

TETRACHLOROETHYLENE

Part I - Environment

CAS No: 127-18-4

EINECS No: 204-825-9

Summary Risk Assessment Report

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SUMMARY RISK ASSESSMENT REPORT

Final report, 2005

United Kingdom

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PREFACE

This report provides a summary, with conclusions, of the risk assessment report of the substance tetrachloroethylene that has been prepared by the United Kingdom in the context of Council Regulation (EEC) No. 793/93 on the evaluation and control of existing substances.

For detailed information on the risk assessment principles and procedures followed, the underlying data and the literature references the reader is referred to the comprehensive Final Risk Assessment Report (Final RAR) that can be obtained from the European Chemicals Bureau¹. The Final RAR should be used for citation purposes rather than this present Summary Report.

¹ European Chemicals Bureau – Existing Chemicals – <http://ecb.jrc.it>

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1 GENERAL SUBSTANCE INFORMATION

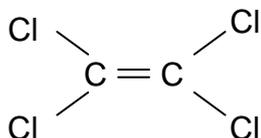
1.1 IDENTIFICATION OF THE SUBSTANCE

CAS No: 127-18-4
EINECS No: 204-825-9
Annex 1 Entry: 602-028-00-4
IUPAC name: Tetrachloroethene
Synonyms: Tetrachloroethene 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-Tetrachloroethene, Ethene, tetrachloro-, Ethylene, tetrachloro-, Perchloroethene, Per, Perstabil®, Ankilostin®, Didakene®, Perclene®, Dowper®, Perklone®

Molecular weight: 165.85

Molecular formula: C₂Cl₄

Structural formula:



1.2 PURITY/IMPURITIES, ADDITIVES

Tetrachloroethylene as produced is >99% pure. Impurities that may be present include 1,1,1-trichloroethane, carbon tetrachloride, dichloromethane, trichloroethylene and water. Stabilisers may be added to tetrachloroethylene.

1.3 PHYSICO-CHEMICAL PROPERTIES

Tetrachloroethylene is a colourless liquid with an ethereal odour. The physico-chemical properties are summarised in **Table 1.1**.

Table 1.1 Summary of physico-chemical properties

Property	Value
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.
Flammability	No flash point under experimental conditions.
Explosive properties:	Not explosive.
Oxidising properties:	Not considered as an oxidising agent but can oxidise in presence of air and light.

1.4 CLASSIFICATION

Current classification

The current EU classification is

- Carcinogen category 3; R40; N:R51/53
and the current labelling requirement is
- Xn; N; R40-51/53; S23-36/37-61
- Xn; R40 indicates “Limited evidence of a carcinogenic effect”.
- N indicates “Dangerous for the Environment”
- R51 indicates “Toxic to aquatic organisms”
- R53 indicates “May cause long-term adverse effects in the aquatic environment”
- S23 states “Do not breathe dust”.
- S36/37 states “Wear suitable protective clothing and gloves”.
- S61 states “Avoid release to the environment. Refer to special instructions/safety data sheet.”

Carcinogen category 3 indicates a substance which causes concern for man 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 $\geq 1\%$ of tetrachloroethylene.

Proposed classification

In addition to the above classification and labelling the following is proposed for human health:

- Xi: R38; R67
- Xi indicates “Irritant”.
- R38 indicates “Irritating to skin”.
- R67 indicates “Vapours may cause drowsiness and dizziness”.

2 GENERAL INFORMATION ON EXPOSURE

2.1 PRODUCTION

Tetrachloroethylene is produced by six manufacturers within the European Union (EU). 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 were exported and the remainder used as a chemical intermediate within the chemical industry².

Tetrachloroethylene is produced by oxychlorination, chlorination and/or dehydrochlorination reactions of hydrocarbons or chlorinated hydrocarbons. The most common methods of production are the chlorination of propylene and the oxychlorination of 1,2-dichloroethane. Production is carried out in closed systems limiting human and environmental exposure under normal operating conditions.

2.2 USES

The major uses of tetrachloroethylene are as a dry cleaning agent (62,400 tonnes/year), as a chemical intermediate (30,000 tonnes/year) and in metal cleaning (14,000 tonnes/year).

Tetrachloroethylene accounted for approximately 90% of the total solvent used within the dry cleaning industry in 1994. The total number of dry cleaning establishments in the EU is estimated at 60,000 units. Different types of equipment are employed in dry cleaning and include open circuit machines, open circuit machines fitted with filters and closed circuit machines.

The amount of tetrachloroethylene used within the EU has decreased in recent years. This reduction is attributed to the use of more efficient dry cleaning machines, improved recycling of tetrachloroethylene in the dry cleaning industry and better housekeeping. Use as a chemical intermediate has also declined due to restrictions on the end products.

² By 2003, there were five manufacturers in an enlarged EU; production 127,000 tonnes, sales 53,000 tonnes, exports 46,000 tonnes (Personal communication (ECSA), 2005).

3 ENVIRONMENT

3.1 ENVIRONMENTAL EXPOSURE

3.1.1 Environmental releases

The assessment considers releases from the production of tetrachloroethylene, its use as an intermediate and in dry cleaning and metal cleaning. Emission estimates are based on specific information from industry where available and considered representative, together with default assumptions. The local emissions for each life cycle step are included in **Table 3.1**, together with the overall emissions on the regional and continental scales.

3.1.2 Environmental fate

Tetrachloroethylene may be released into the environment during its production and subsequent use. Emissions to air and water are the most important environmental routes of exposure.

On release to the atmosphere tetrachloroethylene reacts with a number of photochemical produced species in the troposphere. The major reactions occur with hydroxyl radicals (half-life for reaction 3.2 months) and chlorine radicals (half-life for reaction 6-12 months). During the photochemical degradation of tetrachloroethylene a number of products may be formed including phosgene, trichloroacetyl chloride and carbon tetrachloride. Trichloroacetyl chloride can further react in the atmosphere to form trichloroacetic acid. Tetrachloroethylene has the potential to dissolve in atmospheric water droplets and be deposited by rainout.

Tetrachloroethylene undergoes anaerobic biodegradation by a process of reductive dechlorination. The extent to which this occurs depends on the local conditions. Tetrachloroethylene does not appear to undergo aerobic biodegradation. Tetrachloroethylene may be removed from surface waters by photolysis and volatilisation, the major removal process being dependent upon the specific conditions. The amount of tetrachloroethylene adsorbed to soils is negligible; hence it is relatively mobile in groundwater in the absence of any removal process.

Tetrachloroethylene has a low potential for bioaccumulation based upon measured levels in fish (BCF 40-50) and Log Kow of 2.53. Highly fatty substances may adsorb tetrachloroethylene. Therefore foodstuffs exposed to atmospheric tetrachloroethylene may contain relatively high levels of tetrachloroethylene and be a route of indirect exposure of man via the environment.

3.1.3 Environmental concentrations

Predicted Environmental Concentrations (PECs) have been calculated for specific sites involved in the production of tetrachloroethylene and its use as an intermediate. For other uses a combination of specific information and default values has been used. Calculations were performed using the Technical Guidance document and EUSES. The PECs for air and water are summarised in **Table 3.1**.

For surface water measured concentrations are generally below 5 µg/l and the majority of these are below 1 µg/l. However, measurements made at contaminated sites and taken near point source releases are higher suggesting that significant releases of tetrachloroethylene

have occurred previously. Current data show levels in line with the PECs. Measurements of tetrachloroethylene in air are in line with the PECs for air. Most measured levels are below 0.01 mg/m^3 with the majority of these below 0.001 mg/m^3 .

Table 3.1 PECs for air and water for tetrachloroethylene

	Emission to water (kg/day)	PEC _{water} ($\mu\text{g/l}$)	Emission to air (kg/day)	PEC _{air} ($\mu\text{g/m}^3$)	Notes
Production and use as a chemical intermediate	0.02 to 0.81	0.011 to 9.1	0.002 to 733	0.88 - 36	Based upon site specific data and default values
Dry cleaning	$3 \cdot 10^{-3}$	0.02	15.5	4.4	1
Metal cleaning	0.48	1.6	42	7.7	2
Regional	44	0.011	33,120	0.88	
Continental	398	0.0015	149,488	0.32	

- 1 Releases of tetrachloroethylene during dry cleaning will vary depending upon the type of system in use. The two most common types of machine are open-circuit machines in which the drying air is vented to atmosphere in the final drying stage and closed circuit machines where solvent vapours are recovered in the drying cycle. Releases from open circuit machines are generally higher and are used here as a reasonable worst case scenario.
- 2 Releases of tetrachloroethylene are calculated for a reasonable worst case scenario based upon current industry practice within the United Kingdom.

Direct releases to soil are unlikely to occur. Tetrachloroethylene levels in soil are therefore due to application of sewage sludge containing tetrachloroethylene or to aerial deposition. These are likely to be low due to the rapid loss of tetrachloroethylene from soil by volatilisation and negligible adsorption to soil. A worst case PEC_{local,soil} is calculated as $3.9 \mu\text{g/kg}$ (wet weight).

Tetrachloroethylene has been measured in a range of biota and food products. The concentrations observed are due to exposure to tetrachloroethylene (via surface water for aquatic species, surface water and atmospheric deposition for plants and atmospheric emissions for foodstuffs) not accumulation in the food chain. The daily human dose due to indirect exposure to tetrachloroethylene via the environment is calculated as $1,443 \mu\text{g/kg bw/day}$ for people living near dry cleaners, $23.7 \mu\text{g/kg bw/day}$ for people living near production plants and $0.34 \mu\text{g/kg bw/day}$ for background exposure. These calculations are based upon a mixture of measured levels and predicted environmental concentrations and are meant to represent reasonably worst case scenarios.

Due to concern over possible effects of atmospheric breakdown products from tetrachloroethylene, the concentrations of trichloroacetic acid in soil are considered in the assessment. Measured levels in soil are generally below $1 \mu\text{g/kg}$, but at some locations, typically upland forest sites, higher concentrations have been measured. A sampling exercise carried out for the assessment at such sites found levels from 0.46 to $10.9 \mu\text{g/kg}$, with significant variation at sites through the year.

3.2 EFFECTS ASSESSMENT

Acute and chronic toxicity data are reported for fish, daphnia and algae, and the valid studies are summarised in **Table 3.2**.

Table 3.2 Aquatic toxicity of tetrachloroethylene

Species	Parameter	Concentration (mg/l)
Fish		
<i>Jordanella floridae</i>	96-hour LC ₅₀	8.4
	10-day NOEC (survival, larvae)	1.99
	28-day NOEC (survival, fry)	2.34
<i>Oncorhynchus mykiss</i>	96-hour LC ₅₀	5
Invertebrates		
<i>Daphnia magna</i>	48-hour EC ₅₀	8.5
	28-day NOEC (reproduction)	0.51
Algae		
<i>Chlamydomonas reinhardtii</i>	72-hour EC ₅₀ (cell multiplication inhibition)	3.64
	72-hour EC ₁₀ (cell multiplication inhibition)	1.77

The most sensitive species in a chronic toxicity test is *Daphnia magna* with a 28 day NOEC based upon reproduction of 0.51 mg/l. Based upon this result and applying an assessment factor of 10 the PNEC_{aquatic} is calculated as 51 µg/l for tetrachloroethylene.

A PNEC_{micro-organisms} of 11.2 mg/l is derived using a 24 hour IC₅₀ of 112 mg/l for the nitrifying bacteria *Nitrosomonas sp.*

No toxicity data is available for benthic organisms, therefore the PNEC_{sediment} is derived by a partition coefficient method from the PNEC_{aquatic}. The PNEC_{sediment} is calculated as 318 µg/kg wet weight.

Short term and long term toxicity studies on terrestrial invertebrates, plant and soil dwelling bacteria are reported. A PNEC_{terrestrial} is calculated from these studies. The lowest long term toxicity test reported is a bacterial NOEC of ≤0.1 mg/kg (wet weight) for nitrification in a loam soil. Based upon this result and applying an assessment factor of 10 the PNEC_{terrestrial} is calculated as 0.01 mg/kg wet weight. For comparison, the equilibrium partitioning method gives a PNEC of 0.24 mg/kg wet weight.

The effects of tetrachloroethylene on plants exposed through the air have been studied. Twelve plant species were exposed in open top chambers, with exposure over a growing season. The species were selected to represent the range of European flora, and included crops (bean, wheat and kale), trees (spruce, pine and beech), wild species and mosses. Effects of some kind were seen in ten of the species used, with the bean (*Phaseolus vulgaris*) the species affected at the lowest concentration. Seasonal effects were noted, in that both bean plants and clover were affected by exposures during the spring but showed no effects in similar exposures during the summer. A number of approaches were used to determine a PNEC from the results of the study, with the value selected being 8.2 µg/m³.

Due to concern over the possible effects of the atmospheric breakdown products of tetrachloroethylene on the environment, toxicity of trichloroacetic acid is also considered in this assessment. The effects of trichloroacetic acid on aquatic organisms are considered in the OECD SIAR on trichloroacetic acid and used to derive PNEC_{aquatic} of 0.17 µg/l. The PNEC for trichloroacetic acid for terrestrial organisms is derived, from data given in the SIAR on trichloroacetic acid, as 2.4 µg/kg dry weight.

3.3 RISK CHARACTERISATION

3.3.1 Aquatic compartment (incl. sediment)

A comparison of the $PNEC_{\text{aquatic}}$, $PNEC_{\text{sediment}}$ and $PNEC_{\text{microorganisms}}$ for tetrachloroethylene with the PECs in water, sediment and waste water treatment plants respectively gives rise to PEC/PNEC all below 1 (see **Table 3.3**). The same is true for measured levels in water, sediment and waste water treatment plants.

Table 3.3 PEC/PNEC ratios for tetrachloroethylene

Activity	Water	Soil	Air
Production/use as an intermediate	0.18	0.39	4.4
Dry cleaning	<0.001	0.006	0.54
Metal cleaning	0.03	0.25	0.94
Regional	<0.001	<0.001	0.11

A comparison of the $PNEC_{\text{aquatic}}$ for trichloroacetic acid with the measured concentrations of trichloroacetic acid in surface water and predicted concentrations, due to the atmospheric breakdown of tetrachloroethylene and subsequent rainout of trichloroacetic acid, gives rise to PEC/PNEC ratios less than 1. **Conclusion (ii)**.

3.3.2 Terrestrial compartment

A comparison of the $PNEC_{\text{terrestrial}}$ for tetrachloroethylene with the PECs and measured levels of tetrachloroethylene in soil gives rise to PEC/PNEC ratios less than 1. The PNEC for trichloroacetic acid for terrestrial organisms is given as 2.4 $\mu\text{g}/\text{kg}$ dry weight. When this is compared to measured TCA levels in soils from a small number of sites a risk is identified for certain regions (e.g. the Black Forest in Germany). Detailed studies on the levels of TCA in soils and on possible sources have been carried out for the assessment. Based on these, it appears that TCA from the breakdown of tetrachloroethylene in the atmosphere is not by itself responsible for the higher levels found in soil. These appear to be due to a combination of deposited TCA and natural formation in soil. **Conclusion (ii)**.

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

3.3.3 Atmosphere

Tetrachloroethylene reacts in the atmosphere to form potentially harmful species. The risks of trichloroacetic acid formed by this route are considered for aquatic and terrestrial species, as this is where the effect is observed.

Tetrachloroethylene is not thought to contribute significantly to tropospheric ozone formation. Its potential as an ozone depletor in the stratosphere is thought to be significantly less than other ozone depleting chemicals.

Tetrachloroethylene has been shown to have effects on plants through exposure via air. This was discussed in Section 3.1.2; 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 3.1.1 and the ratios are presented in **Table 3.2**. The highest concentration, 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, for dry cleaning, for metal cleaning, and for the regional background all give ratios less than 1. **Conclusion (ii)**.

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

Conclusion (iii)

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.

3.3.4 Secondary poisoning

Tetrachloroethylene has a low potential for bioaccumulation in aquatic species. The data also indicates that it has a low potential to biomagnify. The concentrations observed in biota and food arise have occurred due to direct exposure to tetrachloroethylene. **Conclusion (ii)**

4 HUMAN HEALTH

(will be added later)

5 RESULTS

5.1 INTRODUCTION

Tetrachloroethylene is made by six companies within the EU, with an estimated production tonnage of 164,000 tonnes in 1994. Of this, 78,000 tonnes were sold within the EU, for use mainly in dry cleaning and metal cleaning. Exports amounted to 56,000 tonnes and 30,000 tonnes used as an intermediate.

5.2 ENVIRONMENT

The environmental risk characterisation considers the production of tetrachloroethylene and its use as an intermediate, in dry cleaning and in metal cleaning. It also considers the potential formation and effects of a breakdown product, trichloroacetic acid.

For the aquatic compartment the PEC/PNEC ratios are less than one for all of the life cycle steps considered for water and sediment. The ratios for waste water treatment plants are also less than one. For trichloroacetic acid, the concentrations in surface waters are expected to be less than the PNEC.

For the terrestrial compartment, the PEC/PNEC ratios are less than one for trichloroethylene exposure in soil through sewage sludge application or aerial deposition. The measured concentrations of trichloroacetic acid in soil at a small number of sites are higher than the PNEC estimated for trichloroacetic acid, but the evidence indicates that these are due to the combination of natural production of TCA in soil with that deposited from the air and that deposition alone does not lead to levels above the PNEC.

For the atmospheric compartment a PNEC has been derived for the effects of tetrachloroethylene on plants. This indicates possible effects on plants from emission to air from one site producing tetrachloroethylene and using it as an intermediate. Dry cleaning and metal cleaning give rise to concentrations below the PNEC.

Overall results of the environmental risk assessment

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.

This conclusion applies to the aquatic compartment (including sediment), to waste water treatment plants, and to the terrestrial environment for all stages in the production and use of tetrachloroethylene; to the air compartment for dry cleaning and metal cleaning; and to all compartments for trichloroacetic acid produced by the photodegradation of tetrachloroethylene.

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.

