leaf/stem crop (reasonable worst case)	2 $\mu\text{g}/\text{kg}$	1.20 $\text{kg}/\text{day}$	0.03	McConnell et al. (1975) Highest reported level
Leaf/stem crop (background)	$4.86 \cdot 10^{-3}$ $\mu\text{g}/\text{kg}$	1.20 $\text{kg}/\text{day}$	$8.3 \cdot 10^{-5}$	Regional model EUSES

Table 3.24 continued overleaf

Table 3.24 continued Daily human intake via indirect exposure to tetrachloroethylene in the environment

Medium	Concentration	Daily intake	Dose ( $\mu\text{g}/\text{kgbw}/\text{d}$ )	Reference
Root crop (reasonable worst case)	2 $\mu\text{g}/\text{kg}$	0.384 kg/day	0.011	McConnel et al. (1975) Highest reported level
Root crop (background)	$5.18 \cdot 10^{-3}$ $\mu\text{g}/\text{kg}$	0.384 kg/day	$2.8 \cdot 10^{-5}$	Regional model EUSES
Meat (reasonable worst case)	1,150 $\mu\text{g}/\text{kg}$	0.301 kg/day	4.95	Zimmerli et al. (1982) Consumption-weighted average
Meat (background)	$9.2 \cdot 10^{-4}$ $\mu\text{g}/\text{kg}$	0.301 kg/day	$4 \cdot 10^{-4}$	Regional model EUSES
Milk/Dairy products (high background levels)	~10 $\mu\text{g}/\text{kg}$	0.561 kg/day	0.08	Zimmerli et al. (1982)
Milk/Dairy products (reasonable worst case)	~1,000 $\mu\text{g}/\text{kg}$	~1,000 $\mu\text{g}/\text{kg}$	8.01	Vieths et al. (1987) Vieths et al. (1988)
<b>Total daily intake</b>				
Living near dry cleaners			1,443	Reasonable worst case
Living near manufacturer			23.7	assumptions
Background			0.34	

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

### 3.2.1 Aquatic compartment (incl. sediment)

#### 3.2.1.1 Toxicity test results

A wide range of acute and chronic aquatic toxicity tests are reported and these are summarised in **Tables 3.25-3.30**. In these tables (n) indicates nominal concentrations and (m) indicates measured concentrations where specified; for other studies this information was not reported, and nominal concentrations have been assumed. The validity of the toxicity tests has been assessed in accordance with Chapter 3 and Appendices IV and V of the TGD.

##### 3.2.1.1.1 Toxicity tests to fish

**Tables 3.25** and **3.26** summarise acute toxicity and long term toxicity tests to fish.

The most sensitive freshwater species in acute toxicity tests appears to be *Oryzias latipes* with a 48-hour LC<sub>50</sub> of 1.6 mg/l. However this study is not considered to be valid. The experimental details are poorly described in the paper, therefore it is not possible to determine if appropriate measures were taken to minimise evaporation of tetrachloroethylene from the test solution. The reported effect concentration appears to be based upon nominal concentrations in the test solution. The next most sensitive species appears to be *Oncorhynchus mykiss* with a 96-hour LC<sub>50</sub> of 5 mg/l. This study is considered to be valid because the test conditions are fully described in the paper and the effect concentration is based upon measured levels.

In long-term toxicity tests *Poecilia sphenops* appears to be the most sensitive species with a 60-day LOEC of 1.6 mg/l. This study is not considered to be valid because no measures appear to have been taken to monitor concentrations or to minimise evaporation of tetrachloroethylene from the test solution; the resultant effect concentrations are based on nominal concentrations. The next most sensitive species appears to be *Jordanella floridae* with a 10-day NOEC of 1.99 mg/l based upon survival and a 28-day NOEC based on survival of 2.34 mg/l. These results are considered to be valid as test conditions are fully reported and the effect concentrations are based upon measured levels.

##### 3.2.1.1.2 Toxicity tests to aquatic invertebrates

**Tables 3.27** and **3.28** summarise the acute and long-term toxicity tests to aquatic invertebrates.

The lowest 48-hour EC<sub>50</sub> reported for *Daphnia magna* is 8.5 mg/l (Richter et al., 1983) and is based on measured concentrations. The test conditions are fully described for this result and the test is therefore considered valid. A 24-hour EC<sub>50</sub> of 3.2 mg/l is reported by Bazin et al. (1987) based upon nominal concentrations. No details are given as to the test method used, therefore this study is considered not valid.

Table 3.25 Acute toxicity to fish

Species	Age/size	pH	Dissolved Oxygen	Water hardness (as CaCO <sub>3</sub> )	Temperature	Flow/Static	Parameter	Concentration (mg/l)	Reference
Fresh water									
American flagfish <i>Jordanella floridae</i>	2-4 days	6.95	>90 %	48 mg/l	25°C	Flow	96-hour LC <sub>50</sub>	(m) 8.4	Smith et al. (1991) See note A.
Fathead minnow <i>Pimephales promelas</i>	Adult, 49 mm	7.8-8.0	> 5 mg/l	> 5.0 mg/l	12°C	Flow	96-hour LC <sub>50</sub>	(m) 18.4	Alexander et al. (1978)
						Static	96-hour LC <sub>50</sub>	(m) 21.4	
	30-35 days	6.7-7.6	8 mg/l	45.1 mg/l	25°C	Flow	96-hour LC <sub>50</sub>	(m) 13.4	Wallbridge et al. (1983)
	28-34 days	7.6	> 8 mg/l	44.6 mg/l	25°C	Flow	96-hour LC <sub>50</sub>	(m) 23.8	Broderius and Kahl (1985)
Rainbow trout <i>Oncorhynchus mykiss</i>		7.1	8.2 mg/l	44 mg/l	12°C	Flow	96-hour LC <sub>50</sub>	(m) 5	Shubat et al. (1982)
Bluegill <i>Lepomis macrochirus</i>	0.32-1.2 g	6.5-7.8	7.0-8.8 mg/l	32-48 mg/l	21-23°C	Static	96-hour LC <sub>50</sub>	(n) 13	Buccafusco et al. (1981)
Killifish <i>Oryzias latipes</i>	3 cm/0.3 g		≥ 3 mg/l	80 mg/l	20°C	Static	48-hour LC <sub>50</sub>	1.6	Yoshioka et al. (1986)
Guppy <i>Poecilia reticulata</i>	2-3 months	Static		> 5 mg/l	25 mg/l	22°C	7 day LC <sub>50</sub>	17.8	Könemann (1981)
Golden orfe <i>Leuciscus idus</i>							96-hour LC <sub>50</sub>	(m) 130	Knie et al. (1983)
Salt water									
Dab <i>Limanda limanda</i>	15-20 cm					Flow	96-hour LC <sub>50</sub>	(m) 5	Pearson and McConnell (1975)
Sheepshead minnow <i>Cyprinodon variegatus</i>	juvenile				25-31°C	Semi-static	96-hour LC <sub>50</sub>	(n) 29-52	Heitmuller et al. (1981)

A A semi static test was also reported, giving a 96-hour LC<sub>50</sub> of 4 mg/l, although the range of values measured with toxic effects was 18-32 mg/l. Due to the conflicting nature of the result it is not reported in the table of results

Table 3.26 Chronic toxicity to fish (freshwater)

Species	Age/ Length	Flow/ Static	pH	Dissolved Oxygen	Water hardness (as CaCO <sub>3</sub> )	Temperature	Parameter	Concentration (mg/l)	Reference
American flagfish <i>Jordanella floridae</i>	Larva	Flow	6.95	> 90%	48 mg/l	25°C	10 day survival NOEC	(m) 1.99	Smith et al. (1991)
	Fry						28 day survival NOEC	(m) 2.34	
Fathead minnow <i>Pimephales promelas</i>	Embryo, larva						MATC	1.4-2.8	USEPA (1980)
Black mollie <i>Poecilia sphenops</i>	Adult	Static					60 day LOEC	1.6	Lökle (1983)

Table 3.27 Acute toxicity to aquatic invertebrates

Species	Age/ Size	pH	Dissolved Oxygen	Water hardness (as CaCO <sub>3</sub> )	Temperature	Flow/ Static	Parameter	Concentration (mg/l)	Reference
Water flea <i>Daphnia magna</i>							24-hour EC <sub>50</sub>	(n) 3.2	Bazin et al. (1987)
							48-hour EC <sub>50</sub>	(m) 22	Knie et al. (1983)
		6.8-7.4	2.4-8.5 mg/l		14.4-18.6°C		4 day lethality	(m) 25-250	Lay et al. / (1984)
	24 hour	7.6-7.7	> 2 mg/l	70 mg/l	20-22°C	Static	24-hour EC <sub>50</sub>	123-176	Bringmann and Kühn (1982)
	Juvenile	7.1-7.7	7.9-9.9 mg/l	43.5-47.5 mg/l	20°C	Static	48-hour EC <sub>50</sub>	(m) 8.5	Richter et al. (1983)
	Juvenile (24 hour)	6.7-8.1	6.5-9.1 mg/l	72 mg/l	22°C	Static	48-hour EC <sub>50</sub>	(n) 18	LeBlanc (1980)
Mysid shrimp <i>Mysidopsis bahia</i>						Static	96-hour EC <sub>50</sub>	(n) 10.2	USEPA (1980)
Water flea <i>Moina macrocopa</i>	5 days				20°C	Static	3-hour EC <sub>50</sub>	(n) 1.8	Yoshioka et al. (1986)
Barnacle <i>Elminius modestus</i>						Static	48-hour EC <sub>50</sub>	(n) 3.5	Pearson and McConnell (1975)
Midge <i>Tanytarsus dissimilis</i>	2-3.5 mm	7.5	95.3-99.8 %	46.4 mg/l	20°C	Static	48-hour EC <sub>50</sub>	(m) 30.8	Call et al. (1983)

Table 3.28 Chronic toxicity to aquatic invertebrates

Species	Age/ Length	pH	Dissolved Oxygen	Water hardness (as CaCO <sub>3</sub> )	Temperature	Flow/ Static	Parameter	Concentration (mg/l)	Reference
Water flea <i>Daphnia magna</i>	24 hour	6.6-7.9	5.4-8.9 mg/l	43.5-47.5 mg/l	20°C	Static	28-day NOEC (Reproduction)	(m) 0.51	Richter et al. (1983)
	24 hour	7.4	98.1 %	44.5 mg/l	20°C	Static	28-day NOEC (Reproduction and length)	(m) 1.11	Call et al. (1983)
Mysid shrimp <i>Mysidopsis bahia</i>							EC (Lethality)	0.45	USEPA (1980)

Table 3.29 Toxicity to aquatic plants (algae)

Species	Parameter	Concentration (mg/l)	Reference
<i>Chlamydomonas reinhardtii</i>	72-hour EC <sub>50</sub>	3.64	Brack and Rottler (1994)
	72-hour EC <sub>10</sub>	1.77	
<i>Haematococcus pluvalis</i>	4-hour EC <sub>10</sub>	>36	Knie et al. (1983)
<i>Phaeodactylum tricornutum</i>	EC <sub>50</sub>	10.5	Pearson and McConnell (1975)
<i>Selenastrum capricornutum</i>	96-hour NOEC	816	USEPA (1980)
<i>Skeletonema costatum</i>	7-day EC <sub>50</sub>	>16	Erickson and Freedman (1978)
	96-hour EC <sub>50</sub>	500	USEPA (1980)
Estuarine phytoplankton	48-hour NOEC	1	Erickson and Hawkins (1980)

For other aquatic invertebrates a 3-hour EC<sub>50</sub> of 1.8 mg/l is reported for *Monia macrocopa* (Yoshioka et al., 1986) and a 48-hour EC<sub>50</sub> of 3.5 mg/l is reported for *Elminius modestus* (Pearson and McConnell, 1975). Both of these tests results are based upon nominal concentrations; the test methods used are also poorly described, therefore these results are considered not valid.

In longer term studies a 28-day NOEC based upon reproduction of 0.51 mg/l is reported (Richter et al., 1983). The test concentrations are measured, the test conditions are fully described and so the result is considered as valid. A lower value of 0.45 mg/l is reported for *Mysidopsis bahia* (USEPA, 1980); no indication is given as to the test conditions and the result is therefore considered not valid.

### 3.2.1.1.3 Toxicity to aquatic plants (algae)

**Table 3.29** summarises the toxicity test results for aquatic plants. A 72-hour EC<sub>50</sub> of 3.64 mg/l is reported for the algae *Chlamydomonas reinhardtii* by Brack and Rottler (1994). The test conditions are fully described in the paper, and the test can be considered valid. In the same study Brack and Rottler (1994) report a 72-hour EC<sub>10</sub> of 1.77 mg/l for the algae *Chlamydomonas reinhardtii*. The TGD suggests that this EC<sub>10</sub> may be considered as a NOEC and for algae that a 72-hour NOEC may be considered as a long term study. A 48-hour NOEC of 1 mg/l is reported by Erickson and Hawkins (1980) for estuarine phytoplankton. No indication is given as to the species tested therefore the result is not considered valid.

### 3.2.1.1.4 Toxicity to micro-organisms

For tetrachloroethylene toxic effects upon micro-organisms are observed at around 100 mg/l. All of the studies reported appear to be valid, but the test with *Photobacterium* is not relevant for micro-organisms in treatment plants. The other tests are suitable for use in the risk assessment. Results are summarised in **Table 3.30**.

Table 3.30 Toxicity to micro-organisms

Species	Parameter	Concentration (mg/l)	Reference
<i>Nitrosomonas sp</i> (Bacteria)	24-hour IC <sub>50</sub>	112	Blum and Speece (1991)
<i>Photobacterium phosphoreum</i>	10-minute EC <sub>10</sub>	(m) 68	Bazin et al. (1987)
<i>Tetrahymena pyriformis</i>	24-hour EC <sub>50</sub>	100	Yoshioka et al. (1986)

### 3.2.1.1.5 Field study data

Results from field studies have been reported. Lay et al. (1984) applied tetrachloroethylene to a natural pond at 25 and 250 mg/l. The initial concentrations were measured at 0.44 mg/l and 1.2 mg/l and after seven weeks the concentrations were below the detection limit of 0.1 mg/l. Adverse effects were noted in the phyto- and zooplankton communities under the conditions of the experiment. The numbers of *Daphnia* declined to zero within one day at the higher concentration and within 3.5 days at the lower concentration. Some of the plankton communities were unaffected by exposure to tetrachloroethylene, some were found to increase in number and

others were found to decrease in number during the study. Changes were also observed in the untreated control areas; *Spyrogyra* sp died out in these within five to seven days.

In a follow up study, Lay and Herrmann (1989) divided an experimental pond into four sub-systems (enclosures) using open-ended PVC cylinders sunk into the pond sediment. Two enclosures were continuously dosed with tetrachloroethylene for eleven weeks. The concentrations in the water of these two enclosures were measured regularly, and reached the target levels of 0.8 and 1.6 mg/l after five days.

Primary production in the treated enclosures showed a decrease in the short term, but a marked increase from the second week. Within this group, some individual species disappeared while others increased in number. The population of copepods was greatly reduced at the higher treatment level; at the lower treatment level an initial decrease was followed by an increase in reproduction rate towards the end of the experiment. Among rotifers, an initial increase in population for some species was followed by their later disappearance.

These field studies show that tetrachloroethylene can have an impact on aquatic ecosystems. It is not possible to derive a NOEC from either of these studies, but they will be considered as supporting information in the derivation of the PNEC.

### 3.2.1.2 Calculation of PNEC for aquatic organisms

The most sensitive aquatic toxicity data from the available valid studies are summarised in **Table 3.31**.

Table 3.31 Summary of toxicity to aquatic species

Species	Parameter	Concentration (mg/l)
Fish		
<i>Jordanella floridae</i>	96-hour LC <sub>50</sub>	8.4
	10-day NOEC (Survival, Larvae)	1.99
	28-day NOEC (Survival, Fry)	2.34
<i>Oncorhynchus mykiss</i>	96-hour LC <sub>50</sub>	5
Invertebrates		
<i>Daphnia magna</i>	48-hour EC <sub>50</sub>	8.5
	28-day NOEC (Reproduction)	0.51
Algae		
<i>Chlamydomonas reinhardtii</i>	72-hour EC <sub>50</sub> (Cell multiplication inhibition test)	3.64
	72-hour EC <sub>10</sub> (Cell multiplication inhibition test)	1.77

For most existing chemicals, the pool of data from which to predict ecosystem effects is limited. In these circumstances empirically derived assessment factors are used to calculate a predicted no effect concentration (PNEC). The PNEC is the level below which the probabilities suggest that an adverse environmental effect will not occur. It is not intended to be a level below which the chemical is considered as safe. The PNEC is calculated by dividing the lowest L(E)C<sub>50</sub> or NOEC value by the appropriate assessment factor.

For tetrachloroethylene short term L(E)C<sub>50</sub>s from validated sources are reported for fish, invertebrates and algae. For fresh water fish the lowest LC<sub>50</sub> from validated data is 5 mg/l (*Oncorhynchus mykiss*), for invertebrates the lowest EC<sub>50</sub> from validated data is 8.5 mg/l (*Daphnia magna*) and for algae the lowest EC<sub>50</sub> from validated data is 3.64 mg/l (*Chlamydomonas reinhardtii*).

In addition to short-term toxicity data, longer term toxicity data are reported for fish, *Daphnia* and algae. For fish a 10-day NOEC of 1.99 mg/l and a 28-day NOEC of 2.34 mg/l are reported for the larvae and fry of *Jordanella floridae* respectively. Although these studies did not follow recognised testing protocols for chronic tests as described in the Technical Guidance on testing strategies, they do cover three different stages in the life cycle of fish, including the early stages. Thus taken together the results are considered to give sufficient evidence as to the chronic effects that are observed in fish. For *Daphnia* a 28-day NOEC based upon reproduction of 0.51 mg/l is reported from validated sources. For fresh water algae a 72-hour EC<sub>10</sub> of 1.77 mg/l is reported, and this is taken as a long-term NOEC value.

An assessment factor of 10 may be applied when three long-term NOECs have been determined from different trophic levels and one of these long-term NOECs is from the species with the lowest L(E)C<sub>50</sub> from the short-term tests. When the assessment factor of 10 is applied to the 28-day NOEC for *Daphnia magna* of 0.51 mg/l, a PNEC of 51 µg/l is obtained. This value is an order of magnitude below the concentrations where effects were seen in field studies (Section 3.2.1.1.5).

### 3.2.1.3 Calculation of PNEC for micro-organisms in wastewater treatment plants

Since chemicals can have an adverse effect on microbial activity in WWTPs, a PNEC<sub>micro-organisms</sub> is derived. The PNEC should be calculated at the concentration at which significant effects occur, in particular short term measurements equivalent to the retention time of the chemical in the WWTP are preferable.

The assessment factor to be used depends upon the microbial effect data available. If the test has been performed on nitrifying bacteria the effect concentration may be compared directly with the effluent concentration. For other tests assessment factors in the range of 10 to 100 maybe applied.

For tetrachloroethylene toxic effects upon micro-organisms are observed at around 100 mg/l. Toxic effects are observed with *Nitrosomonas sp* which are nitrifying bacteria. This test is thought to be more relevant for WWTPs than the test with *Tetrahymena pyriformis*. A 24-hour EC<sub>50</sub> of 112 mg/l is reported; the TGD recommends that this be divided by an assessment factor of 10 giving a PNEC<sub>micro-organisms</sub> for tetrachloroethylene of 11.2 mg/l.

### 3.2.1.4 Calculation of PNEC for sediment-dwelling organisms

In the absence of data on the toxic effects of tetrachloroethylene on sediment dwelling organisms the equilibrium partitioning method is used to calculate a PNEC<sub>sediment</sub> as an initial screen. The PNEC<sub>sediment</sub> is given by the following equation:

$$PNEC_{sed} = \frac{K_{susp-water}}{RHO_{susp}} \times PNEC_{water} \times 1000 \quad (\text{TGD 54})$$

For tetrachloroethylene the suspended matter-water partition coefficient ( $K_{\text{susp-water}}$ ) is  $7.18 \text{ m}^3/\text{m}^3$ , the bulk density of wet sediment ( $\text{RHO}_{\text{susp}}$ ) is  $1,150 \text{ kg}/\text{m}^3$  and the  $\text{PNEC}_{\text{aquatic organisms}}$  is  $51 \text{ }\mu\text{g}/\text{l}$ . This gives a  $\text{PNEC}_{\text{sediment}}$  of  $318 \text{ }\mu\text{g}/\text{kg}$  wet weight.

By using this method only uptake via the water phase is taken into account and it should be noted that uptake may also occur via ingestion of sediment.

### 3.2.2 Terrestrial compartment

This section considers the toxicity of tetrachloroethylene to terrestrial organisms. The toxicity of the degradation product trichloroacetic acid is discussed in Appendix B.

#### 3.2.2.1 Mammalian toxicity test results

A wide range of test results for laboratory mammals is reported. These tests are reviewed in Section 4 (which will be added later), human health effects. The effects observed vary with the dose and species exposed. The levels at which these effects occur appear to be at higher concentrations than measured or predicted in the environment and it is unlikely that adverse effects will be noted in typical conditions.

#### 3.2.2.2 Other terrestrial toxicity data

The results of toxicity studies on terrestrial organisms (invertebrates and plants) and soil bacteria are summarised in **Table 3.32**. It should be noted that it is very difficult to test for toxicity to terrestrial species due to the volatilisation of tetrachloroethylene from the test medium and for some systems it is not easy to test organisms in sealed systems which minimise the effects of volatilisation.

Soils used in ecotoxicological tests differ in characteristics like organic matter, clay content, soil pH and soil moisture content. The TGD recommends that results are converted to a standard soil, which is defined as having an organic matter content of 3.4%. This has been done for those tests where the fraction of organic matter in the test soil is reported.

##### 3.2.2.2.1 Terrestrial invertebrates

Vonk et al. (1986) investigated the acute toxicity of tetrachloroethylene to the earthworm (*Eisenia foetida*) using OECD guideline No. 207. They used an artificial soil (10% peat, 20% Kaolin clay and 70% industrial sand) with a pH of 6. The exposure period was extended from 14 days (as recommend in the guidelines) to 28 days. Production of cocoons was observed in addition to mortality. To overcome the problem of evaporation, tetrachloroethylene was tested in closed containers supplied with sufficient oxygen for the worms to breathe and the soil and substrate were replaced weekly. The 14-day  $\text{LC}_{50}$  was  $100\text{-}320 \text{ mg}/\text{kg}$ , the 28-day NOEC (based upon cocoons) was  $\leq 18 \text{ mg}/\text{kg}$  and the 28-day NOEC (based upon appearance) was  $18\text{-}32 \text{ mg}/\text{kg}$ .

Table 3.32 Toxicity to soil dwelling bacteria, terrestrial invertebrates and plants

Species	Parameter	Concentration	Reference
Terrestrial Invertebrates			
Earthworm <i>Eisenia foetida</i>	14-day LC <sub>50</sub>	100-320 mg/kg	Vonk et al. (1986)
	28-day NOEC (Production of cocoons)	≤ 18 mg/kg	
	28-day NOEC (Appearance of worms)	18-32 mg/kg	
	14-day NOEC (Mortality, weight and behaviour)	577 mg/kg	Römbke et al. (1991)
	14-day LC <sub>50</sub>	945 mg/kg	
Carabid beetle <i>Poecilus cupreus</i>	14-day NOEC	5.0 mg/kg	Römbke et al. (1991)
Springtail <i>Folsomia candida</i>	1-day LC <sub>50</sub>	113 mg/kg (549 mg/kg)	Heimann and Härle (1993)
Terrestrial Plants			
Lettuce <i>Avena sativa</i>	16-day NOEC (Growth)	100 mg/kg (148 mg/kg)	Bauer and Dietze (1992)
	16-day NOEC (Sublethal effects)	1 mg/kg (1.48 mg/kg)	
	16-day EC <sub>50</sub> (Growth)	580 mg/kg (861 mg/kg)	
Soil dwelling bacteria			
<i>Pseudomonas putida</i>	16-hour EC <sub>10</sub>	> 45 mg/l	Knie et al. (1983)
Other bacteria	Soil respiration: NOEC	< 2,000 mg/kg (wet)	Vonk et al. (1986)
	Nitrification with humic sand: NOEC	< 40 mg/kg (wet)	
	Nitrification with loam: NOEC	≤ 0.1 mg/kg (wet)	

Note Figures in brackets refer to standardised test results.

Römbke et al. (1991) investigated the acute toxicity of tetrachloroethylene to the earthworm (*Eisenia foetida*) using OECD guideline No. 207. The earthworms used were 2 months old and weighed between 246-585 mg. They were exposed to tetrachloroethylene in glass jars containing an artificial soil (10% peat, 20% Kaolin clay and 70% industrial sand) with a pH of 6 and absolute water content of 34%. The exposure period was 14 days at 20°C. Mortality, changes in biomass, behaviour and morphology were recorded, and the LC<sub>50</sub> was determined by probit analysis. The highest test concentration causing no mortalities was found to be 577 mg/kg, the lowest test concentration causing 100% mortalities was >1,000 mg/kg and the LC<sub>50</sub> was determined as 945 mg/kg. At 1,000 mg/kg worms refused to crawl into the substrate. The concentrations reported are nominal concentrations, and no precautions were taken to prevent evaporation of tetrachloroethylene from the soil. Therefore, these results may underestimate the toxicity.

Römbke et al. (1993) studied the effect of tetrachloroethylene on the carabid beetle (*Poecilus cupreus*). The beetles were exposed to tetrachloroethylene for 14 days in sand (99.7% silicon dioxide) moistened to 70% of its holding capacity with water containing tetrachloroethylene (1.25 mg/l equivalent to 5 mg/kg). Mortality and behavioural changes were observed. After the 14-day exposure period there was a 6-day rest period; the beetles were then exposed to tetrachloroethylene for a further 11 days, with tetrachloroethylene applications (3 mg/kg)

occurring every 2 days. In the acute tests no mortality or behavioural changes were observed although there was an 18% reduction in feeding rate. In the chronic study no mortality or behavioural changes were observed although a 14% reduction in feeding rate was observed.

Heimann and Härle (1993) studied the effect of tetrachloroethylene on *Folsomia candida* (springtail) in an acute test and a reproduction test. The test on reproduction was a modification of the 'Richlinienentwurf der Biologischen Bundesanstalt für Land - und Fortwirtschaft'. The test was modified by using a standard soil (LUFA Speyer) instead of an artificial soil. The test was carried out over 5 weeks and the concentrations tested were 6.25, 9.3, 25.0, 50.0 and 100 mg/kg dry weight. In the acute tests the springtails were exposed in a similar test system to the reproduction test over 24 hours to tetrachloroethylene concentrations of 0.1, 1.0, 10, 100 and 1,000 mg/kg dry weight. In the acute test the 24-hour EC<sub>50</sub> was calculated as 113 mg/kg. There were problems with the reproduction test results, in particular mortality in the control tests, therefore the reproduction tests are regarded as invalid. The organic matter content of the test soil was reported as 0.7%, this gives a 24-hour EC<sub>50</sub> of 549 mg/kg when converted to a standard organic matter content.

#### **3.2.2.2.2 Terrestrial plants**

Bauer and Dietze (1992) studied the early development stage of the lettuce (*Avenia sativa*) when exposed to tetrachloroethylene. Germinated plants were exposed for 16 days to tetrachloroethylene (1, 10, 100 and 1,000 mg/kg dry weight) in a standard soil. The 16-day NOEC (growth) was 100 mg/kg, the 16-day NOEC (sublethal effects) was 1 mg/kg and the 16-day EC<sub>50</sub> (growth) was 580 mg/kg. The organic matter content of the test soil was reported as 2.29%. This gives a 16-day NOEC (growth) of 148 mg/kg, a 16-day NOEC (sublethal effects) of 1.48 mg/kg and a 16-day EC<sub>50</sub> (growth) of 861 mg/kg when converted to a standard organic matter content.

Dietz and Schnoor (2001) exposed cuttings of hybrid poplar (*Populus deltoides x nigra* DN34) to tetrachloroethylene in hydroponic solutions. Exposures were carried out in closed vessels in order to reduce volatilisation and maintain concentrations. Solutions were replaced every two days, and the concentrations were confirmed by analysis. The mass of the cuttings was determined after two weeks exposure. The use of water by the plants was also monitored at two-day intervals as a measure of the transpiration rate. The results were presented as the concentration which resulted in no increase in the mass of the plants over the two week period (45 mg/l) and as the concentration producing a 50% reduction in the transpiration rate over the same period (38 mg/l).

The effect of atmospheric tetrachloroethylene on plants has also been investigated. As the route of exposure is via the air these studies are considered in the atmospheric effects section (see Section 3.2.3).

#### **3.2.2.2.3 Soil dwelling bacteria**

Vonk et al. (1986) studied the effect of tetrachloroethylene on micro-organisms responsible for soil respiration, ammonification and nitrification. Short-term oxygen consumption was measured with a Warburg respirometer. A loam soil and a humic sand were used in the test. Measurements were taken with and without glucose added as an external source of carbon (basal and stimulated soil respiration). Nitrification was measured by addition of ammonium sulphate to the soils and monitoring the conversion of ammoniacal nitrogen. A NOEC of <2,000 mg/kg (wet weight) was

determined for soil respiration and NOECs of  $< 40$  mg/kg (wet weight) and  $\leq 0.1$  mg/kg (wet weight) determined for nitrification with humic sand and loam soil respectively.

Kanazawa and Filip (1987) studied the effect of tetrachloroethylene on soil biomass and microbial counts. In the experiments an arable brown soil was used (pH 6.8, carbon 1.44%, nitrogen 0.12%). This was air dried, large particles were discarded, and water was added to obtain a soil moisture content of 50% of the soil maximum. The soil was placed in flasks, which were closed with rubber stoppers. Tetrachloroethylene was then added to the soil by micro-syringe (test concentrations 0.1 mg/kg, 1 mg/kg and 10 mg/kg). The samples were incubated for 8 weeks in the dark at 25°C. Samples were taken at 3, 7, 14, 28, and 56 days and analysed microbiologically and for soil biomass. All the concentrations of tetrachloroethylene tested decreased the amount of soil biomass, the greatest effect being observed at 10 mg/kg. Very little effect on the population of soil fungi was observed at 0.1 mg/kg and 1 mg/kg levels, although at 10 mg/kg the growth of soil fungi was inhibited. Both copiotrophic and oligotrophic aerobic soil bacteria were inhibited at 10 mg/kg after 3 days, this was followed by an increase in the populations up to 28 days. The organic matter content of the soil was reported as 1.44%.

The effect of tetrachloroethylene on the dehydrogenase activity of soil micro-organisms was studied by Danneburg (1993). Two concentrations were tested: 0.5 and 5 mg/kg (dry weight). Initially an increase (42-62%) in dehydrogenase activity was found. This was followed by a decrease (11-18%) after 14 days and an increase (6-13%) after 28 days in dehydrogenase activity. The data show no consistent effect.

#### 3.2.2.4 Summary of terrestrial toxicity data

With toxicity tests it is preferable to have constant exposure of the organisms to the test chemical during the whole of the test period. In the studies presented in **Table 3.32** this is not the case. Because exposure can not be guaranteed and chemical analyses were in most cases not conducted, the studies can not be considered as valid. Nevertheless they do give an estimate of the toxicity of tetrachloroethylene. It should be noted that a method for soil toxicity tests with volatile chemicals, which ensures a constant exposure during the whole test period, has not yet been developed. The test using poplar hybrids did have better control of exposures, but did not use exposure through soil as such. Tetrachloroethylene in the presence of UV light may be involved in the bleaching of chlorophyll from the needles of spruce trees (see Section 3.2.3.).

#### 3.2.2.3 Calculation of PNEC for terrestrial organisms

For tetrachloroethylene enough terrestrial toxicity data are reported to allow the PNEC to be derived from actual data, although these are of questionable validity. Long-term studies have been conducted with three trophic levels/species; invertebrates (*Eisenia foetida*), plants (*Avena sativa*) and soil dwelling bacteria. The lowest NOEC reported is for nitrification in a loam with a NOEC of  $\leq 0.1$  mg/kg wet weight. Applying an assessment factor of 10 results in a  $PNEC_{soil}$  of 0.01 mg/kg wet weight.

A PNEC for terrestrial species can also be derived from the  $PNEC_{aquatic\ species}$  using an equilibrium partitioning method (as described in the TGD). For tetrachloroethylene this gives a PNEC for terrestrial species of 0.24 mg/kg wet weight.

Although the exposure of plants in hydroponic solutions is not a soil exposure, it could be considered as equivalent to exposure through the pore water. This study also took precautions to

reduce the possible volatilisation from the exposures. The two week exposures could be considered as acute tests; applying a factor of 1,000 to the lower result of 38 mg/l gives a value of 38 µg/l; this converts to a soil concentration of 0.18 mg/kg.

The PNEC derived from actual soil organism toxicity data is lower than the PNEC derived from aquatic species data, and so it will be used in the risk assessment.

### **3.2.3 Atmospheric effects**

This section deals with the direct effect of tetrachloroethylene on plants and with abiotic effects such as ozone depletion. The possible effects of trichloroacetic acid, a breakdown product of tetrachloroethylene, are discussed in Appendix B.

#### **3.2.3.1 Effects on plants**

##### **3.2.3.1.1 Older studies**

Possible effects of tetrachloroethylene on plants, especially conifers, have been investigated. Frank and Frank (1985) exposed a ten-year old spruce tree to trichloroethylene and perchloroethylene in the field (Black Forest). Exposures were uncontrolled, the substances being allowed to evaporate from a bottle below the tree, but air samples were taken from between the branches of the tree at 1 m above the source at intervals for analysis. The effect observed was bleaching of chlorophyll from sun-exposed surfaces. This only occurred in needles on the upper face of twigs and only during sunny periods. There was some recovery of partly damaged needles during cloudy periods. Needles on shaded twigs remained dark green. Similar symptoms were seen on the sun exposed leaves of a hornbeam shrub at a distance of 2 m from the pine tree. The authors suggest that the combined action of the chloroethylenes and UV light was required. As UV is attenuated at lower altitudes by smog etc, the effect is only observed at higher altitudes. They comment that effects due to other halogenated species or synergism with other pollutants such as sulphur dioxide or nitrogen oxides could not be ruled out; these other species were not monitored.

Frank and Frank (1986) investigated further the possible link between the destruction of photosynthetic pigments and chloroethylenes, by exposing single needles from spruce trees to airborne concentrations of tetrachloroethylene under direct irradiation. They found that the needles changed colour from dark green to a dirty brown green (in a 5-hour exposure). The concentrations of pigments in the exposed needles were found to be reduced, particularly chlorophyll-a and β carotene. Exposure to the higher concentration did not have any greater effect than the lower concentration. The nature of the radiation used in this study has been questioned, as it may have contributed significant amounts of radiation sufficiently energetic to cause direct photolysis of the substance. The report also observes that exposure to UV alone led to a reduction in one of the pigments studied, so it is possible that the needles were under stress as a result of the UV exposure alone.

In a further experiment (reported only in a progress report to the Bavarian State Ministry) spruce trees in pots were exposed in purpose built exposure chambers. Several 3 year old trees were exposed for a period of months. In all cases acute phytotoxicity was seen at a concentration of 130 µg/m<sup>3</sup>. After one or two months exposure an earlier and heavier yellowing of the directly irradiated needles was observed compared to the controls. Continuing exposure led to heavy

needle loss and eventually the deaths of the experimental trees. There have again been questions about the lighting conditions, which appear likely to include higher levels of UV than under natural conditions. There were also problems of pests on the trees, indicating non-ideal growing conditions. The author commented that it was not possible to derive any statistical values from these studies.

It is not possible to derive any kind of effect concentration or NOEC from these studies, and so they cannot be used directly in the risk assessment. However, taken together they were seen as an indication of possible effects of tetrachloroethylene on plants. As a result, a new study was designed and carried out to establish a no effect concentration for plants exposed to tetrachloroethylene through the air (see Section 3.2.3.1.2).

#### 3.2.3.1.2 Plant Research International study

The study (Plant Research International, 2000) was conducted using open-top chambers, which are considered to be the best technique currently available for providing near-field exposures. Details of the construction of the chambers are included in the report. The polyacrylate sheets from which the chambers are made allow 85% of the photosynthetically active light to pass. Air is blown continuously into the chambers through a perforated floor. In this study, the ambient air was filtered through charcoal, then a stream of nitrogen containing the tetrachloroethylene was added to the air stream before blowing into the chambers. Tetrachloroethylene concentrations were monitored through trapping on Tenax; sampling was for short periods totalling 15 minutes each day, with samples for seven days taken on the same tube to give an average level for each week's exposure. Samples were taken at plant height within the chambers, at less than 100 cm high. From other experiments in these chambers, concentration gradients do occur in the top 100 cm, but there are only very slight gradients in the bottom 100 cm.

The observed concentrations were different from the nominal concentrations intended, but the exposures at each concentration level were considered consistent. All results are based on the measured concentrations. The overall range of the exposures was 7-2,140  $\mu\text{g}/\text{m}^3$ , expressed as seasonal average concentrations. There was some variation in the concentrations over the course of the experiment, due to meteorological conditions affecting the outdoor chambers. As the aim of the study was to investigate the effects of long-term exposure, the use of average concentrations over the exposure period is considered appropriate. The concentrations used in the derivation of effect concentrations are those over the exposure period up to the point at which the relevant observations were made. This means that the concentrations for plants in the same chamber can be different, as the exposure periods were different.

The lowest of the exposure levels was intended to be a zero exposure control, but a small degree of contamination meant that a low level of tetrachloroethylene was present in this chamber. This was not considered to adversely affect the performance of the test; the mean weight of bean pods in the 'clean' chamber in this study was the same as that from an earlier study (1992) under the same conditions but with no tetrachloroethylene involvement in the exposures.

Twelve plant species were chosen for the study, to represent a range of European flora. These are shown in **Table 3.33**. Also shown are the sources of the plants used in the experiments and the duration of the exposures used for each species.

**Table 3.33** Plant species used in the experiments, origin of plants and duration of exposure

Scientific Name	Common Name	LifeCycle	Origin of Plants	Exposure From/to
Crops				
<i>Phaseolus vulgaris</i>	Bean	annual	Seeded	31 May-14 July *
<i>Triticum aestivum</i>	Wheat	annual	Seeded	10 May-28 July
<i>Brassica oleracea</i>	Kale	annual	Seeded	10 May-3 Aug
Trees				
<i>Picea abies</i>	Spruce	perennial	Nursery	10-May-8 Nov
<i>Pinus sylvestris</i>	Pine	perennial	Nursery	10-May-8 Nov
<i>Fagus sylvatica</i>	Beech	perennial	Nursery	10-May-8 Nov
Wild species				
<i>Trifolium repens</i>	White clover	perennial	Seeded	31 May-14 July *
<i>Molinia caerulea</i>	Purple Moorgrass	perennial	Clones	10 May-2 Sep
<i>Vaccinium myrtillus</i>	Blueberry	perennial	Nursery	10-May-8 Nov
Mosses				
<i>Polytrichum formosum</i>	Haircap Moss	perennial	Forest	4-Jun-12 Oct
<i>Pleurozium schreberi</i>	Schreber's Moss	perennial	Forest	4-Jun-12 Oct
<i>Rhytidiadelphus squarrosus</i>	Goose Neck Moss	perennial	Forest	4-Jun-12 Oct

\* Bean and clover were used in a second experiment, which started on 19 July and ended on 19 August for bean and 12 October for clover.

Six individuals of each species were used at each exposure level. Plants were grown in pots and arranged in the chambers so the trees did not overshadow the crop plants. Pots were rearranged at random in the chambers once a month.

After the end of the exposures, the trees and the mosses were moved to a wind-sheltered location and monitored over the winter for any carry-over effects.

A range of observations and measurements were made on plants during the exposures. Plants were checked daily for the occurrence of foliar injuries. A visual assessment was carried out in the first week of each month of exposure, looking at:

- the percentage of injured or senescent leaves (wilting and yellowing);
- numbers of flowers, pods, berries;
- stem diameters of trees;
- and plant heights (for most species).

Measurements on chlorophyll content were conducted on beech and kale in June, as these species were not showing any signs of foliar injury (in other species, chlorophyll reduction could be seen by injury or yellowing of leaves).

The exposures were terminated for each species when the plants had flowered and developed seed, so they were harvested at different dates. (Trees and mosses were not harvested at the end of the exposure but kept for continued observation as noted above.) A number of measurements were made at this stage, including numbers of flowers, pods, ears and berries, and the weight of

biomass as appropriate. Samples of the biomass were analysed for trichloroacetic acid for some species (spruce, pine, kale and beans).

The measured response parameters for the different species are shown in **Table 3.34**.

**Table 3.34** Measured response parameters per species

Plant species	Importance	Relevant response parameters
Bean	Yield/survival	Total pod weight, number of pods, mean pod weights
Wheat	Yield/survival	Total ear weight, 1,000-grain weight
Kale	Yield/survival	Total shoot weight, weight of leaves
Blueberry	Yield/survival	Aboveground weight, number and weight of berries
Pine	Growth/survival	Aboveground weight, stem diameter, bud-break
Spruce	Growth/survival	Aboveground weight, stem diameter, bud-break
Beech	Growth/survival	Aboveground weight, stem diameter, bud-break
White Clover	Growth/survival	Aboveground weight, number of flowers
Purple Moor Grass	Growth/survival	Aboveground weight, number of inflorescences
Haircap Moss	Growth/survival	Post-exposure-growth, survival
Schreber's Moss	Growth/survival	Post-exposure-growth, survival
Goose Neck Moss	Growth/survival	Post-exposure-growth, survival

### NOEC values in the study report

NOEC values were derived where possible from the quantified measurements, and these are shown in **Table 3.35**.

**Table 3.35** NOECs for adverse effects of tetrachloroethylene in different plant species

Plant Species	Representative Variable	NOEC [ $\mu\text{g m}^{-3}$ ]
Seed/fruit production		
Bean I	Pod dry weight	46 *
Bean II	Pod dry weight	$\geq 2,056$

Table 3.35 continued overleaf

Table 3.35 continued NOECs for adverse effects of tetrachloroethylene in different plant species

Plant Species	Representative Variable	NOEC [ $\mu\text{g m}^{-3}$ ]
Wheat	Ear dry weight	747-1,966 **
Kale	Shoot dry weight	$\geq 1,955$
Blueberry	Weight of berries	252-1,009 **
Growth/timber production		
Pine	Stem diameter	319 *
Spruce	Stem diameter	387 *
Beech	Stem diameter	$\geq 2,104$
Growth/survival		
Haircap Moss	Re-growth	$\geq 2,101$
Schreber's Moss	Re-growth	$\geq 2,101$
Goose Neck Moss	Re-growth	$\geq 2,101$
Clover I	Shoot dry weight	1,034 *
Clover II	Shoot dry weight	$\geq 2,179$
Moor Grass	Shoot dry weight	$\geq 2,029$

\* NOECs could be derived from the exposure-response relationships

\*\* Significant difference between two treatments

Where a dose-response relationship could be established, a logistic curve was fitted to the data. The NOEC was derived as the concentration at which the curve crossed the lower 95% confidence limit of the control response (the asymptote to the curve). In two cases, a dose-response could not be established but there was a significant difference between treatments. For the other cases, the response of the variable was not significantly different from the controls at the highest exposure level used.

Note that two experiments were carried out on beans and clover. The first exposures of beans in the spring showed strong effects of tetrachloroethylene, with the pod yield reduced to zero at the three highest concentrations. In a repeat experiment in the summer, no adverse effects were seen at any concentration. Clover was not affected as strongly in the spring experiment, and was also not affected at any concentration in the summer repeat. Possible reasons for the different results between these repeat studies are discussed in Section 3.2.3.1.2.

From the observations on foliar injury, there did not appear to be any significant effects at concentrations up to and including  $100 \mu\text{g/m}^3$ . The first concentration at which most species showed noticeable effects (>20% of the surface area affected) was  $257 \mu\text{g/m}^3$ . (Two of the species showed higher than 20% effects in the controls, but no exposure related increase (if there was one) was noted until  $257 \mu\text{g/m}^3$ .)

### Revised NOEC values

Due to criticism about the way the NOECs were derived in the study report, a re-evaluation of the data was carried out by the rapporteur. Where a dose-response relationship could be established,  $\text{EC}_{10}$  values were estimated; these were the same four endpoints as indicated in **Table 3.35**, together with the ear dry weight for wheat. For bean, wheat and clover an  $\text{EC}_{10}$  value with reasonable confidence intervals could be established. The large degree of background biological variation with pine and spruce meant that this approach was unreliable, as shown by

the very wide confidence limits obtained (over two orders of magnitude either side for spruce). The resulting values are shown in **Table 3.36**.

**Table 3.36** EC<sub>10</sub> values for adverse effects of tetrachloroethylene in plants

Plant species and effect	EC <sub>10</sub> (µg/m <sup>3</sup> )	P95 confidence limits
Bean, pod dry weight	48	31-74
Wheat, ear dry weight	1,239	312-4,912
Spruce, increase in stem diameter	14	0.1-1,442
Pine, increase in stem diameter	43	1.6-1,990
Clover, shoot dry weight	543	89-3,317

A more classical approach to estimating NOECs was also adopted, by establishing the highest concentration tested where the effect in the exposed group was not significantly different from that in the controls. This allowed some of the other endpoints to be considered, such as foliar injury and senescence. As many of the endpoints monitored as could be considered were included in this, and the results for the most sensitive endpoint for each species are included in **Table 3.37**.

**Table 3.37** NOEC values for most sensitive endpoint for each plant species

Plant species	Endpoint	NOEC	Remarks
<i>Phaseolus vulgaris</i> (bean)	Pod dry weight	46	See Table 6
<i>Triticum aestivum</i> (wheat)	Ear dry weight	747	
<i>Brassica oleracea</i> (kale)	Stem dry weight	758	Report, Fig. II-4
<i>Picea abies</i> (spruce)	Foliar injury	109	Report, Fig. 5
<i>Pinus silvestris</i> (pine)	Foliar injury	109	Report, Fig. 5
<i>Fagus sylvatica</i> (beech)	Foliar injury	750	Report, Fig. 5
<i>Trifolium repens</i> (white clover)	Shoot dry weight	543	EC10 instead of NOEC (708)
<i>Molinia caerulea</i> (purple moor grass)	Senescence	109	Report, Fig. 5
<i>Vaccinium myrtillus</i> (blueberry)	Senescence	109	Report, Fig. 5
<i>Polytrichum formosum</i> (haircap moss)	Post-exposure-growth	2,101	Report, Fig. 14
<i>Pleurozium schreberi</i> (Schreber's moss)	Post-exposure-growth	984	Report, Fig. 14
<i>Rhytidiadelphus squarrosus</i> (goose neck moss)	Post-exposure-growth	2,101	Report, Fig. 14

Note Remarks relate to the location of information in the original report.

For the bean, the value from the analysis of the dose-response relationship has been retained. There is no strict NOEC for the bean, as effects were noted at the lowest of the test concentrations, 82 µg/m<sup>3</sup>. Both the logistic curve-fitting method and the EC<sub>10</sub> approach gave similar figures, 46 and 48 µg/m<sup>3</sup>, and the lower of these values has been used. For clover, the two methods again gave similar results, but in this case the lower value is the EC<sub>10</sub> result and this has been used. As noted above, the EC<sub>10</sub> values estimated for pine and spruce are not considered to be reliable in view of the wide confidence limits obtained. Values for foliar injury are used for these two species; these are lower than those derived from the curve-fitting method.

### Trichloroacetic (TCA) levels

As noted above, some species were analysed for trichloroacetic acid (TCA). TCA was found in significant amounts in all four species analysed (pine, spruce, bean and kale). The highest concentrations were found in conifer needles, with levels up to 1,000 times those reported for samples collected in the field. Although the levels of TCA in the biomass increased with the exposure concentration of tetrachloroethylene there was not a linear relationship. New needles in spruce in spring 2000 (with the exposure to tetrachloroethylene having ended in November 1999) contained measurable TCA on trees which had been exposed to the highest tetrachloroethylene concentrations in the previous season. In contrast, pine needles formed in spring 2000 had very low levels. Beans from the first experiment in spring 1999 had higher levels than beans from the later exposure in summer.

### Factors affecting the toxicity of tetrachloroethylene to plants

A number of possible factors that could affect the toxicity of tetrachloroethylene to plants are discussed in the Plant Research International (2000) report.

The physiological difference between plants at different seasons - beans in the second (summer) experiment grew more quickly than those in the first (spring) exposure. Higher metabolic rates could lead to more rapid detoxification, and also to more dilution through growth.

High UV levels - in the first bean experiment UV levels were higher (sum of UV-A was  $607.8 \text{ J cm}^{-2}$  in the first experiment,  $401.1 \text{ J cm}^{-2}$  in the second), which could lead to more combined effects. The combination of UV and pollutants has been suggested as necessary for more pronounced effects.

Photo-inhibition - the primary photosynthetic pathway can be affected by a range of stress factors including air pollution. This can lead to the formation of large numbers of free radicals, which overwhelm the normal defence mechanisms in the plant and can enhance the effects of pollutants. Conditions in the first bean experiment may have contributed to or produced this effect; the bean prefers higher temperatures, and so would be under more stress growing at the lower temperature of this experiment. Other species like kale which prefer lower temperatures would not be affected as much.

It is also possible that TCA produced the effects seen in the plants. The report notes that TCA uptake or metabolism was thought to take place via or in the leaves, and not via the roots (tetrachloroethylene is not considered to degrade to TCA in soil). The observation of surface effects in the plants supports this idea. TCA is unlikely to have been formed in the air of the chambers, as the ventilation rate was too high and hence the residence time of tetrachloroethylene too short. Therefore TCA formation is assumed to have taken place in the plants after uptake of tetrachloroethylene from the air.

#### **3.2.3.2 PNEC plant**

There is no established framework within the Technical Guidance Document with which to generate a PNEC for plants. This section will use the available test information to derive a PNEC, taking into account the characteristics of the test conditions and the nature of the organisms tested. The PNEC derived here is only applicable to plants exposed to tetrachloroethylene through the air.

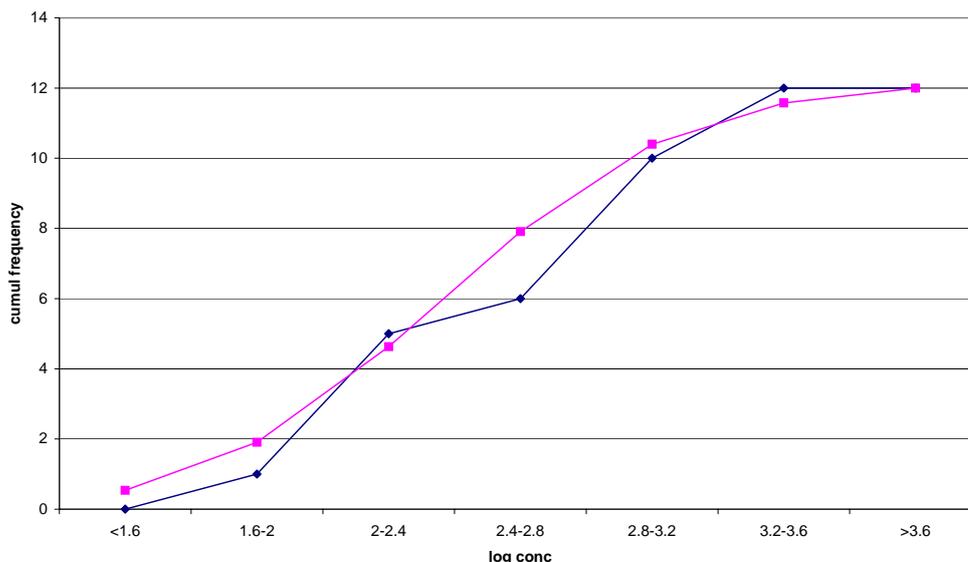


sensitive conditions. The endpoint on which the NOEC is based is the production of seed pods, which as well as being a measure of yield is also a measure of reproduction. Though not stated explicitly, it can be assumed that the reduced biomass of the seed pods resulted from reduction in weight of the seeds rather than reduction in numbers of seeds developing; that is, the seeds were fertile but grew smaller under the treatment. The effect, therefore, is consistent with other findings on other species showing reduced photosynthetic capacity with a resulting reduction in growth and there is no suggestion of reproductive effects. The study as a whole looked at twelve species of plant chosen to cover the important groups and those previously considered to be potentially susceptible. Taken together, the range of species covered and the near-field exposure conditions cover at least some of the usual uncertainty in extrapolating from experiments to the environment, and so the use of an assessment factor less than 10 on the NOEC from beans could be considered. There are no previous examples to follow in this case, so as a conservative approach a factor of 5 is proposed. This leads to a PNEC of  $9.2 \mu\text{g}/\text{m}^3$ .

The initial concerns over effects of tetrachloroethylene related to possible effects on pine and spruce trees. These were included in the study for this reason and a further species of tree (beech) was also included. Measurements on spruce and pine showed that the higher concentrations of tetrachloroethylene affected their growth (stem girth and height) and NOECs of  $319 \mu\text{g}/\text{m}^3$  (pine) and  $387 \mu\text{g}/\text{m}^3$  (spruce) were determined by the logistic curve-fitting method. The endpoint of stem girth is widely used in forestry. Observations on foliar damage indicated effects at lower concentrations, with a NOEC of  $109 \mu\text{g}/\text{m}^3$  for both spruce and pine. In terms of the full life span of the trees, the exposure period used was a small fraction. However, it did cover a complete growing season, and the trees were over-wintered to look for effects the following spring. The trees used were young plants (three-year old saplings), whereas effects have been noted in older needles in other studies. Against this, there is evidence in the experimental results that immature foliage is more sensitive than mature foliage. The youngest needle age class is the most important for the growth of the plants, with at least 70% of the photosynthetic capacity being present in the needles of the most recent year, even in species which have needles up to seven years old. Again the exposure conditions are considered to be very close to those in the field. Balancing these aspects, but taking into account the relatively short proportion of the lifetime exposed, it is considered prudent to apply a factor to the NOECs for trees. In the absence of a firm indication of what factor to apply, a value of 10 will be used as applied to 3 NOECs for trees. This gives a PNEC of  $11 \mu\text{g}/\text{m}^3$ . This is based on the yellowing of needles and it is not clear how significant this degree of yellowing is for the survival or growth of the trees, so this is to some degree conservative.

A third possible approach to the PNEC is to use a statistical extrapolation method. The revised set of NOEC values contains actual values for ten species. For two species there were no effects at the highest concentration tested; in these cases the limit value of the highest tested concentration was used. The Aldenberg and Slob method, assuming a log-normal distribution, gives an HC5 (50%) value of  $41 \mu\text{g}/\text{m}^3$ . The fit of the data set to the assumed distribution is not rejected by the Kolmogorov-Smirnov test; the cumulative frequency plot is shown in **Figure 3.2**. (For comparison, the data set without the two unbounded values (so including ten values) gives an HC5 (50%) of  $37.5 \mu\text{g}/\text{m}^3$ .)

Figure 3.2 Cumulative frequency plot for tetrachloroethylene plant toxicity



An assessment factor may need to be applied to this result. The number of values available meets the requirements of the method from a statistical viewpoint. In terms of the representation of species, criteria developed for aquatic organisms are not directly applicable, since only plants are being considered here. The data set includes twelve species, covering a range of types of plant considered to be reasonably representative of those in the EU. The number is less than the 15 species indicated as preferred for aquatic species; however, plants should be a more homogeneous group than aquatic organisms as a whole. The most sensitive of the measured endpoints has been taken in each case. The endpoints are mostly related to growth (although the foliar effects are at a level below growth as such) or reproduction (pod weights, etc.). Against this there is little experience in this area. The data set also includes two ‘unbounded NOEC’ values for moss species. Therefore a conservative approach is taken in using an assessment factor of 5 on the HC5. This gives a PNEC of  $8.2 \mu\text{g}/\text{m}^3$ . (For comparison the HC5 (95%) value is  $10 \mu\text{g}/\text{m}^3$ .)

All three approaches give similar results: 9.2, 11 and  $8.2 \mu\text{g}/\text{m}^3$ . The lowest of these is selected for risk assessment, so the PNEC for plants exposed through the air is  $8.2 \mu\text{g}/\text{m}^3$ .

### 3.2.3.3 Abiotic effects

The reactivity of tetrachloroethylene in the troposphere (the half-life is around 5 months) is such that it is not thought to contribute significantly to tropospheric ozone formation. Gas phase photolysis and rain out are thought to be of negligible importance in the removal of tetrachloroethylene from the troposphere.

The lifetime of tetrachloroethylene in the troposphere is such that the amount entering the stratosphere is low. Studies into stratospheric ozone depletion mention that tetrachloroethylene is a possible ozone depleter, although its potential is significantly less than other ozone depleting chemicals. Degradation products of tetrachloroethylene in the troposphere may enter the stratosphere, of these carbon tetrachloride is a known ozone depleter. The amounts of carbon tetrachloride entering the stratosphere due to tetrachloroethylene degradation are thought to be negligible when compared to other sources of carbon tetrachloride emissions.

No data has been found quantifying the contribution tetrachloroethylene makes to ozone depletion either directly or indirectly via its degradation products. Expert working groups on ozone depletion (WMO, 1991) consider the contribution that tetrachloroethylene makes to ozone depletion to be negligible when compared to other ozone depleting chemicals such as CFCs, HCFCs, carbon tetrachloride and 1,1,1-trichloroethane.

Tetrachloroethylene is not expected to contribute significantly to global warming.

### **3.2.4 Secondary poisoning**

As discussed in Section 3.1.8 tetrachloroethylene shows no indications of accumulating in the food chain, and therefore an assessment of secondary poisoning has not been carried out.

### 3.3 RISK CHARACTERISATION

As noted in Section 2, the quantities considered to be produced and used in the EU for this assessment are largely based on data from 1994. It is recognised that some changes have occurred to the overall tonnages and the relative amounts in each area since this time. This needs to be kept in mind in interpreting the conclusions. These changes are most likely to affect the regional concentrations. However, the local concentration estimates are based on more specific information relating to emissions and/or to the sizes of sites using tetrachloroethylene, and these are considered to be less likely to have changed significantly.

#### 3.3.1 Aquatic compartment (incl. sediment)

##### 3.3.1.1 Water

A PNEC of 51 µg/l is obtained for aquatic species exposed to tetrachloroethylene as detailed in Section 3.2.1. Measured levels and PECs of tetrachloroethylene in water are detailed in Section 3.1.8. **Table 3.38** summarises these PECs and measured levels, along with the PEC/PNEC ratios.

Table 3.38 PECs and measured levels of tetrachloroethylene in water

Parameter	Concentration (µg/l)	PEC/PNEC
PEC (Surface water)		
Production and processing sites		
Site A	0.02 (Direct, based on detection limit)	0.0004
Site B	0.01 (via WWTP)	0.0002
Site C	5 (Direct)	0.098
Site D	0.85 (Direct)	0.017
	0.07 (via WWTP)	0.0014
Site E	9.1 (Direct)	0.18
	0.6 (via WWTP)	0.012
Site F	4.2 (Direct)	0.082
	0.28 (via WWTP)	0.0058
Dry cleaning	0.02	0.00039
Metal cleaning	1.6	0.03
Regional	0.011	0.0002
Continental	0.0016	0.00003
Measured levels		
Surface water (realistic worst case)	5	0.1

When the PECs and PNEC are compared the PEC/PNEC ratio is less than 1 for all life cycle stages and for each use category. On the basis of the PECs and measured data, tetrachloroethylene should not present a risk to the aquatic (surface water) environment. The risk to groundwater has not been addressed in this assessment.

For sediment dwelling organisms a  $PNEC_{\text{sediment}}$  of 318  $\mu\text{g}/\text{kg}$  is calculated. The highest  $PEC_{\text{local(sediment)}}$  is calculated as 57  $\mu\text{g}/\text{kg}$  and the maximum measured level is 50  $\mu\text{g}/\text{kg}$ . When these values are compared with the PNEC the PEC/PNEC ratio is less than 1, it is therefore unlikely that tetrachloroethylene is a risk to sediment dwelling organisms.

Appendix B also indicates that there is no concern for regional surface water concentrations of TCA formed through the degradation of tetrachloroethylene in air.

## Result

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

### **3.3.1.2 Sewage treatment processes**

For micro-organisms in sewage treatment processes a  $PNEC_{\text{microorganisms}}$  of 11.2 mg/l has been derived. The highest  $PEC_{\text{stp}}$  is calculated as 16  $\mu\text{g}/\text{l}$  and the maximum measured level for municipal WWTP is 23  $\mu\text{g}/\text{l}$ . When these values are compared with the PNEC the PEC/PNEC ratio is less than 1, and so it is unlikely that tetrachloroethylene is a risk to micro-organisms in the WWTP.

## Results

**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.

### **3.3.2 Terrestrial compartment**

A  $PNEC_{\text{soil}}$  of 0.01 mg/kg is calculated for terrestrial organisms. The  $PEC_{\text{local}}$  values for tetrachloroethylene in soil from production/processing, dry cleaning and metal cleaning (see Section 3.1.7.1) are 0.39, 0.06 and 2.5  $\mu\text{g}/\text{kg}$  respectively. The PEC/PNEC ratios are less than 1, and so it is unlikely that tetrachloroethylene will be a risk to terrestrial organisms.

In Appendix B the risk to the environment from the breakdown of tetrachloroethylene in the atmosphere is assessed. The main degradation product to show adverse effects on terrestrial species is trichloroacetic acid (TCA). The  $PNEC_{\text{soil}}$  for TCA is 2.4  $\mu\text{g}/\text{kg}$  dry weight. When this is compared to measured TCA levels in soils, a risk is identified in some cases. Based on the available evidence, it appears that tetrachloroethylene is not by itself responsible for the TCA levels that exceed the PNEC. These higher levels of TCA in soil appear to be due to the combination of natural production in the soil and deposition from the atmosphere. The degradation of tetrachloroethylene in air is considered unlikely to lead to risks to terrestrial organisms (see Appendix B for further details).

## Results

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

This applies to risks from the direct effects of tetrachloroethylene itself, and from the breakdown product trichloroacetic acid formed through the degradation of tetrachloroethylene in air.

### 3.3.3 Atmosphere

There are three aspects to consider in the risk characterisation for the atmospheric effects of tetrachloroethylene. The first of these is the direct effect of tetrachloroethylene on plants. This was discussed in Section 3.2.3.2 where a PNEC of  $8.2 \mu\text{g}/\text{m}^3$  was derived.

This experimental result can be compared with calculated and measured levels in the environment. The selected values were described in Section 3.1.8.3. The highest value, measured for a production and processing site, is  $36 \mu\text{g}/\text{m}^3$ , which gives a PEC/PNEC ratio of 4.4. The calculated values for other production sites are below the PNEC. The calculated values for dry cleaning ( $4.4 \mu\text{g}/\text{m}^3$ ), metal cleaning ( $7.7 \mu\text{g}/\text{m}^3$ ) and the regional background ( $0.88 \mu\text{g}/\text{m}^3$ ) all give ratios less than 1 (0.54, 0.94 and 0.11 respectively).

The second aspect concerns breakdown products. Tetrachloroethylene undergoes reaction with reactive species in the troposphere, in particular with hydroxyl radicals and chlorine radicals, leading to the formation of a number of degradation products. These products are acidic in nature. The production of these breakdown products is discussed in detail in Section 3.1.8, and their significance is discussed in Appendix B. The potential risk to soil from these products has been considered in Section 3.3.2.

The third aspect relates to more indirect effects such as low level ozone formation, and stratospheric ozone depletion. Tetrachloroethylene's reactivity is such that it is not thought to contribute significantly to tropospheric ozone formation.

The lifetime of tetrachloroethylene in the troposphere is such that the amount entering the stratosphere is low. Studies into stratospheric ozone depletion mention that tetrachloroethylene is a possible ozone depleter, though its potential is significantly less than other ozone depleting chemicals. Degradation products of tetrachloroethylene in the troposphere may enter the stratosphere, and of these carbon tetrachloride is a known ozone depleter. The amounts of carbon tetrachloride entering the stratosphere due to tetrachloroethylene degradation are thought to be negligible when compared to other sources of carbon tetrachloride emissions.

Expert working groups on ozone depletion (WMO, 1991) consider the contribution that tetrachloroethylene makes to ozone depletion to be negligible when compared to other ozone depleting chemicals such as CFCs, HCFCs, carbon tetrachloride and 1,1,1-trichloroethane.

#### Results

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

This conclusion applies to the risk of harm to plants from air emissions of tetrachloroethylene from sites producing and processing tetrachloroethylene as an intermediate. It should be noted that only one of the sites considered in the assessment gives rise to a ratio greater than 1, but this is based on measured concentrations.

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

This conclusion applies to the risk of harm to plants from the use of tetrachloroethylene in dry cleaning and metal cleaning.

### 3.3.4 Secondary poisoning

The low octanol-water partition coefficient indicates that the bioaccumulation potential of tetrachloroethylene is low. This is supported by reported data. It is therefore unlikely that tetrachloroethylene will accumulate in aquatic species, and the predicted and measured levels in biota appear to support this assumption. The data also indicate that accumulation through the food chain is unlikely to occur.

#### Result

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

## **4 HUMAN HEALTH**

(to be added later)

## 5 RESULTS

### 5.1 INTRODUCTION

Tetrachloroethylene is produced by six manufacturers within the European Union.<sup>10</sup> In 1994 the total production of tetrachloroethylene was 164,000 tonnes. Of this amount, 78,000 tonnes was sold for use within the EU, 56,000 tonnes was exported and the remainder was used as a chemical intermediate within the chemical industry. Tetrachloroethylene is mainly used as a solvent in dry cleaning and metal cleaning and as a chemical intermediate.

Tetrachloroethylene is a colourless liquid with an 'ethereal' odour at normal temperature and pressure. It has a high vapour pressure and low water solubility.

### 5.2 ENVIRONMENT

Local releases of tetrachloroethylene to the environment may occur from use as a solvent in dry cleaning and metal cleaning and from production and chemical intermediate use sites. These releases have been quantified in the assessment and used to calculate PECs for various environmental compartments.

For the aquatic compartment the PEC/PNEC ratio is <1 for water and sediment from local sources, background levels and measured data. Similarly, there is no risk to STP or predators via the food chain for any life cycle step. No further information and/or testing or risk reduction measures are required beyond those which are already being applied. This conclusion also applies to the regional aquatic compartment for TCA formed through the degradation of tetrachloroethylene in air.

For the terrestrial compartment the PEC/PNEC ratio is <1 from local sources, background levels and measured data. No further information and/or testing or risk reduction measures are required beyond those that are already being applied. The breakdown of tetrachloroethylene in the atmosphere is also assessed. The main degradation product is trichloroacetic acid (TCA). When levels of TCA in soil are compared to the PNEC for TCA for terrestrial organisms a risk is identified for some local scenarios. Based on the available evidence, it appears that tetrachloroethylene is not by itself responsible for the TCA levels that exceed the PNEC. These higher levels of TCA in soil appear to be due to the combination of natural production in the soil and deposition from the atmosphere. The degradation of tetrachloroethylene in air is considered unlikely to lead to risks to terrestrial organisms (see Appendix B for further details). The implementation of the Solvent Emissions Directive (1999/13/EC) will reduce the emissions of tetrachloroethylene, but this has not been formally quantified in this assessment.

This assessment does not address risks arising from groundwater contamination.

For the atmospheric compartment, air levels measured at a production/chemical intermediate site exceed the PNEC for effects on plant life from atmospheric exposure. Therefore a risk to plants is identified for this life cycle step.

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<sup>10</sup> There are now five producers in the enlarged EU (in the Czech Republic, France, Germany, Spain and UK) (Personal communication (ECSA), 2005). No calculations have been performed for the production site located in the Czech Republic, because this part of the assessment was completed before the accession took place.

Tetrachloroethylene's reactivity is such that that it is not thought to contribute significantly to tropospheric ozone formation. The life-time of tetrachloroethylene in the troposphere is such that the amount entering the stratosphere is low. Studies into stratospheric ozone depletion mention that tetrachloroethylene is a possible ozone depleter, though its potential is significantly less than other ozone depleting chemicals. Degradation products of tetrachloroethylene in the troposphere may enter the stratosphere, and of these carbon tetrachloride is a known ozone depleter. The amounts of carbon tetrachloride entering the stratosphere due to tetrachloroethylene degradation are thought to be negligible when compared to other sources of carbon tetrachloride emissions.

### 5.2.1 RESULT

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

This applies to the aquatic compartment (including sediment and STP), the terrestrial compartment and secondary poisoning for tetrachloroethylene. It also applies to the air compartment for dry cleaning and metal cleaning for direct effects on plants. The conclusion also applies to the regional aquatic and terrestrial compartments for TCA formed through the degradation of tetrachloroethylene in air.

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

This conclusion applies to the risk of harm to plants from air emissions of tetrachloroethylene from sites producing and processing tetrachloroethylene as an intermediate. Based on site-specific data the conclusion relates to one site.

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## ABBREVIATIONS

ADI	Acceptable Daily Intake
AF	Assessment Factor
ASTM	American Society for Testing and Materials
ATP	Adaptation to Technical Progress
AUC	Area Under The Curve
B	Bioaccumulation
BBA	Biologische Bundesanstalt für Land- und Forstwirtschaft
BCF	Bioconcentration Factor
BMC	Benchmark Concentration
BMD	Benchmark Dose
BMF	Biomagnification Factor
BOD	Biochemical Oxygen Demand
bw	body weight / <i>Bw</i> , <i>bw</i>
C	Corrosive (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)
CA	Chromosome Aberration
CA	Competent Authority
CAS	Chemical Abstract Services
CEC	Commission of the European Communities
CEN	European Standards Organisation / European Committee for Normalisation
CEPE	European Committee for Paints and Inks
CMR	Carcinogenic, Mutagenic and toxic to Reproduction
CNS	Central Nervous System
COD	Chemical Oxygen Demand
CSTEE	Scientific Committee for Toxicity, Ecotoxicity and the Environment (DG SANCO)
CT <sub>50</sub>	Clearance Time, elimination or depuration expressed as half-life
d.wt	dry weight / <i>dw</i>
dfi	daily food intake
DG	Directorate General
DIN	Deutsche Industrie Norm (German norm)
DNA	DeoxyriboNucleic Acid
DOC	Dissolved Organic Carbon
DT50	Degradation half-life or period required for 50 percent dissipation / degradation
DT90	Period required for 90 percent dissipation / degradation
E	Explosive (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)
EASE	Estimation and Assessment of Substance Exposure Physico-chemical properties [Model]

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

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

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

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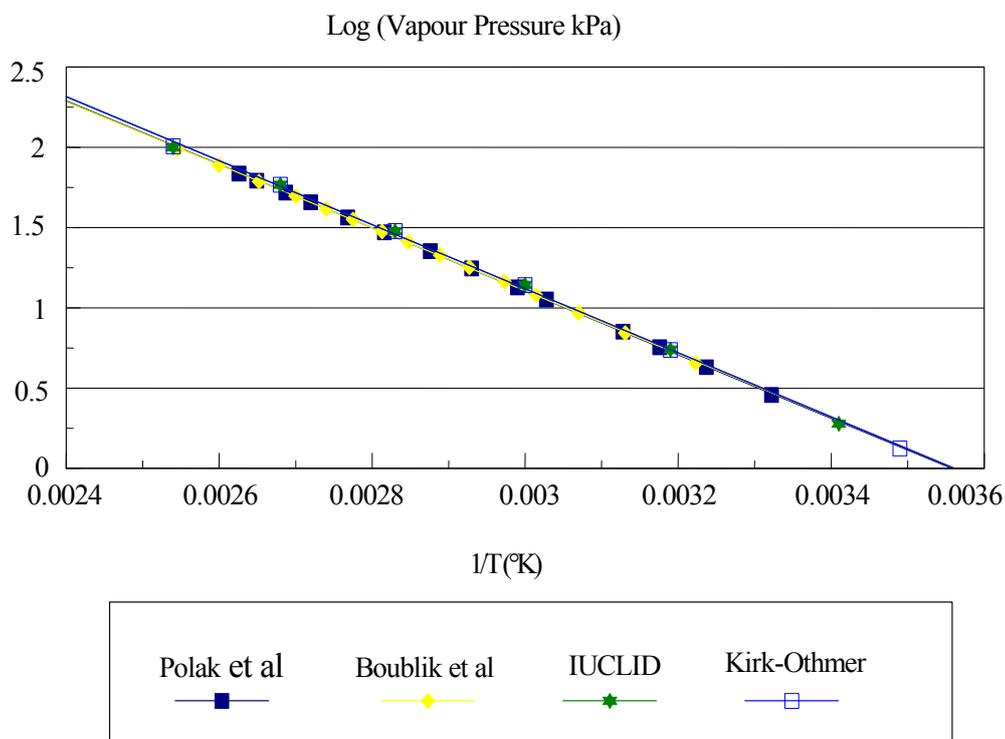
US EPA	Environmental Protection Agency, USA
UV	Ultraviolet Region of Spectrum
UVCB	Unknown or Variable composition, Complex reaction products of Biological material
vB	very Bioaccumulative
VOC	Volatile Organic Compound
vP	very Persistent
vPvB	very Persistent and very Bioaccumulative
v/v	volume per volume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

## Appendix A Vapour pressure data

Table A.1 Vapour pressure of tetrachloroethylene at varying temperatures

Polak et al (1970)		Boublik et al (1972)	
Temperature (°C)	Vapour pressure (kPa)	Temperature(°C)	Vapour pressure (kPa)
27.89	2.87	37.09	4.52
35.76	4.27	46.24	6.97
41.7	5.69	52.67	9.31
46.5	7.1	58.7	12.05
57.07	11.28	63.27	14.55
61.25	13.41	68.55	17.92
68.07	17.62	73.06	21.31
74.53	22.54	78.17	25.78
81.96	29.56	82.29	29.92
88.06	36.56	87.18	35.49
94.57	45.47	91.79	41.47
98.92	52.32	97.29	49.7
104.27	61.88	103.93	61.3
107.79	68.69	111.55	77.13
		119.65	97.34

Figure A.1 Graph of  $1/T(^{\circ}\text{K})$  v  $\text{Log}(\text{Vapour Pressure kPa})$



## **Appendix B Risk assessment for trichloroacetic acid arising as a breakdown product from degradation of tetrachloroethylene in air**

Section 3.1.3.1 of the main report describes the reactions by which tetrachloroethylene can break down in the atmosphere. One of the possible products is trichloroacetic acid (hereafter referred to as TCA). This has been the subject of an assessment under the OECD SIDS programme (OECD, 2000), which dealt with the production and use of the substance as an industrial chemical. That assessment concluded that levels of TCA found in soil could have adverse effects on soil organisms, and that these levels could be due to the breakdown of tetrachloroethylene. TCA has also been the subject of a BUA report (1996). Further information on TCA can be obtained from those two reports.

This appendix considers the potential production of TCA from tetrachloroethylene and the levels of TCA found in the environment. These are compared with the effects data from the OECD SIDS report to assess whether there is a risk to soil organisms that can be related to the use of tetrachloroethylene.

### **B1 Estimation of the production of TCA from tetrachloroethylene**

The potential pathways and products from the reaction of tetrachloroethylene with species in the atmosphere are described in Section 3.1.3.1 of the main report. The extent to which TCA may be produced is estimated in this section of the appendix. The methodology is based on that developed by Franklin (1994) and Sidebottom and Franklin (1996) and in the ECETOC JACC Report (1999) on tetrachloroethylene. The production of TCA from tetrachloroethylene depends on the relative reaction rate of tetrachloroethylene with hydroxyl and chlorine radicals. Values for the rate constants for these reactions at a temperature of 277 K are:

$$\begin{aligned}k_{\text{OH}} &= 1.23 \cdot 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1} \\k_{\text{Cl}} &= 4 \cdot 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}\end{aligned}$$

The average concentrations of hydroxyl and chlorine radicals in the atmosphere are taken as:

$$\begin{aligned}[\text{OH}] &= 5 \cdot 10^5 \text{ molec/cm}^3 \\[\text{Cl}] &= 500 \text{ molec/cm}^3\end{aligned}$$

Hence the pseudo-first-order reaction rates are:

$$\begin{aligned}k[\text{OH}] &= 6.15 \cdot 10^{-8} \text{ sec}^{-1} \\k[\text{Cl}] &= 2.0 \cdot 10^{-8} \text{ sec}^{-1}\end{aligned}$$

The split between the two reaction rates is 75:25 (the overall lifetime for tetrachloroethylene from these rates is 0.39 years).

The reaction with Cl eventually leads to two products, trichloroacetyl chloride (TCAC) and phosgene, in the ratio 85:15. The maximum yield of TCAC is therefore 85% of 25%, or 21.25%.

TCAC can hydrolyse with water in the atmosphere to give TCA (half-life 20 days) or it can photolyse (giving largely phosgene). The half-life for this last process has been given as 6 days by the World Meteorological Organisation (WMO, 1994) or 50 days by Behnke and Zetsch (1991) (the shorter of these agrees with the half-life for the related substance dichloroacetyl chloride (DCAC) of 9 days). The hydrolysis:photolysis ratio is thus 23:77 or 71:29, depending on which half-life is selected for photolysis. The final yield of TCA is therefore 23% or 71% of 21.25%, i.e. 5% or 15%.

McCulloch and Midgley (1996) estimated that around 295,000 tonnes/year of tetrachloroethylene were released to the atmosphere worldwide in 1992. If this reacted in the atmosphere as described above the amount of TCAC produced would be around 62,700 tonnes/year. This amount would give 13,000 - 40,000 tonnes of TCA based on the yields above.

From the estimates of tetrachloroethylene release in the EU (~59,000 tonnes/year), the amount of TCA generated in the EU atmosphere is 2,910-8,720 tonne/year.

It should be recognised that there are likely to be considerable uncertainties in some of these figures.

## **B2 Measured levels of TCA in the environment**

This section provides an overview of reported levels in a variety of environmental media (i.e. air, precipitation, surface water, soil and vegetation).

### **B2.1 Levels in air**

There are only a few available measurements of TCA in air. BUA (1996) quotes levels of 0.4-3 ng/m<sup>3</sup> for air samples from the Black Forest area in the early 1990s. Somewhat lower values have been presented more recently (Klein, 1997, reference not seen). As part of a study on levels of TCA in soil, Peters (2000) measured the concentration of TCA in air samples from two locations in The Netherlands. The levels found were <0.5 and 0.7 ng/m<sup>3</sup>. Heal et al. (2003) measured concentrations of TCA in air in Scotland from a forest site (Glentress Forest, Dunslair Heights) and in central Edinburgh. The mean level in forest air was 33 pg/m<sup>3</sup> (range <10-110 pg/m<sup>3</sup>). The concentration in urban air was higher, with a mean value of 83 pg/m<sup>3</sup> (range <10-632 pg/m<sup>3</sup>). These are total air measurements; particulates were separated from the urban air samples, and found to contain on average 23% of the total load.

### **B2.2 Levels in precipitation**

Measured levels of TCA in rainwater are summarised in **Table B.1**.

Table B.1 Measured levels of TCA in rainwater

Year	Location	Concentration ( $\mu\text{g/l}$ )	Notes	Reference
1988-9	Hessen, Germany	0.2-6.5; mean 1.7	94 samples, 8 locations	Schleyer et al., 1991
1990-1	Berlin, Germany	0.1-20; mean 2.1 throughfall, 0.9 open field		Plumacher and Renner, 1993
1990-1	Bonn, Germany	$\leq 7.5$ ; mean 0.8, median 0.25		Schöler et al., 1991
1991-2	Grossenbach, Germany	$< 0.1$ -2.0; annual average 0.57	Near to metal industry; peak in June	Haiber et al., 1996
1992	Hau, Germany	0.08-0.3; mean 0.15, median 0.12	30km from above location; no seasonal variation	Haiber et al., 1996
1991-3	Bleche, Germany	0.05-9.7; median 0.16	2 high values Nov 1991, rest below 1 $\mu\text{g/l}$ . Rural area, no seasonal dependence	Schöler, 1998
1993-4	Southwest Germany	0.37-2.3, means 0.2-0.85 (throughfall); 0.33-0.47, means 0.17-0.28 (open field)	9 rural and semi-rural sites	Schleyer et al., 1996
1991-3	Austria	0.01-0.3	7 sites, 85 samples	Lorbeer et al., 1994
1991-6	Austria	Range $< 0.01$ -0.86; median 0.14	9 sites, rural and urban. Seasonal variation	Sattelberger et al., 2000
1994-5	Eastern Finland	0.02-0.21, mean 0.1	4km from centre of Kuopio	Juuti, 1997
1999	Netherlands	0.16, 0.15	Two open locations, Speulderbos and Vlaardingen	Peters, 2000
1993	Switzerland	$< 0.03$ -0.9; average 0.3		Muller et al., 1996
1993	Switzerland	0.044-0.71; average 0.3	No significant difference between urban and semi-rural area. Seasonal dependence	Reimann et al., 1996
1998-9	Germany	Average 0.13	Forest area, Waldstein in Fichtelgebirge, NE Bavaria	Römpp et al., 2001
1998-2000	Scotland	0.13-1.7, mean 0.8, median 0.76 (602 m height) 0.15-1.6, mean 0.72, median 0.68 (275 m height)	Two rural upland forest sites, sampled weekly for 2 years.	Heal et al, 2003
2002	Southern Germany and North-west France	0.02-0.45, mean 0.16	10 sites, monthly samples over July-December	de Winkel et al., 2003
2001-2	Scotland	0.32 – 2.3, median 0.81	Upland moorland and forest area	Stidson et al., 2004

Notes Throughfall is rainfall sampled after passing through the tree canopy

### *Geographical variation*

The higher measured levels - with means of 2,000 ng/l or higher - appear to come from forest areas in earlier studies (i.e. those conducted around 1988-90). Data for 1993-4 (particularly Schleyer et al., 1996) show mean levels up to 850 ng/l in spruce forest areas. Open areas have values closer to 200 ng/l.

The concentrations of tetrachloroethylene would not be expected to differ significantly between the forest and open areas. One reason for the increased concentration of TCA in forest areas might be that foliage may retain atmospheric TCA during dry periods. The next shower of rain would then wash this off. Another explanation is that TCA may be taken up from soil by the tree roots, and transported through the tree until it passes out through the stomata in solution. As it cannot evaporate with the water it would remain on the leaf surface until the next rainfall.

Levels of TCA have also been measured in more remote locations, usually in snow samples. Ice and snow cores can be used to show historical levels. Results from these analyses are in **Table B.2**.

**Table B.2** Levels of TCA in remote and older precipitation samples

Source	Concentration (ng/l)	Notes	Reference
Arctic snow	ND	Spitzbergen	Haiber et al., 1996
Alpine snow	400±50	February 1992	
Alpine glacier	100±40	Approx. age 100 years	
Swedish ice	1-13	Pre-industrial, 3 samples	Grimvall et al., 1995
Snow, Norway & Sweden	5-40	16 samples	
Russian tundra snow	5-55	10 samples, 7 ND	
British Columbian snow	10-45	4 samples, 1 ND	
Antarctic snow	20-120	6 samples	
Older Antarctic firn	7-10	3 samples	

ND Not detected

In general the remote samples show lower levels than those measured in central Europe. The samples from Russia and British Columbia in which TCA was not detected were taken after major snowmelt periods.

The levels measured in older samples indicate the presence of TCA in the atmosphere before the widespread industrial use of chlorinated solvents.

### *Seasonal variation*

A number of the studies show seasonal variations in concentrations. Schöler (1998) notes that the seasonal variations are more noticeable in industrial areas while rural areas, especially in central and northern Europe, do not show seasonal trends. Sattelberger et al. (2000) commented that TCA occurred in rainwater throughout the year, but the highest concentrations were mostly detected in the summer.

De Winkel et al. (2003) detected a gradual decrease in the concentration of TCA in rain from July to December. The average concentration over ten sites in France and Germany was 230 ng/l

in July, decreasing to 110 ng/l by December 2002 (see Section 2.3 (this Appendix) for further details of the sites). The rain intensity increased over the same period, so that there was a relatively constant deposition of TCA over the period.

In contrast to this, Heal et al. (2003) found no obvious seasonal variation in the concentration of TCA in rainwater measured over two years at two forest sites in Scotland. The rainfall at the sites also showed little seasonal variation, and so the deposition rate was relatively constant, which is in agreement with the findings of de Winkel et al. (2003) in regard to deposition.

### *Fog*

Measurements have also been made on levels of TCA in cloud water or fog. Römpf et al. (2000) reported fog concentrations in the range 20 – 2,000 ng/l from samples from the Fichtelgebirge in northeast Bavaria. These were higher than the corresponding levels in rainwater, with a median fog/rain concentration ratio of 4.4. de Winkel et al. (2003) also measured higher concentrations of TCA in fog samples than in the corresponding rain samples, with an average concentration in fog of 380 ng/l (range 130 – 1,100 ng/l), a factor of 2.8 times that in rain.

Heal et al. (2003) measured TCA in cloud water samples from the higher of two forest sites in Scotland, and found a mean concentration of 1,200 ng/l (median 930 ng/l, range 250-7,200 ng/l). Higher concentrations were found at times of lower deposition. A comparison of the precipitation-weighted concentrations showed an enrichment factor of 1.2 for cloud water over rainwater, which is much lower than found for inorganic ions. Overall, cloud water was estimated to contribute ~13% to the total deposition of TCA at the site, which is not significantly different from the cloud contribution to water deposition at the site, which is 11%.

## **B2.3 Levels in surface water**

TCA in surface waters can arise from a number of sources, including use as an industrial chemical and formation through the chlorination of water. The reported levels of TCA in surface water are reviewed by the OECD (2000). The background (regional) concentration of TCA is 0.12 µg/l, from measurements on lakes in Switzerland. As the production of TCA from tetrachloroethylene is dispersed it will contribute to the regional levels, and so this value will be taken as representing the worst case for surface water concentrations from this source.

## **B2.4 Levels in soil**

The database for measured levels in soil is not very extensive. In Germany, Frank (1988) reported levels of 20-380 µg/kg in Black Forest soils in 1986. Plumacher and Renner (1991, 1993) also measured levels of 0.1-120 µg/kg in coniferous forest soils near Berlin. Hoekstra and de Leer (1993) measured lower levels of 0.2 - 4.6 µg/kg in four soil types (peat moor, peat bog, beech forest and Douglas fir forest) from rural locations in the Netherlands. These concentrations were expressed in terms of soil organic matter, but the soils consisted almost completely of organic matter. Weißflog et al. (1999) reported levels of TCA in soils from a number of sites in south-western Russia. Pine needles were sampled at thirteen sites (see below); soil samples (from the surface soil) were taken from nine sites in April 1997 and eight sites in July/August 1997. The concentrations ranged from 0.04-1.09 µg/kg in April and 0.09-1.06 µg/kg in June/July.

Peters (2000) analysed soil samples from 10 locations across Europe. Most of the sites were selected randomly, but locations in Germany (Freudenstadt in the Black Forest) and in The Netherlands (Apeldoorn) were included to compare results with earlier measurements. At each

location, samples were taken from forest sites (i.e. beneath the tree canopy) and from nearby open locations. Samples were taken at three depths at each location. Average concentrations over the depth profile and a comparison between the results from forest sites and open sites (expressed in terms of dry weight (dw)) are given in **Table B.3**. The individual results are presented in **Table B.4**.

Table B.3 Average levels of TCA in soil (Peters, 2000)

Country	Area	Average TCA conc ( $\mu\text{g}/\text{kg dw}$ )		Ratio (Forest/Open)
		Forest	Open	
Germany	Freudenstadt	6.6	1.3	5.3
	Kiel	0.86	0.25	3.4
The Netherlands	Apeldoorn	0.28	0.35	0.8
	Rotterdam	0.14	0.13	1.0
Italy	Venice	0.31	0.13	2.4
	Rome	0.23	0.11	2.2
Scandinavia	Göteborg	0.46	0.26	1.8
	Oslo	0.34	0.08	4.2
UK	Nottingham	0.54	0.21	2.6
	Glasgow	0.19	0.19	1.0

The open sites generally have levels that are lower than those from the forest sites (as has been observed for rainwater). There is no standard pattern to the concentrations with depth for the forest samples; there are examples of concentrations increasing and decreasing with depth, and some examples of similar levels down the profile. The lack of pattern is also true in the open site samples, although there is more of a tendency for levels to be similar down through the profile.

The overall average concentration in the European soils sampled in this study was  $0.6 \mu\text{g}/\text{kg}$ .

**Table B.4** Levels of TCA in EU soils – individual results at different depths (Peters, 2000)

Country	Area	Forest		Open	
		Depth (m)	Concentration (µg/kg dw)	Depth (m)	Concentration (µg/kg dw)
Germany	Freudenstadt	0.1	2.1	0.1	1.3
		0.3	5.4	0.3	1.9
		0.6	12	0.9	0.63
	Kiel	0.1	0.81	0.1	0.29
		0.3	1.4	0.3	0.18
		0.8	0.33	1.0	0.29
The Netherlands	Apeldoorn	0.1	0.44	0.1	0.26
		0.3	0.18	0.3	0.34
		1.0	0.21	1.0	0.44
	Rotterdam	0.1	<0.05	0.1	<0.05
		0.3	<0.05	0.3	<0.05
		1.0	0.14	0.8	0.13
Italy	Venice	0.1	0.63	0.1	0.17
		0.3	0.16	0.3	0.10
		0.8	0.14	0.8	0.11
	Rome	0.1	0.37	0.1	<0.05
		0.3	0.09	0.3	0.11
		1.0	<0.05	0.8	<0.05
Scandinavia	Göteborg	0.1	0.29	0.1	<0.05
		0.3	<0.05	0.3	0.22
		0.7	0.63	0.8	0.30
	Oslo	0.1	0.23	0.1	<0.05
		0.3	0.46	0.3	0.08
		0.6	<0.05	0.8	<0.05
UK	Nottingham	0.1	1.26	0.1	0.11
		0.3	0.19	0.3	0.23
		0.7	0.18	0.8	0.27
	Glasgow	0.1	<0.05	0.1	<0.05
		0.3	0.20	0.3	0.23
		0.6	0.18	0.8	0.15

De Winkel et al. (2003) analysed TCA levels in soil samples from eleven forest sites across central Europe. The sites were chosen<sup>11</sup> to represent locations where high TCA levels might be expected, based on:

- favourable soil conditions (i.e. high organic matter content and low pH),
- appropriate temperature/altitude, and
- conifer coverage.

All of the sites were selected from a database held by the Forest Intensive Monitoring Coordinating Institute (an EU/UNECE network for monitoring forest health), and therefore had regular measurements of meteorological conditions, rainfall, etc. Two sites were in north-east France (in the Vosges and Ardennes regions). The rest were in southern Germany: five in the

<sup>11</sup> The initial survey for this work included spot samples (at 10-30 cm soil depth) at 18 sites, of which four were in the Freudenstadt area. The selected sites (ten, plus one from Freudenstadt) were chosen on the basis of the results from spot soil samples, site characteristics and logistical considerations.

Rheinland-Pfalz and Baden-Württemberg regions, forming a semi-circle east of Freudenstadt (one of these was close to the industrial area of Ludwigshafen/Mannheim); and three in Bavaria (with one near Munich and another close to the Austrian border). In addition, similar investigations were carried out in the Freudenstadt area of the Black Forest (where high soil levels had been reported in earlier studies).

In the initial survey in June 2002 at the 18 candidate test sites, TCA concentrations were in general below 1 µg/kg dw, except for Abreschviller (at 16 µg/kg dw), Freudenstadt (21-61 µg/kg dw) and Zusmarshausen (17 µg/kg dw). In the main survey, samples were taken at eleven selected test sites on at least two occasions between August and December 2002. The various horizons in the soil profiles were sampled individually at each site. The horizons differed to some extent between the sites, but all sites had a surface litter layer (the L horizon) above the first mineral soil layer (the A horizon). The L horizon was ~3 cm deep in most soils, increasing up to 7-10 cm in a few cases. The A horizon depth varied between 5 and 20 cm. Concentrations for these horizons individually are included in the study report, but have been combined in this assessment (on a depth- averaged basis) as the horizons most related to the endpoints in the TGD (the TGD considers soil concentrations to a mixing depth of 10 or 20 cm depending on soil type). The results are presented in **Table B.5**.

**Table B.5** Levels of TCA in soil (µg/kg dw, combined L and A horizons) from sites across central Europe

Location		Site code	August	October	November	December
France	Abreschviller	SP57	5.4			0.46
	Les Hautes Rivieres	EPC08	2.5			0.44
Germany	Johanniskreuz	707	4.8	1.9		0.6
	Bad Rotenfels	801	2.6			1.0
	Rosenfeld	804	3.2			1.4
	Krichzarten	806	1.1			0.57
	Altensteig	809	1.6			0.6
	Alltötting	902	3.3			0.68
	Ebersberg	906	1.7			0.66
	Zusmarshausen	917	10.9	1.3	0.68	0.61
	Freudenstadt	BZE040		2.8		

Note Site codes are those used in the study report.

The majority of the sites showed a steep decrease in TCA concentration with depth, with lower levels in the lower mineral horizons. This suggests that, in general, TCA is not carried down to deeper soil layers to any great extent (although there are a few examples of higher concentrations at depth – trial samples taken from Zusmarshausen, Freudenstadt and Abreschviller before the main study had concentrations<sup>12</sup> above 10 µg/kg dw in soil samples taken at a depth of 10-30 cm). If it is assumed that removal from the upper layers by leaching was not significant and that there was no formation of TCA in soil over the sampling period, the overall TCA half-life based on the decrease in concentration observed over the period July to December can be

<sup>12</sup> The soil concentration at all other sites from this trial, including those not included in the full study, was below 1 µg/kg dw at the June 2002 sampling date.

estimated to be 30-35 days from the data for the Johanniskreuz and Zusmarshausen sites in de Winkel et al. (2003).

## **B2.5 Levels in vegetation**

There are a number of reports dealing with the levels of TCA in conifer needles. Frank et al. (1994) measured TCA levels in spruce and fir needles (European silver fir, *Albies alba*; Norway spruce, *Picea abies*; and Scots Pine, *Pinus sylvestris*) in Germany in 1990-1; the mean concentrations at six sites ranged from 11.4 to 49 µg/kg. The same authors also reported concentrations from northern Finland; in two stands of trees, 1.2 km apart but with different tree densities, the levels were 9.8-11.4 µg/kg in the more closed stand and 72-90 µg/kg in the more open stand.

Juuti (1997) found a median level of 24 µg/kg fresh weight (fw) in conifer (*Picea abies* and *Pinus sylvestris*) needles in Finland, with 95% of the values below 70 µg/kg fw. The concentration in first year needles was lower (median 9 µg/kg fw) than in needles that were two years older (median 74 µg/kg fw). The concentration varied between the nine sampling sites, even between sites close together. It was noted that elevation did not have a significant impact on concentrations in the pine needles. TCA was also found at 40-320 µg/kg dw in arboreal *Uscneaceae* lichens.

Weißflog et al. (1999) reported the concentration of TCA in Scots pine (*Pinus sylvestris*) needles for a range of sites to the northeast of the Caspian Sea (soil concentrations from some of the sites are reported in Section 2.3 of this appendix). These ranged from 3.15-68.9 µg/kg fw, all in two-year-old needles. The same authors extended the survey to include needles from South America (Chile, Argentina), South Africa, northwest Africa, North America and Europe (Germany and Kola Peninsula, Russia), as well as those from the Caspian Sea area (Weißflog et al., 2003). The samples were all of two-year-old needles, from 7-12 year old trees, largely *Pinus sylvestris* with some *P canariensis*, *P radiata* and *P ponderosa*. The sites were grouped into those with very low background pollution, those with low atmospheric pollution and those with high atmospheric pollution. The concentrations were 1.6–8.2 µg/kg wet weight (WWT) in very low pollution areas, 10.1–19.8 µg/kg WWT in low pollution areas, and 25.0–118.9 µg/kg WWT in polluted areas.

Frank et al. (1998) measured TCA levels in pine needles (species not specified) from sites around Germany in 1993, autumn 1995 and spring 1996. In the most recent samples, needles that were new in 1993 had a mean concentration of 4.7 µg/kg; those that were new in 1994 had a mean concentration of 3.6 µg/kg; and the youngest needles from 1995 had a mean concentration of 2.7 µg/kg (range 0.8–16.7 µg/kg, with only one sample above 5 µg/kg).

Peters (2000) analysed vegetation samples from the forest areas where soil samples were also collected (see Section 2.3 of this appendix). The levels of TCA in these vegetation samples were 10-20 times those found in the soil samples. The average values at each location ranged from 4.7-17 µg/kg dw, and the overall average was 8.0 µg/kg dw.

Weiss et al. (2000) sampled spruce needles (species not specified) from 25 remote forest sites in Austria and analysed them for TCA. In half-year-old needles, concentrations up to 23.3 µg/kg fw (median 7.9 µg/kg fw) were found; in older needles (two and a half years) higher concentrations up to 87.1 µg/kg fw (median 19.6 µg/kg fw) were found. There was no correlation between the TCA levels in the needles and the concentrations of volatile halogenated hydrocarbons

(chloroform, 1,1,1-trichloroethane, tetrachloromethane, trichloroethylene, tetrachloroethylene, bromoform and dibromochloromethane) in the same samples.

TCA has been shown to be taken up by plants from soil (Frank, 1991). Schröder et al. (2003) carried out a series of experiments with Norway spruce (*Picea abies*) and labelled TCA in soil. The uptake of TCA from soil into current year needles of the plants was rapid, and ~70% of the radioactivity was lost from the soil over two weeks after a single application of TCA. Longer term experiments over eight weeks showed an increase in radioactivity in older needles.

Uptake through leaves would appear to be less likely for a hydrophilic substance such as TCA; Juuti (1997) suggested a maximum value of 20% of surface applied TCA taken up from leaves on the basis of experimental results.

Dickey et al. (2004) investigated uptake of TCA from foliar application through branchwood. They exposed 6-7 year old saplings of Sitka spruce (*Picea sitchensis*) to TCA either through direct application to soil or through application as a fine mist to foliage. Application was over two growing seasons, with no application over the winter in between. Two concentrations were used, 10 µg/l (equivalent to annual application to soil of ~900 µg/m<sup>2</sup>) and 100 µg/l (equivalent to 9,000 µg/m<sup>2</sup>). Needles in the 100 µg/l treatments had significantly higher concentrations of TCA than the lower concentration treatment or the controls (which received ~1.5 µg/l in the dilution water). There was no significant difference between the application routes. The uptake from foliar application was considered to occur through the branchwood; levels in the branchwood were significantly higher in the foliar exposures than in the soil exposures. In experiments with excised needles, no significant uptake was seen from TCA solution in 24 hours.

The concentrations in the needles of saplings exposed to 100 µg/l decreased over the winter period when there was no application of TCA; the decrease was to 69% or 75% of the level in autumn, which is equivalent to a half-life of 350 days. This contrasts with a half-life of 50 days determined for an application at the start of the growing season. The saplings exposed to 10 µg/l applications showed no increase in TCA levels over the growing season, and were assumed to be able to degrade whatever amounts were taken up into the saplings, with a half-life apparently of a few tens of days. From the change in concentrations in the needles, less than 6% of the applied TCA was present in the saplings at the end of the first season exposure, and less than 2% of that applied was present at the end of the second season.

Another possible source of TCA in plants is the absorption of chlorinated solvents such as tetrachloroethylene from the atmosphere and subsequent conversion within the plant (Frank and Frank, 1986). Frank (1991) demonstrated uptake of tetrachloroethylene into leaves. In a detailed study on the effects on plants from tetrachloroethylene exposure in air, Plant Research International (2000) measured the concentration of TCA in leaves or needles following exposure to tetrachloroethylene (see Section 3.2.3 in the main tetrachloroethylene report for details). The highest levels were found in pine and spruce needles; after six months of exposure to 252 µg/m<sup>3</sup> tetrachloroethylene the concentrations of TCA in the needles were 70 and 95 mg/kg fw respectively. Kale plants exposed to 1,955 µg/m<sup>3</sup> tetrachloroethylene for 12 weeks had 24 mg/kg fw of TCA in their leaves. It should be noted that these exposure concentrations are far higher than the levels of tetrachloroethylene likely to be found in the environment.

Similarly, Newman et al. (1997) demonstrated that cell cultures from hybrid poplars could degrade trichloroethylene, with TCA being one of the products. They also showed that one-year-old poplar plants could take up trichloroethylene (dosed in water into the soil) and metabolise it to trichloroethanol and other products, one of which was TCA.

### **B3 Estimated levels of TCA in the environment arising from tetrachloroethylene degradation**

In this section a number of methods are used to try to estimate the concentrations of TCA that could arise in the environment from the breakdown of tetrachloroethylene. It should be recognised that some of the methods, such as the EUSES program, do not currently have the ability to accommodate substances that can ionise in the environment. In order to overcome this problem, values for the various properties have been chosen to reflect those of the substance as it exists in the environment. However, it should be noted that this probably leads to greater uncertainty in the results compared to neutral organic substances. These preliminary calculations do not take account of the detailed results of de Winkel et al. (2004) that are presented in Section 4.

#### **B3.1 Global calculation of levels in precipitation**

Estimates of the expected background concentration of TCA arising from the breakdown of tetrachloroethylene in the atmosphere can be made based on the estimated yield of TCA from Section 1 above. From a total release of tetrachloroethylene to the atmosphere of 295,000 tonnes worldwide, the amount of TCA produced from the yields derived in Section 1 would be 13,000-40,000 tonnes.

The lifetime of tetrachloroethylene in the atmosphere is too short to allow mixing between the Northern and Southern hemispheres, and so the concentrations in each hemisphere have to be estimated individually. The measured concentrations of tetrachloroethylene in the Northern and Southern hemispheres were  $13 \pm 6$  pptv (parts per trillion by volume) and  $2.7 \pm 0.4$  pptv respectively in 1989. Assuming the amounts of TCA formed are proportional to the tetrachloroethylene concentrations, the amounts of TCA formed in the Northern and Southern hemispheres would be approximately 10,800-33,100 tonnes and 2,240-6,880 tonnes per year respectively. Assuming the annual rainfall in each hemisphere to be  $2.5 \cdot 10^{14}$  tonnes/year, concentrations in rainwater can be estimated as 43-132 ng/l and 9-28 ng/l for the Northern and Southern hemispheres respectively. These values are of a similar order to those measured in precipitation in remote areas by Grimvall et al. (1995), which are generally in the range 10-100 ng/l. These estimates predict that the concentrations found in the Southern hemisphere at remote locations should be lower than those in the Northern hemisphere. It has been suggested that the measured concentrations in each hemisphere are in fact very similar, and that this points to there being other sources of TCA in the atmosphere than the breakdown of tetrachloroethylene. However, the available measurements do not seem sufficient to allow this hypothesis to be tested.

#### **B3.2 EUSES calculations**

The EUSES model (version 1.0) was run for TCA with an input to the continental model of 2,910 or 8,720 tonnes/year in the air compartment (as estimated above). The values for the various parameters are given in **Table B.6**.

Table B.6 Property values used for EUSES

Property	Value
Melting point (°C)	56
Boiling point (°C)	197
Solubility (g/l)	1,300 (EUSES maximum value is 100)
Vapour pressure (Pa)	6.6 (from OECD (2000), SAMS output)
Log K <sub>ow</sub>	1.33 (measured, for neutral form) -0.27 (measured, presumably mixed neutral and ionised) -2.37 (calculated, KOWWIN, ionised form)
H (Pa m <sup>3</sup> mole <sup>-1</sup> )	1.5 · 10 <sup>-4</sup> (estimated from eqn in Bowden et al., 1997, for 277 K)
pKa	0.7 (from OECD, 2000)
Soil half-life (days)	150 (from OECD, 2000)
Air half-life (days)	446 (from OECD, 2000)*
Water half-life (days)	150 days (assumed, used in some of calculations)
Biodegradation rate in plants (d <sup>-1</sup> )	0.07 (from Frank (1991), used in some of calculations)

\* A more recent value for degradation in air has become available; a half-life of 58 days was estimated from the measured degradation rate with OH radicals (Carr et al., 1996). Using this value has only a small effect on the concentrations.

Three partition coefficient values were used; a measured value for the neutral form of the acid, a calculated value for the ionised form and a measured value taken to represent a mixed form (the range of values makes only a small difference to the results of the calculations for the main compartments). The Henry's law constant was estimated from the equation given by Bowden et al. (1997) based on measurements of partial pressure over aqueous solutions of the acid. The substance was treated as not biodegradable in general, but a half-life of 150 days in soil was used throughout; in addition, the effect of including degradation in water with a similar half-life to soil, and biodegradation in plants were included in some calculations.

The resulting concentrations on the continental scale were:

air	0.07-0.2 ng/m <sup>3</sup>
surface water	1-5.4 µg/l
natural soil	0.24-2.1 µg/kg

On the regional scale the concentrations were:

air	0.6-1.9 ng/m <sup>3</sup>
surface water	4-16 µg/l
natural soil	2.2-20 µg/kg
plant leaves	1.6-379 µg/kg

Comparing these results with the data on measured levels, the predicted concentrations in air are of the same order as the very few measurements available. The surface water levels predicted are considerably higher than the levels taken as the regional background, even when a degradation rate in water is included. The EUSES program does not estimate concentrations in rainwater. The soil concentrations predicted are of the same order as the lower measured values, but are

below the highest measured values by over an order of magnitude. The predicted levels in plants are again similar to the measured levels, but the highest predicted values are somewhat higher than the highest measured values. The levels in plants are particularly sensitive to the value of  $K_{ow}$  used in the calculations, although those in air, water and soil are not.

Overall, some of the predicted concentrations appear to agree reasonably well with the observed levels. However, as there are considerable variations possible in the values of the properties chosen, and in the measured levels themselves, this agreement may well be fortuitous. Therefore this assessment will not draw any conclusions from this comparison.

### **B3.3 Estimation of soil concentration from rainfall**

The following calculation estimates the concentrations in soil that might be expected to arise from the deposition of TCA from the atmosphere. The concentrations of TCA in rainwater for these calculations are taken from the data presented in Section 2.2, in particular from the results of Schleyer et al. (1996).

From the TGD, the standard rainfall is 700 mm/year, or 1.92 mm/day. On an area of 1 m<sup>2</sup> this is a volume of  $1.92 \cdot 10^{-3}$  m<sup>3</sup> per day.

For a concentration of 850 ng/l in rain (taken as representative of the levels in forest areas), the amount deposited per day is 1.63 µg/m<sup>2</sup>

The removal half-life for TCA in soil estimated by OECD (2000) is 150 days ( $k = 4.6 \cdot 10^{-3}$  d<sup>-1</sup>). Assuming steady state, removal rate equals deposition rate, or

$$4.6 \cdot 10^{-3} \text{ (d}^{-1}\text{)} \cdot \text{amount (}\mu\text{g/m}^2\text{)} = 1.63 \mu\text{g/m}^2\text{/day}$$

The amount of TCA at steady state is therefore 354 µg/m<sup>2</sup>.

This amount will fall on 1 m<sup>2</sup> to a depth of 10 cm, for natural soil (taken to be the same as grassland), which is a volume of 0.1 m<sup>3</sup>. With a soil density of 1,700 kg/m<sup>3</sup>, the soil mass in this volume is 170 kg.

Hence, the concentration of TCA in soil =  $354/170 = \sim 2$  µg/kg.

This calculation does not include leaching. From EUSES, the leaching rate is 0.007-0.024 d<sup>-1</sup> for grassland soil. Including this removal rate gives a soil concentration of 0.3-0.8 µg/kg.

For the open area rain concentration of 200 ng/l, the equivalent concentrations are 0.5 µg/kg (degradation only) and 0.08-0.2 µg/kg (degradation and leaching).

The highest concentrations of TCA in rainwater were reported by Schöler (1998), with two values of 9.7 and 8.5 µg/l in a series for which the rest were below 1 µg/l and much closer to other measurements. These high concentrations coincided with increased rainfall at the site in Bleche, Germany, and the estimated deposition rate for TCA for the month in which this occurred was 5.2 g/ha (compared to the usual rate of 250 mg/ha). Using the same assumptions as above, i.e. a half-life for TCA in soil of 150 days, the soil concentration arising from this incident would be 22 µg/kg.

The concentrations estimated by this method are of the same order as the lower measured levels found in soil by some authors, although they tend to be lower than all measurements when leaching is taken into account. They are much lower than the high levels in soil reported for forest areas by Frank (1988) and Plumacher and Renner (1991, 1993). The data from Schöler

(1998) indicate that there may occasionally be much greater inputs into the soil than those expected from general measurements on levels of TCA in rainwater.

### **B3.4 Mass balance calculations reported in the literature**

Attempts have been made to construct a mass balance for the soil in a forest area. Juuti (1997) calculated the amount of TCA deposited to soil from the average concentration in precipitation (100 ng/l for Finland) and the annual rainfall. This deposition rate was doubled to account for the increased concentration found in throughfall in forests. The potential contribution from needle litter fall was also considered, based on an average concentration of TCA in needles of 24 µg/kg and a needle fall rate of 0.1 kg/m<sup>2</sup>/year. These gave an estimated combined input of 103-143 µg/m<sup>2</sup>/year. The uptake of TCA into needles was estimated based on a needle fresh weight of 13-24 tonnes/ha, the average concentration of TCA in needles (24 µg/kg) and the elimination rate in needles (0.07 d<sup>-1</sup>, from Frank (1991)). This equates to an uptake of 800-1,500 µg/m<sup>2</sup>/year, which is around ten times that deposited from rain. It was recognised that there are uncertainties in the calculations. In addition, the author pointed out that this calculation does not include biodegradation of TCA in soil or leaching to groundwater, so that the amount available for uptake into trees would in fact be much less than that deposited to soil.

Schöler (1998) performed a similar calculation. The concentration of TCA in rainwater reaching forest soil was assumed to be 400 ng/l (including the throughfall component) with an annual rainfall of 800 mm/year. These give an input of 3.2 g/ha/year (320 µg/m<sup>2</sup>/year for comparison with the calculations by Juuti (1997)). For the contribution from litter fall, a mean litter fall of 1 tonne/ha was used, with a concentration in needles of 50 µg/kg leading to an input of 50 mg/ha/year. For uptake into trees, the same elimination rate of 0.07 d<sup>-1</sup> was used, but with a needle weight of 18 tonnes/ha and a concentration of TCA in needles of 50 µg/kg (range of 1-180 µg/kg). These lead to a flux of TCA into trees of ~20 g/ha/year (2,000 µg/m<sup>2</sup>/year), with a range of 0.5-83 g/ha/year. The seepage (leaching) from soil was also estimated based on a concentration of TCA in groundwater of 0.04 µg/l (based on a few measurements) and an annual groundwater recharge of 22 mm/year, giving a flux of 80 mg/ha/year. The concentration of TCA in soil was taken as 20 µg/kg, with an elimination rate through degradation assumed as 0.07 d<sup>-1</sup>. In order to balance these figures, a production rate of 1.6 kg/ha/year of TCA in soil was calculated.

There have been criticisms of calculations like these, in that they use monitoring data for the various compartments (rain, soil, needles, etc.) from different locations and times. Clearly a consistent set of data where all values were measured together would give more confidence to the calculations, although those by Juuti (1997) did use mostly data from Finland collected over the same period.

Recently a single catchment study has been conducted on a forest and moorland catchment in Scotland (Stidson et al., 2004). Concentrations and input/output fluxes of TCA were measured in all relevant media over one year. The results indicated that, well-within measurement uncertainties, the catchment was at steady state with respect to TCA. Calculations of the amount of TCA in the catchment indicated a minimum residence time of 1-2 years in relation to the flux out of the catchment. This is much longer than the degradation half-lives in soil and biota found in other studies, which are of the order of weeks. The authors conclude that the results are evidence for the production of TCA within the soil of the catchment, and/or that only a proportion of the TCA in the soil is actively involved in TCA cycling.

## **B4 Experimental Mass Balance Investigations**

The investigations reported in this section were carried out by Industry in accordance with Commission Regulation (EC) No. 2592/2001/EC. The aim was to carry out investigations of the quantitative link between TCA levels in soil and tetrachloroethylene, and to determine the geographical extent of the high TCA levels in central European soils. This programme was overseen by a steering group of experts from Industry, Germany and the UK and was carried out over 2002-2003.

De Winkel et al. (2003) identified a number of sites with high measured levels of TCA in soil in 2002 (see Section 2.3). As a follow-up to this work, the same authors performed more detailed investigations at three of the sites with particularly high levels: Zusmarshausen (site 917), Freudenstadt (site BZE040) (both in southern Germany) and Abreschviller (site SP57, north-east France) (de Winkel et al., 2004). Measurements of TCA in rainwater and soil at these sites were continued. Supplementary investigations at one or more of the sites included the measurement of the sorption of TCA to the different soil horizons, investigation of the significance of the surface layer through shielding and removal, and the use of isotope enhancement of chloride in doping experiments. The aim was to develop a mass balance for TCA in these soils. The soils at the German sites were mainly clay, whereas the French site was sandy.

The fieldwork for this phase took place over the period from February to September 2003. Details of the methods used and the analyses undertaken are included in the study report and are not repeated here. Some of the results from the study conducted in 2002 have also been included in the following discussion. The sampling times have been allocated to months (rather than the actual sampling dates from the report) for ease of presentation. The sampling intervals were four to six weeks, and as a result there was no June sample. The sampling date marked as October here was in fact the last day in September.

### **B4.1 Levels of TCA in soil**

As with the measurements in the earlier investigations in 2002, the highest concentrations of TCA were found in the organic surface layer (the L horizon), and tended to decrease rapidly with soil depth. There are some exceptions to this: for the Abreschviller site (SP57) the concentrations in the first mineral horizon (Ah) were similar to those in the L horizon. This was also noted for the Zusmarshausen (917) site in 2002, but not in 2003. Overall, the concentrations seen in 2003 did not reach such high levels as measured at the start of the study at the end of June 2002.

The measured levels are presented in **Table B.7**. The data from the original report are presented as levels in the L and A horizons. These have been combined for this Appendix (as averages by depth) to make the values more comparable with the soil depths used for the TGD risk assessment method. The same combination was carried out for the data from the earlier 2002 investigation (**Table B.5**)

Table B.7 Soil concentrations of TCA at three central European sites during 2003

Site code	TCA concentration ( $\mu\text{g}/\text{kg dw}$ )						
	March	April	May	July	August	September	October
917	1.4	0.6	0.6	1.4	1.2	1.8	
BZE040	5.7	6.7	2.0	12.1	8.0	9.5	4.8
SP57	1.2	0.85	1.4	1.1	7.8	9.7	

In addition to these three sites, samples were also taken at three other sites from the 2002 study in September 2003. The levels found (L plus Ah horizons combined) were 3.0 (site 707), 1.6 (site 804) and 1.4 (site 902)  $\mu\text{g}/\text{kg dw}$ .

#### B4.2 Levels of TCA in rain and deposition

The rainwater samples were collected over the periods between the soil sampling dates, and so are aggregated samples over the time leading up to the soil sample. Several rainwater collectors were employed at each site; some were positioned to collect rainfall directly, others collected rainfall reaching the ground via foliage (throughfall). The samples were combined before analysis.

The concentrations found in rainwater tended to be higher than those found in 2002 for the same sites. This was at least in part due to the lower rainfall during 2003 when compared to the same period in 2002. The rainfall in the second half of 2002 was generally high in relation to normal rainfall for the sites, whereas the 2003 period was an extremely dry season. The concentration ranges found for TCA in rainwater at the three sites were: Zusmarshausen, 80 – 767 ng/l; Freudenstadt, 91 – 463 ng/l; and Abreschviller, 42 – 424 ng/l.

The monthly deposition flux at the sites varied over the period of 2003. Values for each sampling period are given in **Table B.8**.

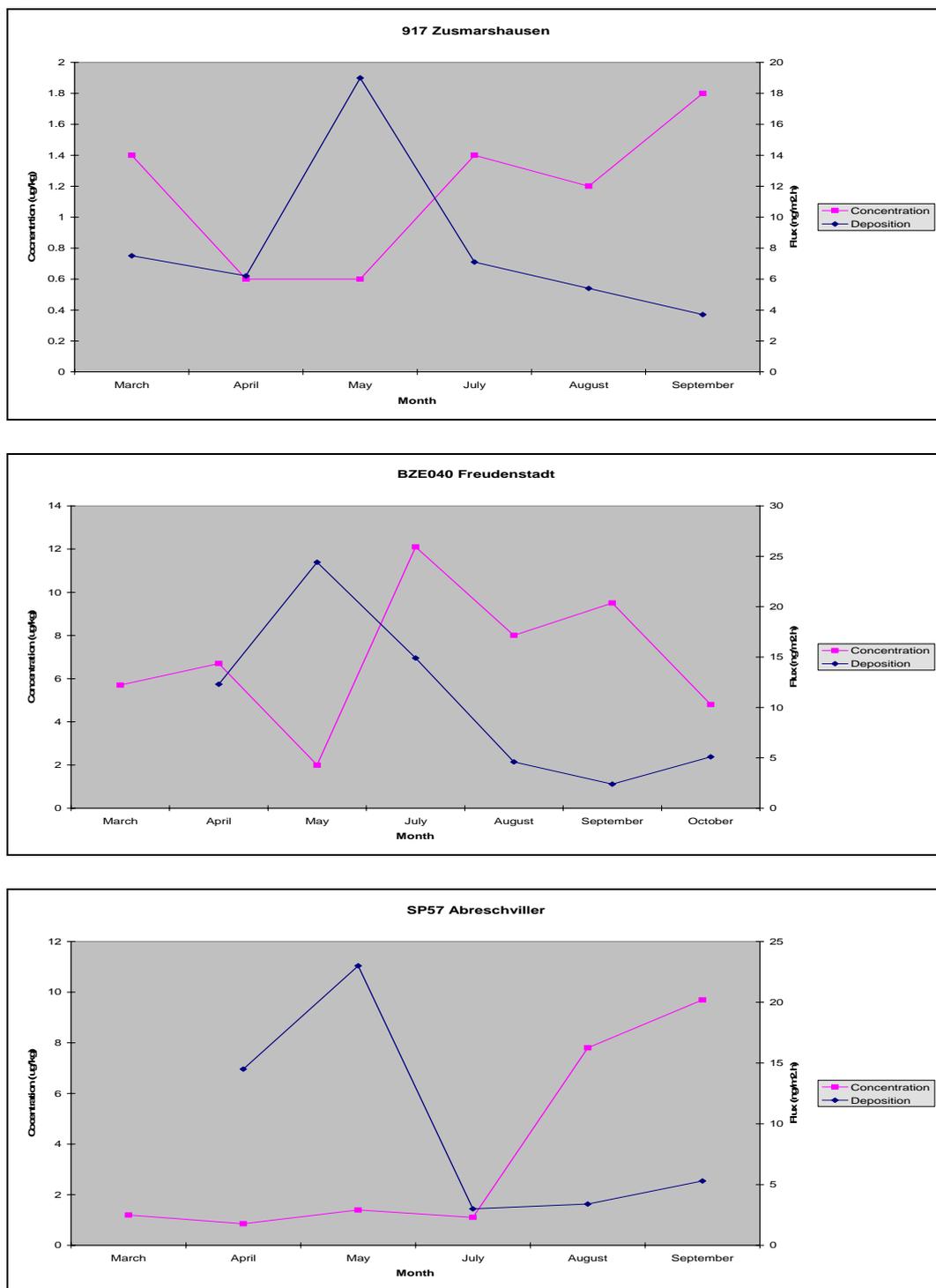
Table B.8 Calculated deposition fluxes ( $\text{ng}/\text{m}^2\cdot\text{h}$ ) for 2003

Site code	TCA deposition flux ( $\text{ng}/\text{m}^2\cdot\text{h}$ )						
	March	April	May	July	August	September	October
917	7.5	6.2	19	7.1	5.4	3.7	
BZE040		12.3	24.4	14.9	4.6	2.4	5.1
SP57		14.5	23	3.0	3.4	5.3	

The average fluxes were  $8.1\pm 5.0$ ,  $10.6\pm 8.3$  and  $9.8\pm 8.7$   $\text{ng}/\text{m}^2\cdot\text{h}$  for sites Zusmarshausen, Freudenstadt and Abreschviller respectively. These correspond to annual fluxes of 70, 93 and 86  $\mu\text{g}/\text{m}^2$ . For comparison, the average deposition flux for all sites studied in 2002 over the June to December period was  $18.2\pm 8.2$   $\text{ng}/\text{m}^2\cdot\text{h}$ , or 160  $\mu\text{g}/\text{m}^2$  annually.

**Figure B.1** compares the input from rain to the concentrations found in soil (the fluxes are for the month preceding the soil sampling). There is no clear correlation between the two.

Figure B.1 TCA concentrations in soil compared to rainwater input rates for three central European sites in 2003



To examine the importance of input from rain more accurately, an area of soil at each of the sites 917 (Zusmarshausen) and BZE040 (Freudenstadt) was covered to prevent rainfall reaching the ground surface. Clean water (concentration of TCA less than 10% that in rainfall) was applied to these areas at the same rate as the measured rainfall at the sites. At Zusmarshausen, the concentrations of TCA measured in the two upper soil horizons (L and Ah) in the shielded patch were similar to those measured in the unshielded areas. There was no notable reduction in concentration in the shielded area, and there was even some evidence of a possible slight

increase towards the end of the study. At Freudenstadt, again for the most part the concentrations were similar between the shielded and unshielded patches, and higher concentrations were measured in the shielded patch on occasion. **Table B.9** shows the concentrations for the shielded and unshielded areas for the two sites.

Table B.9 Concentrations of TCA in shielded (S) and unshielded (US) soils

Site code	S/US	Month					
		March	April	May	July	August	September
917	S	2.5	0.5	0.6	1.0	1.0	1.2
	US	1.4	0.6	0.6	1.4	1.2	1.8
BZE040	S		4.3	2.7	18.1	4.4	3.4
	US		6.7	2.0	12.1	8.0	9.5

The study report concludes that as there is no significant input from rain to the shielded patches, the fact that similar concentrations were measured compared to the unshielded patches strongly suggests that there was another source of TCA in the soil other than from rain or needle fall.

#### **B4.3 Levels of TCA in leaf-fall**

Leaf-fall at the sites was too low to measure over the course of the experiment in 2003 (<50 g/m<sup>2</sup>/month). From other long-term studies in the Bavarian forests, deposition of litter is 2-5 tonnes/ha/year (50 g/m<sup>2</sup>/month would equate to 6 tonnes/ha/year). Based on a maximum litter deposition rate of 50 g/m<sup>2</sup>/month and a maximum concentration of 10 µg/kg TCA in needles (the highest measured value from the sites was 7 µg/kg), the litter deposition rate for TCA would be at most 0.5 µg/m<sup>2</sup>/month, or 6 µg/m<sup>2</sup> annually. Compared to the deposition fluxes from rainwater, which were 83 µg/m<sup>2</sup> in 2003 and 160 µg/m<sup>2</sup> in 2002, leaf-fall will contribute less than 10% to the overall input.

Concentrations of TCA measured in litter samples from two of the sites were higher than those in the L horizon at the corresponding sample time. The decomposition of litter is slow, and it could take around ten years to decompose needles fully to humus (Persson and Anderson, no date). It is therefore possible that the accumulation of needles in the top layer could account for the high concentrations measured there in comparison to the much lower levels in the horizons below. However, the fall of needles is expected to be relatively constant over time, and hence, unless TCA levels in needles vary considerably with time, the level of TCA from needles in the top layer would be expected to be constant. Measurements show considerable variation in the TCA concentration in the top layer, both seasonally and from year to year, so it seems unlikely that needle accumulation can explain the concentrations found in soil.

#### **B4.4 Levels of tetrachloroethylene and ozone in air**

The monthly average concentrations of tetrachloroethylene in the air at the sites ranged from 0.06–0.24 µg/m<sup>3</sup>. Higher concentrations were found in the summer months, and the concentrations in summer 2002 were noticeably higher than those in 2003. There were no great differences in tetrachloroethylene levels between the sites; the average concentrations over the measurement period in 2003 were 0.14 µg/m<sup>2</sup> for Zusmarshausen, 0.11 µg/m<sup>3</sup> for Freudenstadt and 0.13 µg/m<sup>3</sup> for Abreschviller.

The concentrations of tetrachloroethylene in air at these three sites were found to correlate with the wet deposition rate of TCA.

Ozone concentrations in air were also measured at the three sites, and these showed similar behaviour across the sites. The highest concentrations were found in June and July as expected, decreasing to a minimum in November and December (for both 2002 and 2003). Higher concentrations were found in 2003 than in 2002. There was no clear correlation between ozone levels (considered to be an indicator of photochemical activity) and tetrachloroethylene levels – an inverse relation might have been expected (i.e. a higher amount of tetrachloroethylene would be degraded, giving a lower concentration, when more ozone is present). There was also no correlation between ozone levels and the wet deposition rate of TCA.

#### **B4.5 Levels of TCA in fog**

It has been suggested that higher concentrations of TCA may accumulate in fog compared to rainwater, and that these may contribute to higher concentrations of TCA in soil in areas heavily affected by fog. Measurements of average fog:rain TCA ratios vary between 1.2 and 4.4 (see Section 2.2 for details).

The 2003 study used passive samplers to collect fog samples, as was done in 2002. However, it proved difficult to collect sufficient sample in the second part of the study, and volumes were generally low (in the case of the Freudenstadt site, these were too small to be analysed). The fog:rain TCA level ratios obtained over both 2002 and 2003 at Zusmarshausen, Freudenstadt and Abreschviller were mainly in the range 1-5, but the ratio reached 100 at times of very low concentration in rainwater. This is assumed to be due to fog dissolving TCA from the air in periods with no rain. The data indicate an inverse correlation between fog and rain concentrations. Although the concentration in fog can be high, the volumes of water deposited from fog are low based on the data from these studies, so that the overall contribution of TCA from fog is not considered to be significant in relation to the higher TCA levels in soil. Heal et al. (2003) also concluded that fog did not make a significant contribution to overall TCA deposition.

#### **B4.6 Relationships between soil TCA levels and soil properties**

The temperature in soil at the three sites was measured at three depths: 5, 20 and 50 cm. Comparing the temperatures recorded with the concentrations of TCA measured in soil, the higher TCA levels coincide with temperatures above 15°C (Freudenstadt) and 20°C (Abreschviller). There appears to be no distinct relation between the TCA levels and the soil pH – high levels have been found in soils with pHs above and below pH 4.

Samples of soil water were taken at depths of 25, 50 and 75 cm from the sites where possible (on some sampling visits no soil water could be collected due to dry weather conditions). No clear concentration profile for TCA was noted in these samples. The concentration in soil water was in all but one case lower than that in rainwater. The concentrations in soil water from the 25 cm depth, below the Ah horizon, does not seem to correlate with the concentration measured in the upper soil layers (combined L and Ah horizon).

#### **B4.7 Adsorption of TCA to soil**

It has previously been suggested that high levels of TCA in some soils might be due in part to an accumulation mechanism that is not accounted for. Partition coefficient ( $K_d$ ) values were therefore measured in soils from all the sites sampled in 2002, using  $^{13}\text{C}$ -labelled TCA and OECD Guideline 106. The average  $K_d$  value for the L horizon was 2 kg/kg, corresponding to an average sorption of 32-40%. For the A horizons, sorption was 24-38% and for the lower B and C horizons it was 10-22% (so  $K_d$  was less than 1 for these).

The apparent  $K_d$  value derived from the concentrations in rainwater and soil from the L horizon appears to vary with time, from a value of 2.5 early in the year to 150, with an average value of 45.5 from July onwards. The composition of the horizon does not vary significantly and so the value of  $K_d$  would also not be expected to vary to this extent. Hence there must be other factors that affect the concentration of TCA in the soil.

#### **B4.8 Effect of the L horizon**

The significance of the L horizon was investigated by removing this horizon from a patch of soil at the Zusmarshausen and Freudenstadt sites. These patches were watered with clean water (concentration of TCA less than 10% of that in rainfall) at the same rate as the rainfall at the sites, in the same way as for the covered patches described in Section 4.2. The results were compared to those from the full soil exposed to natural rain and to the shielded sites receiving the artificial rain. At Freudenstadt, soils with an intact L horizon showed increases in the concentration of TCA which were not shown in the patch with the horizon removed. Little difference was noted between the patches at Zusmarshausen. The results indicate that processes in the L horizon can be important in relation to soil TCA levels. Experiments were carried out on soil samples from these sites to determine the soil microbial biomass carbon content of the soil layers, as an indication of potential microbial activity. The results showed that the microbial biomass was mainly concentrated in the L horizon.

#### **B4.9 Comparison of TCA levels with chloroform and tetrachloroethylene in soil gas**

Both chloroform and tetrachloroethylene were measured in soil gas at three depths at each of the three sites. The concentrations were compared to those measured in air at 0.6 and 1 m height at the sites, under the tree canopy. At Zusmarshausen, the levels of chloroform found in the soil gas were of a similar order to those found in air. At Freudenstadt, the chloroform levels in soil gas were similar to those in air until July, when the soil gas concentration increased by a factor of 4. At Abreschviller, the chloroform concentration in soil gas was lower than that in air over the first part of the year, but increased in June and July to levels up to 70 times those in air. These changes coincided with increases in the TCA concentration at the sites, and the chloroform concentration in soil gas correlates reasonably well with the TCA mass calculated for the upper two soil layers from the soil TCA concentrations and the properties of the soil layers. In contrast, there was no correlation apparent between the deposition rate of TCA and the chloroform concentration.

The tetrachloroethylene levels in soil gas were generally lower than those in ambient air.

#### **B4.10 Doping study**

A chlorine doping study was carried out at the Freudenstadt site to test whether TCA could be formed *in situ* in soil. An area of soil was shielded from the rain, as described in Section 4.2, and water containing sodium chloride enriched with  $^{37}\text{Cl}$  was added in such a way as to maintain the natural conditions as far as possible. The application rate of sodium chloride solution used was intended to match the average rainfall; it was applied once per week to the patch over a period of 0.5 – 1 hours. The later part of the experiment coincided with a dry period, so that the water application exceeded that actually occurring from rain in this period. The amount of chloride applied exceeded that deposited in rain, but was within a factor of five.

The natural relative abundance of the two chlorine isotopes is 76%  $^{35}\text{Cl}$  and 24%  $^{37}\text{Cl}$ . Adding sodium chloride enriched with  $^{37}\text{Cl}$  alters this ratio in the chloride ions in the soil. If compounds

containing chlorine are produced in the soil, then the chlorine isotope ratio in these will be different from that occurring naturally. In this study, mass spectrometry of the methyl ester of TCA was used to examine the ratio. The ion used for this derived from TCA has two chlorine atoms, and so there are three possible combinations:  $2^{35}\text{Cl}$ ,  $^{35}\text{Cl}^{37}\text{Cl}$  and  $2^{37}\text{Cl}$ . The peak area of the second ion as a percentage of the area of the first ion was used as the measure in this case. From repeated measurements on 'normal' TCA the mixed isotope ion peak was 66% of the  $2^{35}\text{Cl}$  ion, with a standard deviation of 3%. A deviation of more than three standard deviations from the average is considered to be significant, hence a peak area which was 75% or more of the  $2^{35}\text{Cl}$  peak would not be considered to arise from the natural abundance of the isotopes. The results found for the L horizon were 91% after 19 days, 101% after 52 days and 107% after 77 days. For the A horizon the ratio was 69% at 19 days and 90% at 77 days. The results may provide evidence of the *de novo* formation of TCA in the L horizon. However, there is also the possibility of exchange of chlorine between TCA and the soil solution. Any such exchange of chlorine between the chloride in solution and TCA would also lead to an enrichment of the  $^{37}\text{Cl}$  level in TCA. Although such exchange is well known for alkyl halides in solution, there is very little if any information in relation to polyhalogenated species in soils. The conclusion is therefore that the study cannot be taken as clear evidence of in-situ formation of TCA in soil.

Measurements on the isotope ratio of chloroform and tetrachloroethylene in the soil gas were also made. These showed values of 96%, 110% and 115% for chloroform at 19, 52 and 77 days respectively in the L horizon. The isotope ratio for tetrachloroethylene did not change, with values of 65%, 66% and 66% at the same time intervals in the L horizon.

#### **B4.11 Mass balance calculations**

The mass balance developed as part of the study by de Winkel et al. (2004) is of a different form to that presented in Section 3.4. The calculations are performed on time series of data, so allow for variation in the rainfall, concentration of TCA in rain, water movement, etc. The model includes the calculation of TCA input in rain and in fog based on the measurements made at the sites. Water input to the soil comes from rain, and the amount of water lost through evapotranspiration is calculated from weather observations. The balance of these affects whether water moves down through the soil or is drawn up toward the surface. The movement of TCA between the soil horizons is calculated based on the net water movement. TCA input from leaf fall is also included as an average rate.

The model does not include specific terms for the degradation of TCA in soil or for the formation of TCA in soil, as the variation of these parameters with time and conditions is not known. Instead, the other properties are used to calculate a net change in the amount of TCA in each soil horizon, and hence a concentration in each horizon. These are compared to the measured concentrations, to determine whether there has been removal or addition over the period that is not accounted for in the calculations. Data for the three sites in 2003 are combined to give a hypothetical site representing average forest conditions. Details of the model are included in the study report and are not repeated here (de Winkel et al., 2004).

The results show removal in excess of that calculated in the model - assumed to be due to degradation - over the period of late summer and autumn 2002. They show addition in excess of the calculated amounts in the summer period in 2003. This is an overall result, and so is over and above any TCA removed by degradation during this period. The calculations indicate the TCA is formed in both the L horizon and possibly also the A horizon, although the method cannot exclude the possibility that TCA in the A horizon arises through leaching from the L horizon.

It is not possible to use the model to determine a rate of production for TCA, as only the net result of production and degradation is calculated, and there are no independent measurements on the degradation rate for this study. Calculations of the amount of TCA in the soil at each sampling time indicate that at Freudenstadt and Abreschviller the effective flux of TCA into soil required to give the highest concentrations is 400–1,000 ng/m<sup>2</sup>.h. This compares to a maximum flux from rainwater over the same period of less than 25 ng/m<sup>2</sup>.h, indicating a much higher input from formation than from rain at times when the soil concentration is high.

From the calculations it is clear that both formation and degradation vary with time. As a result, the TCA mass change rate in soil is not the product of a constant degradation rate and a seasonally varying formation rate – rather, both processes vary seasonally and possibly with other factors. It may be that both processes are much reduced or stopped in autumn/winter as a result of the reduced temperature. The net loss of TCA from soil seen in this period may then be due to increased leaching caused by higher rainfall. In spring both formation and degradation start again, but with different and independently changing rates.

#### **B4.12 Carbon isotope ratio determination**

The carbon isotope ratio can provide information on the origin of a substance in an environmental sample. Carbon-14 is a radioactive isotope with a half-life of 5,730 years, and it is present at steady-state in the atmosphere. It is incorporated into living organisms as part of the normal assimilation of carbon, and so the level in living matter is essentially the same as that in the atmosphere<sup>13</sup>. When an organism dies, incorporation of new carbon stops and the <sup>14</sup>C decays. Carbon from a petrochemical source, which was living matter millions of years ago, does not contain any <sup>14</sup>C because of this decay. Consequently, TCA formed through the degradation of anthropogenic tetrachloroethylene will not contain any <sup>14</sup>C either. On the other hand, the organic matter in soil was part of living matter only relatively recently and so will contain <sup>14</sup>C at or close to the natural abundance. Any TCA formed from this organic matter will also have a similar level of the isotope. Hence the amount of <sup>14</sup>C in a TCA sample can give information as to its origin. As <sup>14</sup>C is only present at 1.2 parts per trillion in ‘modern’ carbon, a very large amount of sample is needed to detect it (based on current analytical techniques).

Frank and co-workers have carried out developmental work on a method to determine the carbon isotope ratio in TCA extracted from soil samples. The study is reported in Jakubowska-Switaj et al. (2004) and details can be found there. Only an outline of the procedure and results is included here. Around 110 kg of soil were collected from a site at Oberthulba, northwest Bavaria in July 2002. The samples were collected in bags as 4 kg batches, with four bags collected from each of six 1 · 1 metre squares across a circular area of ~30 m diameter. This soil was extracted in one-kilogram batches, and the combined extracts were processed through a multi-stage clean-up procedure, with methylation as the last step. The methyl ester of TCA was then further purified using two-dimensional preparative gas chromatography. The isotope ratio in the sample was determined by accelerator mass spectroscopy, using a modified technique which allowed the analysis of the sample without it being first converted into graphite.

The study detected a level of ‘modern’ carbon in the TCA that was not significantly different from that in the blank. The authors concluded that the TCA extracted from the soil came from an old source, most likely petrochemical.

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<sup>13</sup> The ratio in organisms will differ slightly due to the effects of the different masses of the carbon isotopes on the diffusion of substances. This is considered in the calculation of the results from the study.

The average concentration of TCA in the soil was 1.1 µg/kg. Separate analyses on each collection bag showed a high level of variation between the bags, with individual concentrations ranging from 0.3 to 3.0 µg/kg.<sup>14</sup> These results suggest that all individual measurements (in all studies) should be treated with some caution, as there could be variation over relatively small scales at all sites. The results probably reflect local variations in soil properties, composition, physical nature, etc. Such variations could lead to variation in the rates of degradation and leaching over small scales, and could also mean that conditions suitable for potential natural formation may exist over localised areas.

Radiocarbon measurement is a novel method of analysis for TCA, and the level of ‘modern’ carbon that could be detected by the procedure is not clear at present. The average soil concentration is not much greater than the higher concentrations in soil estimated to result from deposition from the air in the simple calculations in Section 3.3. It is also similar to the concentrations measured at Zusmarshausen in the second stage of the sampling by de Winkel et al, when no real seasonal increase was seen in the TCA concentration over the summer and it appeared that little or no *in situ* production occurred. It seems a possibility, therefore, that deposition could account for much if not all of the TCA in the soil that was sampled. If so, it can be anticipated that little or no modern carbon would be present (since the TCA deposited is likely to come from anthropogenic sources). This interpretation would depend on how small a contribution of modern carbon can be detected with the method. The <sup>14</sup>C content of the soil organic matter was not reported, so no direct comparison can be made with that of the TCA contained in the soil.

The result can be taken as further evidence that TCA formed through the degradation of anthropogenic chemicals contributes to the levels of TCA found in soils.

#### **B4.12.1 Effects of TCA**

The effects of TCA on aquatic organisms are considered by the OECD (2000). Short-term tests are available for fish, invertebrates and algae, and long-term tests for fish and algae. An assessment factor of 50 is used with the long-term algal result to give a PNEC of 0.17 µg/l.

For terrestrial organisms, short-term tests on a range of plants and on earthworms from a ring test are available. There are also two long-term studies, on spruce and fir seedlings and on earthworms. Although some uncertainties about both studies are discussed in the assessment (in particular the reported details of the spruce and fir studies are very limited), they are considered to be good enough to use for risk assessment. An assessment factor of 50 gives a PNEC of 2.4 µg/kg dw. The NOEC of 0.12 mg/kg on which the PNEC is based comes from a 60-day study on pine and spruce seeds, the endpoint being weight of root produced. The assessment discusses the possibility of using a lower assessment factor of 10, but concludes that this would not be justified. For long-lived species such as spruce and pine a 60-day test could not be considered to be a full chronic test, and the test did not include the possible effects of TCA on reproduction.

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<sup>14</sup> Six of the 24 samples had levels above 1 µg/kg. If natural formation were responsible for the higher levels, then there should be some ‘modern’ carbon present in the combined sample. It is not clear whether the method would be able to detect this level of ‘modern’ carbon.

## **B5 Risk characterisation**

### **B5.1 Aquatic risk characterisation**

The aerial deposition of TCA arising from the degradation of tetrachloroethylene contributes to the regional concentration in water. This is estimated to be 0.12 µg/l in the OECD assessment (OECD, 2000), which is below the PNEC of 0.17 µg/l and hence gives no concern. It should be noted that there is scope to refine the aquatic PNEC in any case.

### **B5.2 Terrestrial risk characterisation**

The soil PNEC of 2.4 µg/kg dw gives concern for sites in Germany with measured soil concentrations from studies conducted in the late 1980s and early 1990s (especially in the Black Forest region), and also for one site in The Netherlands at a similar time. In a more recent wider survey by Peters (2000), only two samples had concentrations greater than the PNEC. These both came from the Freudenstadt area in the Black Forest, and were taken from 0.3 and 0.6 m depth. The average concentration from this site was also greater than the PNEC.

Seven of the sites included in the most recent studies by de Winkel et al. (2003) had concentrations above the PNEC (in the combined L and A horizons) in August 2002 (PEC/PNEC ratios 1.04 – 4.5). The Freudenstadt site also had a concentration just above the PNEC in October 2002 (ratio 1.07). All the sites had concentrations below the PNEC in December 2002 (Freudenstadt was not sampled at this time). In 2003, the Freudenstadt site had soil concentrations above the PNEC at each monthly sampling time from March to October 2003, with the exception of May (ratios 0.83 – 5.0). The site at Abreschviller in France had concentrations above the PNEC in August and September 2003 (ratios 3.7 – 4.0), while the soil concentrations at Zusmarshausen in Germany remained below the PNEC (highest ratio 0.75) throughout the whole of the 2003 sampling period

The calculated concentration in soil based on simple deposition (0.3–0.8 µg/kg including leaching, see Section 3.3) would not give rise to concern.

Two individual soil samples from the 24 collected at a single site by Jakubowski et al. (2004) had TCA levels above the PNEC (the highest PEC/PNEC ratio being 1.25). This indicates that the potential risk may vary over relatively short distances.

### Discussion

TCA presents a hazard to soil organisms, and soil levels have been measured in a number of areas across central Europe that exceed the PNEC derived in the OECD assessment (OECD, 2000), which suggests a risk for the terrestrial compartment. Tetrachloroethylene degrades to TCA in the atmosphere (as well as in plants), and so can be expected to make an important contribution to the levels that have been measured in soil. The principal area of uncertainty concerns the significance of this contribution to those higher levels that might be causing a risk.

A number of theories have previously been put forward by a variety of experts to explain these higher levels. These include:

- enhanced atmospheric deposition of TCA at some locations (including from fog and leaf-fall),
- enhanced retention of TCA in soil (e.g. some form of adsorption or complexation which prevents the TCA from being degraded or leached), and

- natural production of TCA in soil<sup>15</sup>.

In an attempt to reduce this uncertainty, detailed investigations of the geographical extent of the high TCA levels in central European soils and the quantitative link between soil TCA levels and atmospheric inputs (related to tetrachloroethylene levels) have been carried out in 2002 and 2003 (de Winkel et al., 2003 and 2004).

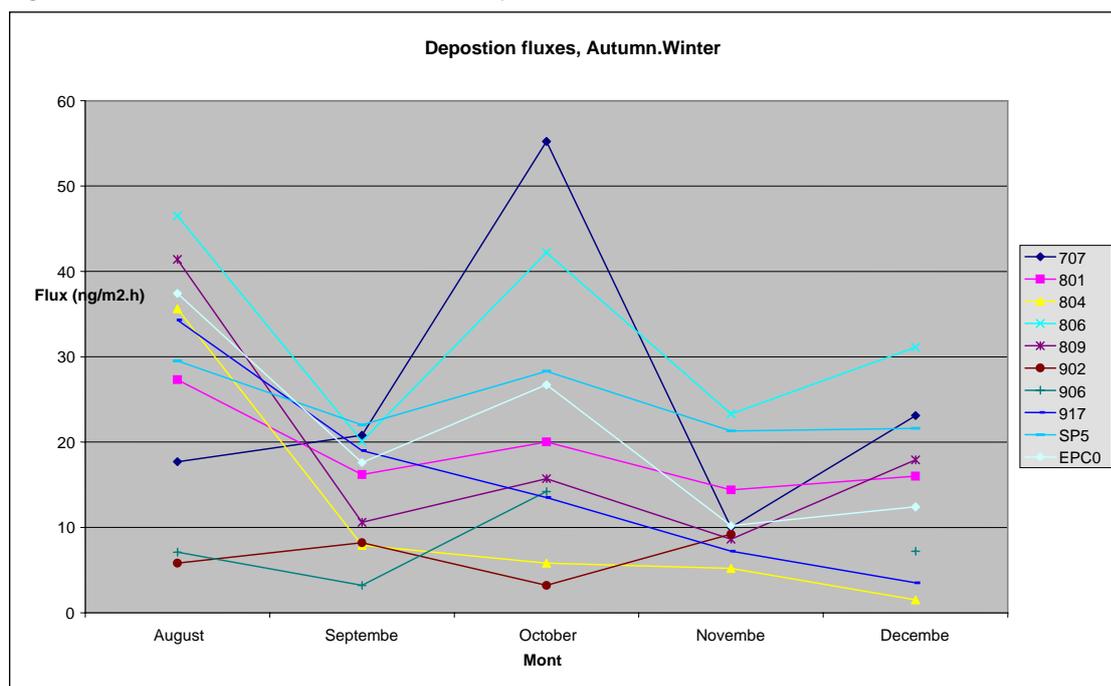
It is clear from this work that TCA levels can still be found that exceed the soil PNEC at a number of forest locations across central Europe (from north-east France and across southern Germany). A risk therefore still appears to exist in some areas. This situation is, however, greatly complicated by seasonal variation. The higher levels were found in samples taken in mid-summer; samples from the same sites in mid-winter had concentrations below the PNEC in all cases. The concentration of TCA in rain at these sites tended to decrease over the same period, but since the rainfall intensity tended to increase, the deposition of TCA did not follow the concentration variation. **Figure B.1** (see Section 4.2) shows the relationship between the actual depositional flux of TCA from rain and the concentration in soil by month at the three sites studied in 2003. The greatest increases in soil concentration coincide with decreases in the input from rain. Peaks of input from rain do not coincide with increases in soil concentration.

**Figure B.2** shows the deposition fluxes by month for the ten sites studied in 2002. The average flux in December is around half of that in August. The figure shows that there can be significant variation in the deposition flux over time. The TCA fluxes from rain in 2002 were generally higher than those measured in 2003, with some exceptions. The average deposition flux over all the sites in 2002 is 160  $\mu\text{g}/\text{m}^2/\text{year}$ , whereas the average for the three sites followed up in 2003 is 83  $\mu\text{g}/\text{m}^2/\text{year}$ . Despite this higher input in 2002, the concentrations in soil decreased over the study period, whereas the concentrations in soil either remained roughly constant or showed clear increases during the 2003 study period.

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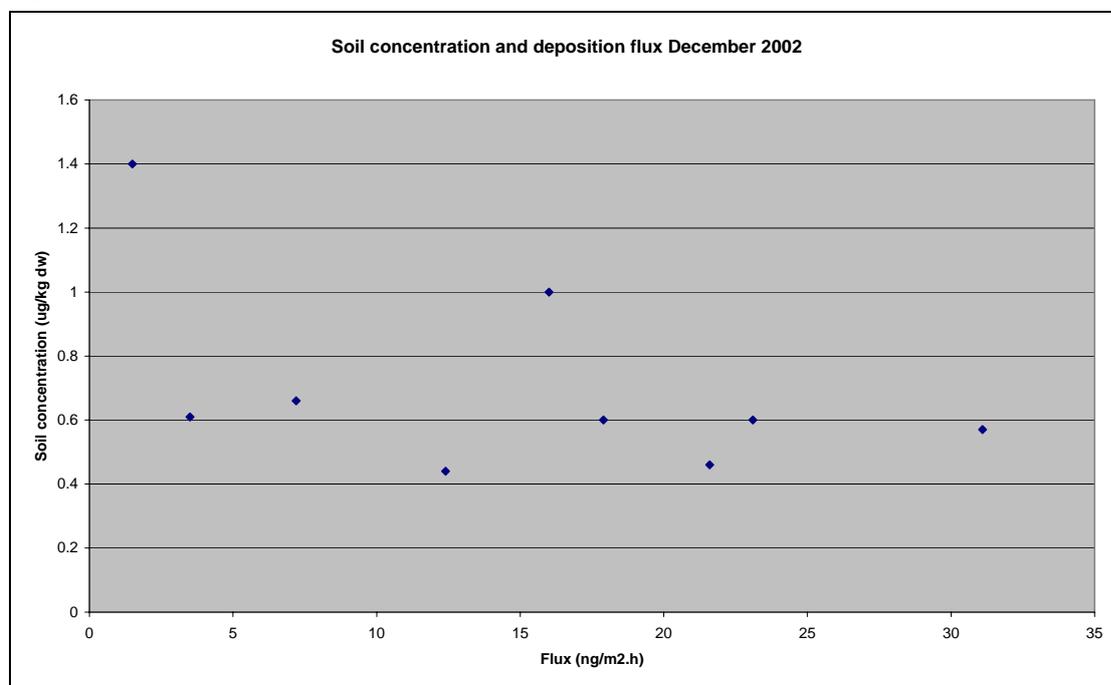
<sup>15</sup> Chlorination of water containing humic substances has been shown to lead to the formation of chloroform and TCA. This is thought to be through the chlorination of phenolic rings in humic substances. Recent studies have shown that similar reactions can occur in soils (Hoekstra and Leer, 1995). Enzymes found in fungi are able to synthesise hypochlorite from inorganic chloride and hydrogen peroxide, which then chlorinates the organic materials. In laboratory studies TCA has been found as the product of such reactions, along with chloroform, dichloroacetic acid, chlorinated acetones, etc. The ability of such reactions to produce chloroform by incorporating chlorine from chloride has been demonstrated in the field, and chloroform levels in soil air have been found to exceed those in the air above the soil by significant amounts. The activity of the chloroperoxidase enzyme has been shown to be higher at lower pHs. The acidic soils found in coniferous forests could therefore lead to greater production of chlorinated species such as TCA. Production of TCA through enzyme activity on short chain aliphatic acids has also been demonstrated (Haiber *et al*, 1996), but under artificial conditions (high levels of peroxide).

Figure B.2 Fluxes of TCA from rainfall at central European sites in 2002



**Figure B.3** shows the concentration in soil in samples taken in December 2002 against the flux of TCA in rainfall for the preceding month. From this figure there appears to be no relationship between the rain input and soil concentration – the level of TCA in the soil samples is similar across most of the sites.

Figure B.3 Soil TCA concentrations and fluxes from rain, December 2002



The reactions that produce TCA from tetrachloroethylene occur relatively slowly and so will take place as the tetrachloroethylene is transported away from the major sources. If the TCA is retained in the air flow for some time after its formation, there is the potential for increased deposition when the air flow reaches mountainous areas with increased rainfall. The Black Forest area of Germany is a possible area where this may occur, and this has been suggested as a reason for the elevated levels of TCA found in the soil in that location. However, there is no evidence of enhanced deposition of TCA due to specific geographical features. Concentrations measured in rainfall in 2002 and 2003 are in reasonable agreement with the majority of the values measured at other locations. Concentrations in fog have been found to be higher than those in rain at the same locations, but the volumes of fog deposited are much smaller than those of rain, so that the input from fog is not significantly higher. Dickey et al. (2004) also concluded this from studies in Scotland.

The mass balance calculations carried out by de Winkel et al. (2004) showed that a further input of TCA over and above that from wet deposition or needle fall was required to account for the levels found towards the end of the study at the Freudenstadt and Abreschviller sites.

Experiments at two sites in which the soil was shielded from rain input showed that the concentration of TCA can increase without this input, indicating that there is a source of TCA within the soil. The studies on soils in which the L horizon was removed indicate that this horizon is important in relation to TCA levels in soil. It is not clear whether it is only the L horizon which is important; the mass balance calculations suggest that the A horizon could also be significant, but to a lesser extent than the L horizon, although the calculations cannot rule out the possible leaching of TCA from the L horizon into the A horizon. Finally, the chlorine isotope enrichment experiment may also indicate that TCA can be formed in situ incorporating inorganic chloride from the soil, although the significance of a possible confounding effect of chlorine exchange cannot be determined at this time.

A recent carbon radioisotope ratio study showed that the TCA found in soil from a site in Germany was derived from anthropogenic sources. It is likely that tetrachloroethylene is the major source of this TCA (noting that TCA also has the potential to be formed from other chlorinated chemicals in the environment (e.g. trichloroethylene – see Section 2.5). However, the study does not provide an answer to the question of the origin of the above-PNEC levels found under some circumstances.

### Summary

The studies of de Winkel et al. (2003, 2004) provide indirect evidence that there can be natural production of TCA in soil under some circumstances, which adds to the levels of TCA from deposition (which are considered to be derived from tetrachloroethylene). The studies do not allow the rate of such production or the specific requirements for it to occur to be identified. From the comparison of soil temperature with concentrations, it would appear that higher temperatures are required. The same may also be true of degradation processes. Assuming that natural formation within soil requires higher temperatures and perhaps summer conditions in general, then measurements in mid-winter should reflect levels arising solely from deposition most closely. Biodegradation would also be expected to be reduced or at a minimum at this time. Measurements made in December 2002 show that most of the sites had soil concentrations around 0.6 µg/kg and all are below the PNEC value. This suggests that under most circumstances, deposition of TCA from rain alone would not lead to soil concentrations that would exceed the PNEC.

Calculations on the mass of TCA in soil at sites with high levels in summer 2003 indicate that the flux required to account for the concentrations is 20-40 times greater than the flux measured from rainfall. At the same time, a similar input from rainfall at the Zusmarshausen site did not lead to a corresponding increase in TCA concentration in soil.

## **B6 Overall conclusions**

Concentrations of TCA in soil exceed the soil PNEC at some locations and at some times of the year, but there are no obvious relationships between these levels and input from the atmosphere arising from tetrachloroethylene. There are no indications of enhanced deposition from rain or from fog, and no indications of enhanced TCA retention in the upper soil horizons sufficient to account for the observed concentrations in soil. The most likely cause of the higher levels of TCA is considered to be natural formation of the substance in the soil, although no conclusive proof of this source is available to date. The specific requirements for this process to occur have not been identified, and there is likely to be significant variation in the importance of this process between sites, over the course of a year at a site, and even between years at the same site. Measurements in the winter, when any formation in soil is likely to be at its lowest but input from deposition is maintained, show levels of TCA below the PNEC value across all of the sites studied in 2002. It is therefore considered unlikely that deposition of TCA from the atmosphere will by itself lead to levels of TCA in soil that pose a risk for terrestrial organisms.

It is of course possible that in certain circumstances the atmospheric input could raise levels in soil above the PNEC when adding to any existing levels formed naturally. However, this will only happen at certain times of the year (mostly in the summer). In addition, from the relative contributions from rain and formation, it appears that at certain times in the year natural formation alone is sufficient to give levels above the PNEC. In such a case, the additional impact of anthropogenic sources might be marginal<sup>16</sup>.

It should also be noted that the PNEC is derived using an assessment factor of 50. Based on recent monitoring data, the PEC/PNEC ratios are 5 or less, so if the natural formation explanation were discounted, it would still be possible to refine the assessment with further toxicity testing (on suitable tree species to include an assessment of reproduction as well as growth). Such a test would potentially take a long time, and a standard protocol does not exist. In the absence of such laboratory data, it is reasonable to consider whether any noticeable impact has been recorded at sites with above-PNEC levels of TCA. Surveys of the ground-level vegetation carried out at one such site (Zusmarshausen) showed that the vegetation was in good condition throughout the studies and that new plants grew during the period. No specific information is currently available about the vegetation quality at the other two sampling sites (Freudenstadt and Abreschviller) during the experimental period, although no specific adverse observations were noted (information provided by the organisations managing the test sites, 2004). The overall benefit of requiring an additional toxicity test would therefore seem low at the present time.

In summary, although much high quality scientific work has been carried out, it is still not possible to provide a full explanation for the variable TCA levels found in certain locations. For example, concentrations in summer 2002 at the Zusmarshausen site were well above the PNEC, whereas in summer 2003 they were barely above those found in the winter. The input from rain was lower in 2003, but not remarkably so, even though the actual amount of rainfall was

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<sup>16</sup> The 'added risk' concept (developed particularly for naturally occurring metals, such as zinc) - where it is assumed that the natural part of the chemical burden has no effect on the local ecosystem - might not be strictly appropriate in this context, due to the apparent seasonal and spatial variability of the 'natural' levels of TCA.

significantly lower. The Freudenstadt site showed an increase in TCA concentration in the spring and then a decrease, before a further increase in the summer. This variability is intriguing, and, based on present knowledge, the most likely explanation would appear to be natural formation processes within the soil.

On the balance of available evidence, it is therefore concluded that the degradation of tetrachloroethylene to TCA in the atmosphere does not pose an unacceptable risk to the terrestrial environment. It is also noted that air levels are expected to decline following the adoption of the Solvent Emissions Directive (1999/13/EC).

**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.

It is recognised that further research on TCA formation and degradation processes in soil would be beneficial to provide firm support for the natural formation explanation. Similarly, the technique for carbon radioisotope ratio determination has the potential to provide additional useful information, and it would be interesting to see results as the method is developed further. However, such additional work is beyond the scope of this current assessment on the role of tetrachloroethylene.

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## **Appendix C EUSES output**

The EUSES program has been used to calculate PEC values in the risk assessment. This appendix contains the output from the program. Some notes are needed to explain how the program was used.

### Local emissions

#### *Production*

The local emissions included in the program are those from site A to air and from site B to water, although site A has a higher emission to water it does not go via an STP. Calculations based on site specific data show that the highest concentration in water for a production site is from site E. The water concentration for this site is used to over-write the calculated water PEC, so that the indirect exposure levels for water and fish are then based on this site. For air, measured concentrations for site A are available, and the annual average PEC in air is over-written with the measured value, again for indirect exposure.

#### *Dry cleaning, metal cleaning*

The emissions are entered as in the risk assessment report, and no subsequent concentrations are over-written

### Regional and continental emissions

The total regional and continental emissions as calculated in the risk assessment report are used to over-write those estimated in the program.

## **Appendix D Potential tetrachloroethylene emission reductions due to implementation of the Solvent Emissions Directive (1999/13/EC)**

### **D1 Important note**

This appendix has been prepared by the European Chlorinated Solvent Association (ECSA) to consider the potential effect of the Solvent Emissions Directive on emissions of tetrachloroethylene. It has been prepared by the manufacturing industry in consultation with some user groups. It does not necessarily reflect the views of the rapporteur or the EU. It is included in this report for information only, to provide further details of current use processes, and to put the conclusions of the environmental risk assessment into some context.



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The EU Risk Assessment Report (RAR) considers three major application areas of perchloroethylene in 1994, plus exports from the EU to other parts of the world and a small amount of other uses. In 1994 these totalled 164,000 tonnes, of which only dry cleaning, metal cleaning and 'other' uses were highly emissive uses in the EU. These applications totalled 78,000 tonnes of sales and 63,405 tonnes of emissions to air.

The Solvent Emission Directive (SED) (1999/13/EC) adopted in 1999, and in force from 1 April 2001, addresses the issue of solvent emissions from a wide variety of industrial applications, and includes in its scope the two major emissive applications of perchloroethylene, metal cleaning (included in the surface cleaning sector of the SED) and dry-cleaning. The requirements of this Directive on these applications are as follows:

Compliance with the Directive is required immediately for new installations, and by 31 October 2007 for existing installations, as follows:

***Dry Cleaning:***            ***All installations must meet maximum overall emissions to air of 20 g/kg of textile cleaned.***

***Surface Cleaning:***    ***Installations consuming more than 1 tonnes/year must meet limits of 20 mg/m<sup>3</sup> for stack emissions, and 10/15% limits for fugitive emissions depending on size of installation.***

Compliance with the Solvent Emissions Directive will have a significant impact on metal cleaning and dry-cleaning installations as described below.

### Dry Cleaning

The largest tonnage of perchloroethylene identified in the RAR in 1994 was used across the EU in dry cleaning. In this application area significant reductions are probable under the Solvent Emissions Directive. Only the most modern machines are capable of achieving routinely the overall 20 g solvent/kg textile cleaned requirement of the SED and many users will need to modernise their existing equipment.

A survey of dry cleaning machine numbers and technologies has been carried out through user associations across EU. Based on this knowledge of the number of perchloroethylene units of each type in each country of EU, and using published data on emissions from each technology, we have assessed the situation for 2000, and the projected situation for 2007.

The dry cleaning industry is generally not currently regulated for environmental emissions, and it is difficult to obtain accurate details of the numbers of machines in use. Various sources of data

were used, and in general, old data, such as the reports for the European Commission, and data in the RAR have been rejected in favour of more up-to-date information from trade associations, machine manufacturers, or solvent producers and distributors.

The pattern of equipment used in the dry-cleaning industry has changed considerably since the risk assessment started, and is different in 2000 from the estimates made in 1994. There are a number of factors responsible for this change:

- A general improvement in design and operation of equipment driven by market forces.
- Regulatory requirements, especially in Germany, have stimulated developments to low emission equipment.
- Discussion on the Solvent Emissions Directive has been in progress since 1994, and manufacturers have anticipated the needs of this regulation.
- As new machines become more sophisticated, it is less likely that old technology remains available.
- New machines will generally always be Best Available Technology.
- A typical life for a dry cleaning machine is 10-20 years, hence in 7 years, significant machine replacement will occur.
- The phase out of use of Fluorocarbon 113 in 1994/5 caused a step change in new machines promoted by conversion to perchloroethylene.

Whilst the emissions we predict may be calculated on a different basis to the RAR, it is evident that as the population of machines improves in emission standards, there will be an overall reduction in emissions of perchloroethylene from the dry cleaning industry.

**Table D.1** shows the available data on machine numbers in each Member State with date and source. Those figures highlighted have been selected as the most reasonable values to use in calculations.

A number of general assumptions have been made regarding the operation of the dry-cleaning units as follows: (Flückiger [14]):

240 working days per year

18 kg typical machine capacity

7 loads per day

5 g/kg of textiles of solvent goes to residues independent of machine type

8% recycled solvent used in dry-cleaning.

Table D.1 Number of Perchloroethylene Dry-Cleaning Machines by Member State

Country	Number of Per Machines	Source of Data	Date	Reference
Austria	225	300 m/c · 75% Per	2000	CINET [1]
Austria	500		2001	Adams [6]
Belgium	1,500		1991	Jourdan & Rentz [2]
Belgium	450		1994	EU Risk Assessment [3]
Belgium	305	500 m/c · 61% Per	2000	CINET [1]
Belgium	610		2001	Adams [6]
Denmark	1,000		1991	Jourdan & Rentz [2]
Denmark	1,000		1994	EU Risk Assessment [3]
Denmark	250	260 m/c · 96% Per	2000	CINET [1]
Denmark	270		2001	Danish Association [4]
Finland	255	300 m/c · 85% Per	2000	CINET [1]
Finland	450		2001	Adams [6]
France	10,000		1991	Jourdan & Rentz [2]
France	9,000		1994	EU Risk Assessment [3]
France	8,000		1997	Hohenstein [5]
France	8,910		2001	CTTN-IREN [12]
France	8,000		2001	Adams [6]
Germany	15,000		1991	Jourdan & Rentz [2]
Germany	6,600		1994	EU Risk Assessment [3]
Germany	4,600		1997	Hohenstein [5]
Germany	2,720	4,000 m/c · 68% Per	2000	CINET [1]
Germany	4,700		2001	DTV [7]
Germany	4,200		2001	Adams [6]
Greece	3,500		1991	Jourdan & Rentz [2]
Greece	3,500		1994	EU Risk Assessment [3]
Greece	1,800		2000	CINET [1]
Greece	2,000		2001	Greek Association [11]
Ireland	800		1991	Jourdan & Rentz [2]
Ireland	800		1994	EU Risk Assessment [3]
Ireland	350		2000	CINET [1]
Ireland (inc NI)	570		2001	Dowling [8]
Italy	20,000		1991	Jourdan & Rentz [2]

Table D.1 continued overleaf

Table D.1 continued Number of Perchloroethylene Dry-Cleaning Machines by Member State

Country	Number of Per Machines	Source of Data	Date	Reference
Italy	25,000		2000	CINET [1]
Italy	24,000		2001	Union [9]
Italy	24,000		2001	Adams [6]
Luxembourg	100		1991	Jourdan & Rentz [2]
Luxembourg	50		1994	EU Risk Assessment [3]
Luxembourg	28	40 m/c . 70% Per	2000	CINET [1]
Luxembourg	20		2001	Adams [6]
Netherlands	750		1991	Jourdan & Rentz [2]
Netherlands	840		1994	EU Risk Assessment [3]
Netherlands	900		1997	Hohenstein [5]
Portugal	1,400		1991	Jourdan & Rentz [2]
Portugal	1,000		1994	EU Risk Assessment [3]
Portugal	900		2001	Adams [6]
Spain	10,500		1991	Jourdan & Rentz [2]
Spain	6,600		1994	EU Risk Assessment [3]
Spain	4,800		2000	CINET [1]
Sweden	500		1997	Hohenstein [5]
Sweden	352	400 m/c . 88% Per	2000	CINET [1]
Sweden	440		2001	Adams [6]
United Kingdom	6,500		1991	Jourdan & Rentz [2]
United Kingdom	6,400		1994	EU Risk Assessment [3]
United Kingdom	6,900		1994	EU Risk Assessment [3]
United Kingdom	5,800		1997	Hohenstein [5]
United Kingdom	5,280	5,500 m/c . 96% Per	2000	CINET [1]
United Kingdom	7,500		2001	Dowling [8]
(exc NI)				

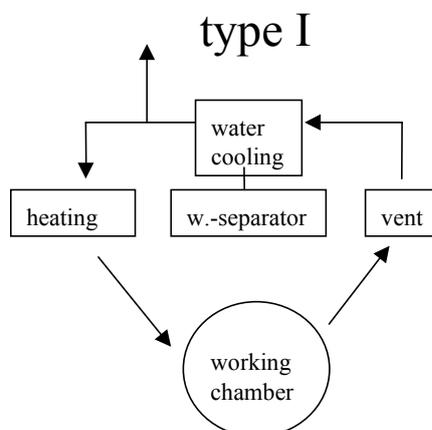
### D1.1 Dry Cleaning Technologies

An assessment has been made of the different technologies in use in the dry cleaning industry, which are described as follows:

**Type I:** As shown in **Figure D.1** this type of machine have only a water cooled unit at a temperature of 20-30°C to condense the perchloroethylene. After water cooling the solvent laden air is exhausted without an activated carbon filter. The emissions to air are assumed to be 105 g solvent / kg textile, which is on the lower side compared with reported average emissions

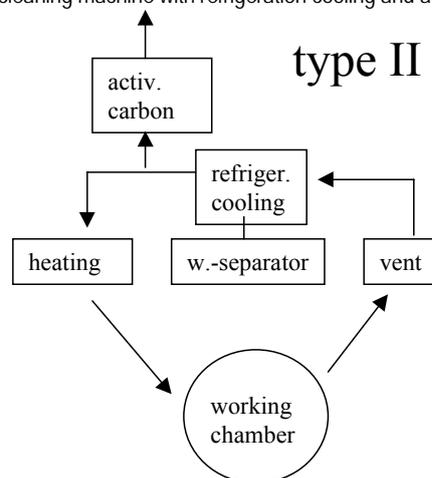
from 100 up to 150 g/kg (Rentz, 1997 [15]). The lower emissions are taken to consider a worst case scenario for the calculated solvent-emissions reduction potential given below. Together with the constant solvent amount to waste of 5 g/kg the total consumption of type I machines is 110 g solvent / kg clothes and therefore it is stated that 95% are emissions to air.

Figure D.1 Dry cleaning machine with water-cooling but without activated carbon filter



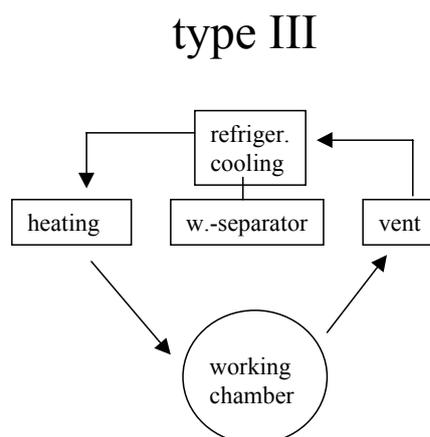
**Type II:** Here the dry cleaning machine has a refrigeration cooling unit condensing perchloroethylene at a temperature of  $-20^{\circ}\text{C}$ . The exhaust air passes an activated carbon filter before being exhausted. The air emissions of perchloroethylene per kg textile are assumed to be 45 g/kg (Zott, 1993 [13]) out of the reported emission range from 40-70 g/kg (Rentz, 1997 [15]). Together with the constant solvent amount in the waste this leads to a total consumption of type II dry cleaning machines of 50 g/kg clothes. The emissions to air are 90% of the total consumption.

Figure D.2 Dry cleaning machine with refrigeration cooling and activated carbon filter



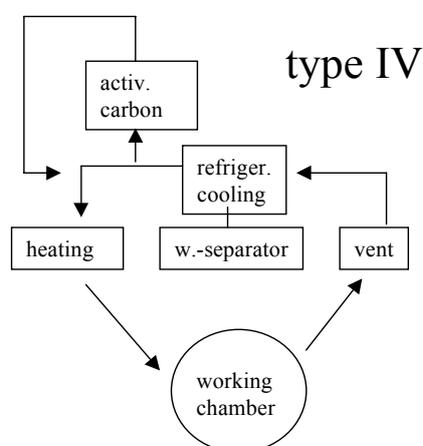
**Type III:** The machine shown in **Figure D.3** is a so-called enclosed machine with a closed drying cycle where the drying air is circulated through the refrigeration cooling unit. There is no exhaust air released to the environment. The assumed emissions to air are 20 g solvent / kg clothes, and the range of emissions are 20-40 g/kg (Zott, 1993 [13], Rentz, 1997 [15]). Together with the constant solvent amount to the waste this leads to a total consumption of 25 g/kg which means that 80% are released to air.

Figure D.3 Closed dry cleaning machine with refrigeration cooling without exhaust air



**Type IV:** The dry cleaning machines of type IV are totally closed with a closed drying cycle similar to type III. In this case the air stream for drying cycles circulates through the refrigeration cooling unit and the activated carbon until the concentration of solvent in the turning cage is below  $2 \text{ mg/m}^3$  (Flückiger, 1999 [14]). The solvent from the desorption phase of the activated carbon adsorber is returned into the machine. With this newest technology of dry cleaning machines the average of emissions to air are 5 g perchloroethylene / kg textile (Zott, 1993 [13], Rentz, 1997 [15]). Together with the constant amount of solvent in waste it results in a total consumption of 10 g/kg, and the emissions to air are therefore 50%.

Figure D.4 Closed dry cleaning machine with refrigeration cooling and activated carbon



## D1.2 Split of Technologies in Use

With the help of trade associations, machine manufacturers, solvent producers and distributors, estimates have been made of the distribution of each of the four types of unit (types 1 to 4). The results of this estimate are shown in **Table D.2**.

Table D.2 Machine Technology Split (Europe, 2000)

Country	Total machines	Type 1	Type 2	Type 3	Type 4	Source
Austria	500				500	[market data Dow] [6]
Belgium	610	10	100	400	100	[market data Dow] [6]
Denmark	270		270			Danish Association [4]
France	8,910	0	450	8,280	180	French Association [12]
Greece	2,000	800		1,200		Greek Association [11]
Ireland	570	315		180	75	Dowling [8]
Italy	24,000	0	3,600	20,200	200	Union [9]
Luxembourg	20				20	[market data Dow] [6]
Netherlands	900		30	500	370	[market data Dow] [6]
Spain/Portugal	5,700	2,900	200	1,500	1,100	[CINET][1] [market data Dow] [6]
Sweden & Finland	890				890	[market data Dow] [6]
UK	7,500	0	2,000	2,000	3,500	Dowling [8]
West Germany	4,700	0	0	0	4,700	DTV [7]
Total Perc Machines	56,570	4,025	6,650	34,260	11,635	
	100%	7%	12%	61%	21%	

### D1.3 Dry Cleaning Conclusion

From the estimated split of different technology machines in use in 2000 and the data on emissions, it is possible to calculate the overall solvent consumption, and emissions.

For 2000 these data give values of 44,309 tonnes/year emissions of perchloroethylene, already a reduction on the estimated emissions for 1994 of 50,805 tonnes/year due to gradual improvement in machine technology, as outlined above.

ECSCA assumes that the dry-cleaning industry will need to invest in Type 4 machines to routinely meet the Solvent Directive Limits. Although Type 3 equipment might be able to meet the 20 g/kg, the quoted range of emissions (20-40 g/kg) suggests that they typically operate above this. The Solvent Emission Directive requires an overall operation within these limits.

Assuming that all machines convert to Type 4 before 31 October 2007 allows us to estimate that under the Solvent Emissions Directive, dry cleaning applications will emit 8,553 tonnes perchloroethylene per year by the end of 2007 to meet the 20 g/kg textiles limit.

Other driving forces might vary these estimates: regulatory pressure on perchloroethylene use may encourage dry cleaners to use other solvents as they invest in new equipment. The estimates above assume no change in the number of perchloroethylene machines.

From the 50,805 tonnes emissions identified in the RAR for dry cleaning use in 1994, we would expect a maximum emission of 8,550 tonnes/year under the Solvent Emissions Directive, a reduction of 83% from this application, due to conversion to modern low emission dry cleaning machines.

### D1.3.1 Surface Cleaning

The Solvent Emissions Directive will require enclosure of cleaning equipment, and abatement of emissions. Consequently the emission levels in 2007 will be substantially lower than the 12,600 tonnes identified in the risk assessment report for metal cleaning, even if all current users of chlorinated solvents continue with their use. Many operators may choose to substitute perchloroethylene by other systems if technically feasible.

A survey of metal degreasing machines using perchloroethylene has been carried out through commercial channels and through machine manufacturers across the EU. Using published data on emissions from each technology, we have assessed the situation for 2000, and the projected situation for 2007 assuming compliance with the limits of the Solvent Emissions Directive (1999/13/EC) and no change in the number of perchloroethylene machines.

The situation for 2000 is shown in **Table D.3**.

A number of general assumptions have been made regarding the operation of the metal cleaning units as follows:

240 working days per year

12 hours per day

2.18 tonnes/year of solvent goes to residues independent of machine type

5% recycled solvent used in metal cleaning.

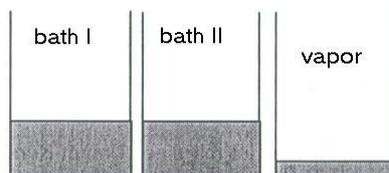
### D1.4 Surface Cleaning Technologies

An assessment has been made of the different technologies in use in the metal cleaning industries, which are described as follows:

**Type I:** As shown in **Figure D.5** this type is a fully emissive open top machine that consists of two baths and one vapour degreasing area with cooling and a suction device without an activated carbon filter. The emissions to air are between 1-16 kg/hour; the average is reported to be 4.7 kg/hour for Germany (Leisewitz and Schwartz, 1994 [19]). The wide spread reflects the fact that type I machines are often customer manufactured and show more variation in emissions than more modern machines depending on operating conditions. To calculate a worst case reduction potential, the emissions to air are assumed to be 2 kg/hour. This also reflects smaller machines typically used elsewhere in the EU. From this average of 2 kg/hour the emissions for type I machines is assumed to be 5.8 tonnes per machine per year. Together with the constant waste of 2.2 tonnes/year the total consumption of the type I machine is 7.9 tonnes/year.

Figure D.5 Fully emissive open top machine

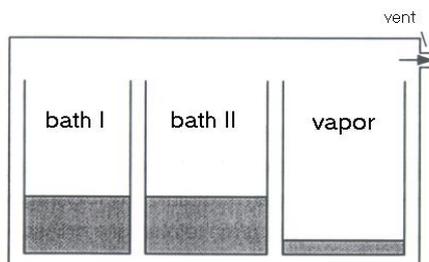
## type I



**Type II:** Here the full emissive open top machine is enclosed (shown in **Figure D.6**). It is distinguished between a Type IIa machine without activated carbon filter and a Type IIb machine with activated carbon filter. The emissions to air are reported to be between 1 and 6.5 kg/hour with an average of 2 kg/hour (Leisewitz & Schwartz, 1994 [19]). For type IIa and type IIb the emissions to air are assumed to be 2.0 kg/hour and 1.0 kg/hour respectively (5.8 tonnes/year and 2.9 tonnes/year.) Together with the constant waste of 2.2 tonnes/year, the total consumption of the type IIa and IIb machines are 7.9 tonnes/year and 5.1 tonnes/year respectively.

Figure D.6 Enclosed machine with or without activated carbon filter

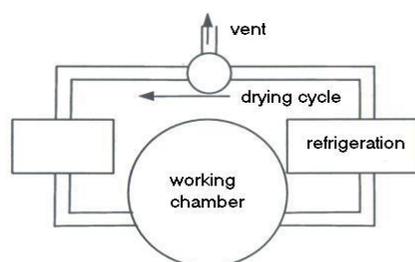
## type II



**Type III:** As shown in **Figure D.7** this type is a closed machine with only one working chamber, a closed loop drying system with refrigeration and suction device with activated carbon filter. These machines are standardised in construction and operation. For this type of machine the emissions to air are said to be 155 g/hour (Göller, 1988 [20]) which results in 0.45 tonne/year per machine. The total consumption is 2.6 tonnes/year per machine.

Figure D.7 Closed machine with exhaust air

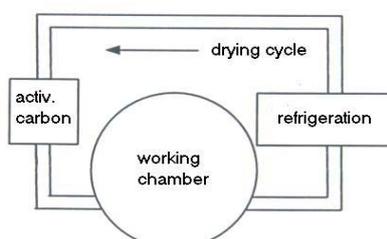
## type III



**Type IV:** This type of machine is a closed machine similar to type III with only one working chamber, a closed loop drying system with refrigeration with activated carbon filter and without exhaust air, which fulfils the requirements of the Solvent Emissions Directive. These machines are standardised in construction and operation. The air emissions are reported to be from 1-100 g/hour with an average of 38 g/hour (Leisewitz, 1994 [19]). For a worst case scenario the average is assumed to be 50 g/hour (Adams, 1993 [21]); this results in total air emissions per machine of 0.14 tonnes/year.

Figure D.8 Closed machine without exhaust air

## type IV



### D1.5 Split of Technologies in Use

With the help of trade associations, machine manufacturers, solvent producers and distributors, estimates have been made of the distribution of the four types of unit (types I to IV). The results of this estimate are shown in **Table D.3**.

Table D.3 Metal Cleaning Machine Split (Europe, 2000)

Country	Total Machines	Type I	Type IIa	Type IIb	Type III	Type IV	Source
Italy	2,000	0		0	1,400	600	(16) , (17)
France	258	250		0	0	8	(18)
UK / Ireland	64	14		0	30	20	(16)
Spain / Portugal	510	50		150	300	10	(16)
West Germany / Austria	1,460				60	1,400	
Greece	10	10					

Table D3 continued overleaf

Table D3 continued Metal Cleaning Machine Split (Europe, 2000)

Country	Total Machines	Type I	Type IIa	Type IIb	Type III	Type IV	Source
Denmark	0						
Netherlands	40				40		(16)
Sweden	15					15	(16)
Belgium	30	10		20	0	0	(16)
Luxembourg	10					10	(16)
Total number per type	4,397	334		170	1,830	2,063	
Percentage per type	100%	8%		4%	42%	47%	
VOC conform		no	no	no	no	yes	
Emission reduction potential by changing to type IV		98%		95%	68%		

Various data estimates are available on solvent emissions from each type of machine, and our assumptions are shown in **Table D.4**.

Table D.4 Assumptions of Solvent Emissions from each Type of Machine

	Type I	Type IIa	Type IIb	Type III	Type IV	
Housing	no	yes	yes	yes	yes	
Cooling/refrigeration	yes	yes	yes	yes	yes	
Exhaust air	yes	yes	yes	yes	no	
Activated carbon	no	no	yes	no	yes	
Closed loop drying	no	no	no	yes	yes	
Emissions	1-16 kg/h	1-6.5 kg/h	155 g/h	50 g/h [21]		
Literature data	aver. 4.7 kg/h [19]	aver. 2 kg/h [19]	[20]	10-100 g/h, aver. 38 g/h [19]		
assumed emission to air [kg/hour]	2	1	0.155	0.05		
<b>Data per Machine</b>	<b>Type I &amp; IIa</b>	<b>Type IIb</b>	<b>Type III</b>	<b>Type IV</b>		
Perc to air [ $t \cdot yr^{-1} \cdot machine^{-1}$ ]	5.760	2.880	0.446	0.144		
Perc to waste [ $t \cdot yr^{-1} \cdot machine^{-1}$ ]	2.185	2.185	2.185	2.185		
total consumption of Perc [ $t \cdot yr^{-1} \cdot machine^{-1}$ ]	7.945	5.065	2.631	2.329		
<b>Waste data</b>			<b>Source</b>			
Perc to waste	1.35	m <sup>3</sup>	oil to waste	0.20	l/h	[19] for type IIa machines
Perc to waste	0.47	l/h	oil content	30	%	Assumed constant for all machines

The risk assessment report assumes an emission rate of 90% into air without making any differentiation between different machine generations. The 90% emission rate, which may describe the emission situation for open top degreasers, is not valid for machines using emission reduction technologies (Type IIb, III and IV machines).

With increasing emission reduction efficiency at a constant soil input (the amount of work to be cleaned is assumed constant) and at a constant soil concentration in the waste, the solvent emissions decline and the ratio of the solvent emitted to air declines as a proportion of the consumption. The change in machine technology is the reason why the ECSA estimates show a lower emission rate and a larger portion of the solvent going to waste, but with consumption comparable to that shown in the RAR.

Solvent to air emissions are composed of emission losses via directed vent streams and diffuse (fugitive) losses into the surrounding air. The diffuse losses are made up of losses from imperfectly enclosed equipment, and solvent dragged out with the cleaned goods. As articles are packed tighter or with more complex surfaces, the risk of solvent being dragged out increases. The Solvent Emission Directive limits the concentration of solvents in the directed air emitted to  $20 \text{ mg/m}^3$  and the fugitive emissions to 10 to 15% of the solvent input depending on the size of the operation. Type I metal cleaning units will not comply with the required  $20 \text{ mg/m}^3$  in the vent and the limit values for fugitive emissions. These units therefore need to be replaced. Units of Type IIa will not comply with the concentration limit of  $20 \text{ mg/m}^3$ . To reduce the concentration in the vent below  $20 \text{ mg/m}^3$  activated carbon filters would be needed. Such installations are however quite expensive, but more important, their performance is not reliable because of oil present in the air of most metal treatment operations. Oil accumulating on the activated carbon reduces the recovery efficiency drastically. It is for this reason, affecting guarantee liability, that machine producers have developed vent free Type IV machines. ECSA has therefore assumed that in 2007 machines will be of Type IV. These are the only machines available in Germany, and are likely to be the standard for the EU under the Solvent Emissions Directive. This assumption is also supported by experience gained in Germany, where the  $20 \text{ mg/m}^3$  concentration limit, similar to the VOC directive, has been required for all surface cleaning installations since 1991. As a consequence most metal cleaning operations have switched to Type IV machines (95% of units in 2000). The 1 tonne/year consumption threshold given in the VOC directive is seen as an additional driving force to switch to Type IV units. Only by using such units and returning the waste solvent for recycling, can smaller cleaning operations get below the 1 tonnes/year consumption threshold value, and thereby avoid the emission controls of the Directive.

The projected average use in 2007 of 2.3 tonnes per year per machine is well in line with the average value found today in Germany, where most machines are already of Type IV. The variation in consumption for type IV machines is mostly related to the amount returned with the waste. Increased oil input and increased depletion of the solvent stabilisation, due to the presence of certain oil additives, increases the amount of solvent in the waste.

## **D1.6 Surface Cleaning Conclusion**

From the numbers of each type of machine in use in EU during 2000, we calculate the perchloroethylene consumption as 13,134 tonnes/year, and emissions as 3,527 tonnes/year.

We have assumed as a worst case that all current users of perchloroethylene continue to use this solvent. However, those users who abandon the use of perchloroethylene may be replaced by others currently using other chlorinated solvents, as a result of changes in acceptability of these other solvents. With uncertainties regarding the future of chlorinated solvents in general, we expect the number of new users of perchloroethylene to be small. These new users will be allowed to work only under fully enclosed, low emission conditions.

We believe that only enclosed machines fitted with refrigeration, activated carbon, and closed loop drying (Type IV) can meet the stringent emission limits under the Solvent Emissions

Directive or escape controls through consumption being reduced below the 1 tonne/year threshold.

We predict a consumption of perchloroethylene in metal cleaning of 10,240 tonnes/year after 2007 compared with 14,000 tonnes/year in 1994 and 13,134 tonnes/year in 2000. This indicates a 27% reduction of perchloroethylene sales into metal cleaning from the 1994 figures.

The predicted emissions to air from perchloroethylene used in metal cleaning after implementation of the Solvent Emissions Directive is 633 tonnes/year, compared to 12,600 tonnes/year of emissions from metal cleaning in 1994, a reduction of more than 95%.

The difference between consumption by users and emissions from these applications implies a considerable quantity of perchloroethylene solvent in residues from cleaning processes. We anticipate that much of this solvent will be recovered for reuse, and hence production of perchloroethylene is likely to decrease.

There are a number of other driving forces which might vary these estimates. Regulatory pressure on perchloroethylene use may encourage metal cleaners to use other solvents as they invest in new equipment. The estimates above assume no change in the number of perchloroethylene machines.

We are convinced that a significant reduction of perchloroethylene emissions will be achieved under the Solvent Emissions Directive (1999/13/EC) in the surface cleaning sector through installation of fully enclosed low emission equipment. Our estimation for emissions after 2007 is 633 tonnes/year, a 95% reduction on the figure of 12,600 tonnes/year for 1994.

#### **D1.6.1 Production and Chemical Intermediate Usage**

The Solvent Emissions Directive (1999/13/EC) will not affect emissions from production of perchloroethylene, or use as a chemical feedstock. In all cases of feedstock use, emissions of a valuable feedstock to atmosphere have economic as well as health and environmental implications, and emissions will be minimal compared to the tonnage in use. Emissions in the RAR amount to 123 tonnes/year from these processes. Assuming no change since 1994, the values are small in comparison with emissions from dry cleaning and metal cleaning.

The ECSA estimates of emissions from dry cleaning and metal cleaning application include assumptions of increased solvent in residues returned for recycling or recovery. This will provide an additional scenario for emissions. We would anticipate that emissions from the recycling stream would be similar to those from production facilities. The operations will be similar, and the value of the product provides incentives to minimise emissions. Closed loop solvent handling systems, using vapour return technology for solvent filling and emptying at user sites, have been developed, and are increasingly in use today. As emissions from production sites are tiny compared to dry cleaning and metal cleaning applications, we believe we are justified in suggesting that emissions from recycling operations will also be insignificant.

#### **D1.6.2 Other Applications**

The RAR mentions other applications such as film cleaning, textile processing, leather treatment and as a biocide. Since the original data were collected these applications have diminished, and will be negligible compared to other uses. However, in the absence of up-to-date data we can only assume similar tonnages.

ECSCA is not aware of any further emissive applications being developed by its members to offset loss of sales in those applications controlled by the Solvent Emissions Directive, and it is probable that the reduction will lead to industry restructuring and closure of certain production units.

### D1.7 Summary

The following table summarises the ECSCA estimates of emission reduction through implementation of the Solvent Emission Directive (1999/13/EC).

Table D.5 Emissions of perchloroethylene in EU – impact of SED

Application	1994	2000	Tonnes per year >2007	% Reduction from 1994
Dry cleaning	50,805	44,309	8,553	83
Metal cleaning	12,600	3,527	633	95
Production and chemical feedstock	123	123	123	0
Other	1,600	1,600	1,600	0
<b>Total</b>	<b>65,128</b>	<b>49,559</b>	<b>10,909</b>	<b>83</b>

We hope that these data provides sufficient evidence for the ECSCA belief that significant levels of risk reduction are likely to be promoted by implementation of existing EU legislation, the Solvent Emissions Directive (1999/13/EC).

We wish to point out that these are predictions based on the best information available, and must not be construed as commitments by ECSCA. The Solvent Emission Directive provides the mechanism for achieving reduced emissions. The actual reductions will be dependent on the transposition of these requirements into Member State law and enforcement.

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European Commission

**EUR 21680 EN      European Union Risk Assessment Report  
tetrachloroethylene, Volume 57**

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Environment and quality of life series

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

#### Part I - Environment

This part of the evaluation considers the emissions and the resulting exposure to the environment in all life cycle steps. Following the exposure assessment, the environmental risk characterisation for each protection goal in the aquatic, terrestrial and atmospheric compartment has been determined.

The environmental risk assessment concludes that there is concern for the risk of harm to plants from air emissions from sites producing and processing tetrachloroethylene as an intermediate. Based on site-specific data the conclusion relates to one site.

There is at present no concern for the aquatic compartment (including sediment and STP), the terrestrial compartment and secondary poisoning for tetrachloroethylene. It also applies to the air compartment for dry cleaning and metal cleaning for direct effects on plants. The conclusion also applies to the regional aquatic and terrestrial compartments for (trichloroacetic acid) TCA formed through the degradation of tetrachloroethylene in air.

#### Part II – Human Health

This part of the report is not yet completed, and will be published later.

The conclusions of this report will lead to risk reduction measures to be proposed by the Commission's committee on risk reduction strategies set up in support of Council Regulation (EEC) N. 793/93.



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European Union Risk Assessment Report

**tetrachloroethylene**

**Part I - environment**

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