



European Chlorinated Solvent Association

Part of Euro Chlor, a Sector Group of CEFIC

WHITE PAPER

Perchloroethylene

EXECUTIVE SUMMARY

The chlorinated solvent, perchloroethylene (also known as PER, PERC, tetrachloroethylene and tetrachloroethene) has been widely used since the 1930s. Major applications are dry-cleaning, metal cleaning and degreasing, and as a chemical intermediate. Sales in the EU 25 countries plus Norway, Switzerland and Turkey totalled 56,000 tonnes in 2005.¹ This figure has fallen substantially since the mid-1980s due to more efficient dry-cleaning processes, greater recycling, use of enclosed systems and other best practices.

Chlorinated solvents have been used extensively for many years. During this time, the only fatalities or serious injuries which have occurred have been due to massive over-exposure through a total disregard for good operating practices, or through deliberate misuse.² When used with due care, perchloroethylene poses no threat to human health, safety or the environment.

There is no evidence that exposure to normal levels of chlorinated solvents increases the risk of cancer in humans, based on extensive toxicological and epidemiological research.^{3,4} Of five studies in laboratory animals, three found a significant increase in formation of liver tumours in mice exposed to the solvent. However, the mechanism of tumour formation is specific to rodents and is not relevant to humans. A small increase in incidence of certain kidney cancers and leukaemia has been reported in rats. In humans, there is no evidence of a link with kidney cancer, liver cancer or leukaemia. However, some studies indicate a higher risk of oesophageal cancer among people exposed to perchloroethylene.

Inhalation of solvent vapour is the most frequent route of exposure: solvent vapours are heavier than air and can accumulate in confined or poorly ventilated areas.⁵ As a result, good ventilation is essential in areas where the product is made or used. ECSA also strongly encourages use of state-of-the-art, contained systems to avoid the release of perchloroethylene into the environment.

¹ <http://www.eurochlor.org/news/detail/index.asp?id=194&npage=1&category=25>

² <http://www.eurochlor.org/facts>

³ <http://www.eurochlor.org/facts>

⁴ Perchloroethylene - ECETOC Report No 37

⁵ <http://www.eurochlor.org/facts>

Perchloroethylene does not deplete the ozone layer, and its contribution to global warming, acid rain and smog formation is negligible.⁶ Chlorinated solvents are unlikely to accumulate in living organisms or the environment. In sediment and soil, perchloroethylene is fairly mobile and can leach into groundwater.

During production, integrated manufacturing methods ensure that waste from one process is used in another process. This keeps manufacturing waste to a minimum, with any toxic or potentially environmentally damaging wastes recycled and converted to useful products, and final waste disposed of properly.⁷ ECSA encourages companies which manufacture and use this solvent to install spillage containment systems in storage and use areas. The Association strongly discourages land filling of waste, even though this may be legal in some areas.

Perchloroethylene use is regulated under the Solvent Emissions Directive (1999/13/EC).^{8,9}

INTRODUCTION

Perchloroethylene (also known as PER, PERC, tetrachloroethylene and tetrachloroethene) is a chlorinated hydrocarbon solvent which is a volatile, non-flammable liquid. This efficient and highly recyclable solvent has been extensively used since the 1930s. When used with due care, it poses no threat to human health, safety or the environment.

The use of perchloroethylene can be broken down as follows: as a chemical intermediate (50%), dry cleaning and textile processing (25%), automotive aerosols (10%), metal cleaning and degreasing (10%), and miscellaneous uses, such as fabrication of industrial glues and rubber formulations (5%).

In Europe, perchloroethylene is manufactured by Dow Europe, Ineos Chlor, Solvay and Spolchemie.¹⁰ Sales in 2005 in the EU 25 countries plus Norway, Switzerland and Turkey totalled 56,000 tonnes.¹¹ This product remains the solvent of choice for more than 80% of dry-cleaning shops and continues to gain market share as a substitute for trichloroethylene in metal degreasing. However, there has been a decline in production since the mid-1980s due to more efficient dry-cleaning processes, greater recycling, use of enclosed systems and other best practices.

⁶ <http://www.eurochlor.org/facts>

⁷ <http://www.eurochlor.org/facts>

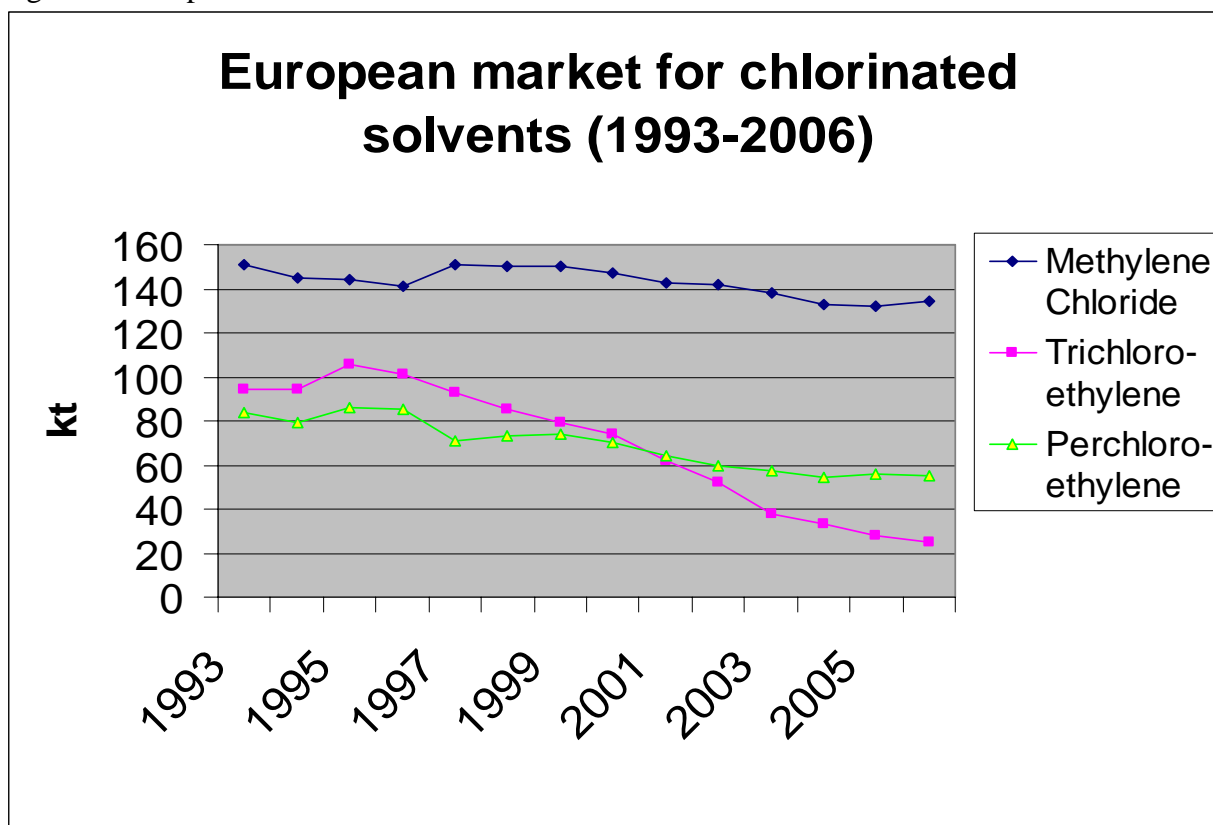
⁸ <http://www.eurochlor.org/solventsemissionsdirective>

⁹ http://eur-lex.europa.eu/LexUriServ/site/en/oj/1999/l_085/l_08519990329en00010022.pdf

¹⁰ <http://www.eurochlor.org/solvents>

¹¹ <http://www.eurochlor.org/news/detail/index.asp?id=194&npage=1&category=25>

Figure 1: European “non feedstock” market for chlorinated solvents



Industrial production of perchloroethylene began in 1914 in the UK and Germany – which are still Europe’s major producers - and in 1925 in the US. Four grades are made for different applications: an alkaline/dry-cleaning grade, an alkaline/vapour degreasing grade for metal degreasing, a technical grade for formulation purposes, and a high purity grade for extraction. Small quantities of used perchloroethylene from a variety of industries are recycled, usually re-entering commerce for metal degreasing applications.

Stabilizers are normally added to perchloroethylene to prevent its decomposition during storage and use. The total concentration of stabilisers is normally less than 0.05% in dry-cleaning grade, with highly stabilized grades for metal cleaning applications containing up to 0.5%. Due to its relatively high stability, PER requires less stabiliser to be added than other chlorinated solvents. To be effective during use, the stabilisers - which include exposides (metal degreasing), alkylamines and phenols (inhibiting antioxidation of PER by air), and secondary and tertiary alcohols - must vaporise at the same rate as perchloroethylene, so that both are present in the liquid and vapour phases.

During the production of chlorinated solvents, integrated manufacturing methods are employed so that waste from one process is used in another process. As a result, waste from the manufacturing plant is kept to a minimum, any toxic or potentially environmentally damaging wastes are recycled and converted to useful products, and final waste is disposed of properly.¹²

¹² <http://www.eurochlor.org/facts>

HEALTH EFFECTS

Chlorinated solvents have been used extensively for many years. During this time, the only fatalities or serious injuries which have occurred have been due to massive over-exposure through a total disregard for good operating practices, or through deliberate misuse.¹³ When solvents are stored, used and disposed of correctly, there is no risk to human health.

Inhalation of solvent vapour is the most frequent route of exposure: solvent vapours are heavier than air and can accumulate in confined or poorly ventilated areas.¹⁴ As a result, good ventilation is essential in areas where the product is made or used.

Cancer risk

There is no evidence that exposure to normal levels of chlorinated solvents increases the risk of cancer in humans, based on extensive toxicological and epidemiological research.^{15,16}

Five studies of the potential of perchloroethylene to cause cancer in laboratory animals have been conducted. Three of these showed a significant increase in formation of liver tumours in mice exposed to the solvent. However, the ways these tumours form have been identified and the mechanisms are specific to rodents and not relevant to humans. A small increase in incidence of certain kidney cancers and leukaemia has been reported in rats. In humans, there is no evidence of a link with kidney cancer, liver cancer or leukaemia. Some studies indicate a higher risk of oesophageal cancer among people exposed to perchloroethylene, which may not be entirely attributable to lifestyle factors such as smoking and drinking alcohol.¹⁷ However, the overall epidemiological data suggests that there is no cancer link.

CNS and behavioural effects

Individuals exposed in their work to perchloroethylene have been studied over many years. Prolonged exposure to perchloroethylene at concentrations of 200 ppm or more has been linked to dizziness, confusion, headache, nausea, and irritation of the eyes and mucous membranes. These effects become more pronounced at higher exposure (>600 ppm). In addition to central nervous system (CNS) effects, there may also be transient, minor alterations in liver or kidney function. Prolonged exposure to extremely high levels (>1,500 ppm) may lead to unconsciousness or even death from respiratory depression. (Indeed, perchloroethylene was used as a human anaesthetic in the past.) Large accidental intakes (estimated at 1.6 - 4.8 g/kg) in children have led to effects such as vomiting, gastrointestinal bleeding, shock and in one case, death.

The effects of prolonged or repeated exposure to perchloroethylene on the nervous and sensory systems have been examined in studies with dry cleaners as well as with volunteers. Some have reported minor neurobehavioural effects in people exposed to low levels of the solvent. These studies are difficult to interpret, however, since the changes observed (e.g. visual contrast

¹³ <http://www.eurochlor.org/facts>

¹⁴ <http://www.eurochlor.org/facts>

¹⁵ <http://www.eurochlor.org/facts>

¹⁶ Perchloroethylene - ECETOC Report No 37

¹⁷ Vaughan *et al*, 1997 (<http://oem.bmj.com/cgi/content/abstract/54/9/692>): this case control study suggested an increased risk of oesophageal cancer linked to working in the dry cleaning sector. However, this result was based on only two out of a total of 404 cases; these two cases of oesophageal squamous cell carcinomas had worked in dry cleaning for a short time.

sensitivity, colour vision, reaction time, visual memory) are small, their toxicological significance is uncertain and the methodologies used are inconsistent. To date, no clear association has been seen between neurobehavioural effects and exposure to perchloroethylene.

Skin effects

A few case reports show perchloroethylene to be a skin irritant, but not to be corrosive. In one case, extensive redness (erythema) and blistering were seen on a worker who had lain unconscious in a pool of solvents for about five hours. In a second case, another worker who had been unconscious for half an hour while wearing clothes soaked in perchloroethylene showed similar symptoms. Considerable reduction of the symptoms was seen within five days, but some dryness, staining and irritation of the injured areas continued. Slight, transient eye irritation developing within the first hours of exposure and subsiding before the end of a work shift has been reported at exposure levels around 100 ppm. Mild nasal irritation was reported by volunteers exposed at 216 ppm for two hours, but not by those exposed at 106 ppm for one hour. Two case reports mention asthma-like symptoms at high levels of perchloroethylene exposure, attributed to respiratory irritation.

Liver and kidney effects

In laboratory animals, acute inhalation exposure of to high levels of perchloroethylene causes kidney and liver effects. Temporary liver and kidney effects are also reported in cases of acute inhalation poisoning of people with high levels of this solvent. Short term inhalation or oral exposure of animals causes cell biology changes, most likely due to the presence of trichloroacetic acid, which is a breakdown product of perchloroethylene.

In people, liver effects have been seen after prolonged perchloroethylene exposure by inhalation at levels of 200-400 ppm. Males seem to be more sensitive to these effects than females. Reversible effects on liver function have been seen in people exposed to high levels of this solvent over extended periods of time. No effects on the liver or kidney were seen in human volunteers exposed to perchloroethylene at levels of up to 150 ppm, 7.5 hours per day, 5 days per week for 11 weeks. In occupational settings, mild liver and kidney function alterations are reported in some studies; others have reported no detectable effects.

It is strongly recommended that users stay within legislative or manufacturers' guidelines to keep human and environmental exposures to a minimum. Compliance with applicable regulations, use of engineering controls, best available work practices and occupational health surveillance, will help ensure that perchloroethylene can continue to be used in a safe and environmentally sound manner.

Genetic, reproductive and developmental effects

A large number of studies have found no overall evidence that perchloroethylene or its major metabolites cause mutations or damage to genetic material in bacteria, cell culture or laboratory animals. Commercial formulations of the solvent have produced weakly positive responses in some yeast and bacterial assays, but only at levels of exposure high enough to be toxic, and with no apparent dose-response relationship. In humans, three studies found no evidence of genotoxicity caused by occupational exposure.

Epidemiological studies of workers in the dry-cleaning sector have found very limited and inconsistent evidence for effects on fertility (quality of semen) and foetal development (spontaneous abortions). It is unclear whether any such effects may be related to perchloroethylene alone, or to a mixture of solvents. There is no evidence that perchloroethylene

causes congenital malformations (teratogenicity) even at high levels in laboratory animals, but the product may be toxic to animal foetuses. An animal reproduction study found no decrease in nest size or early survival following exposure to 300 ppm of perchloroethylene, but a significant decrease in nest size and early survival with exposure to 1,000 ppm five days a week for six hours a day during the 11 weeks prior to mating.

This confirms the need for all users of perchloroethylene to comply with regulations and to implement best practices at all times.

ENVIRONMENTAL EFFECTS

Perchloroethylene does not deplete the ozone layer, and its contribution to global warming, acid rain and smog formation is negligible.¹⁸ In many applications, it performs as well or better than suggested alternatives, which may themselves have significant impacts on the environment and on human health. Chlorinated solvents account for less than 8% of total solvent emissions to the atmosphere from all sources in Western Europe.

Chlorinated solvents are unlikely to accumulate in living organisms or the environment. Perchloroethylene has a half-life in the atmosphere of around three months, and any spills to water or soil are most likely to re-evaporate into the atmosphere within a few days to one month, depending on water movement, depth and wind speed. Here, perchloroethylene breaks down into phosgene, which is taken up by cloud, rain or ocean water and further broken down to carbon dioxide, hydrogen chloride, and possibly trichloroacetic acid. These substances may occur in rain or sea water, but perchloroethylene's contribution to "acid rain" is negligible.

In sediment and soil, perchloroethylene is fairly mobile and can leach into groundwater. Under these conditions no physico-chemical breakdown has been reported. The solvent is not biodegradable under standard test conditions, and may be resistant to breakdown in the presence of oxygen (aerobic conditions). However, if methane is present but not oxygen (strictly anaerobic conditions), some breakdown has been seen.

ECSA encourages companies which manufacture and use this solvent to install spillage containment systems in storage and use areas. The Association strongly discourages land filling of waste, even though this may be legal in some areas.

Environmental levels

Perchloroethylene has been detected at levels of parts per billion (ppb) in all environmental compartments in aquatic organisms and in plants. Background levels in air in remote regions is typically much lower (< 0.1 ppb) than in urban areas (up to 3 ppb). The solvent has been found in indoor air at concentrations of up to one part per million (ppm), mostly due to its use in dry-cleaning; it may also occur in drinking water and foods.

Ecotoxicity

In the aquatic environment all trophic levels show similar sensitivity to the acute toxic effects of perchloroethylene, with the lowest acute Lethal Concentration for 50% of the test population (LC50) and Effective Concentration for 50% of the test population (EC50) values occurring in

¹⁸ <http://www.eurochlor.org/facts>

the range of 1 to 10 mg/l. EC50 values for freshwater and marine algae are reported at higher levels (>500 mg/l).

In fish, chronic exposure to this solvent does not increase its toxicity significantly.

No adverse affects on the aquatic ecosystem have been reported at concentrations below 0.1 mg/l. No Observed Effect Concentration (NOECs) are of the order of 1 mg/kg soil (dry weight).

Several soil organisms, including micro-organisms, invertebrates and plants have been used to assess the toxicity of perchloroethylene after acute or prolonged exposure, but mostly these studies have not been conducted under standardised conditions.

It has been suggested that perchloroethylene may have an adverse effect on the photosynthetic mechanisms of conifers and other higher plants following prolonged exposure.

Based on its octanol-water partition coefficient, no significant bioaccumulation of perchloroethylene is expected. On the basis of measured bioconcentration factors, there is no evidence of biomagnification along the food chain.

REGULATION

Perchloroethylene use is regulated under the Solvent Emissions Directive (1999/13/EC).^{19,20} ECSA welcomes the implementation of this directive, with its goals of reducing workplace exposures and environmental emissions. Modern equipment allows more efficient use of chlorinated solvents, and will continue to contribute to the sustainability of this class of product.

Dry-cleaning is an activity that is within the scope of the EU Solvent Emissions Directive, with complete compliance required by 2007.²¹ An ECSA analysis of the effects of this directive on EU perchloroethylene use and emissions from dry-cleaning found that even if the number of perchloroethylene dry-cleaners remained unchanged, emissions would be reduced significantly through use of modern equipment. An 81% reduction in emissions was forecast for 2007 compared with the 2000 baseline.

Occupational exposure

The current Permissible Exposure Limit (PEL) for perchloroethylene is 100 ppm for 8 hours time-weighted average (TWA), 200 ppm as a ceiling value and 300 ppm as a peak limit (US Occupational Safety and Health Administration).

The American Conference of Governmental Industrial Hygienists (ACGIH) currently recommends a Threshold Limit Value (TLV) of 25 ppm (170 mg/m³ - 8 hour TWA) and 100 ppm (685 mg/m³) as a 15 minute short time exposure limit.

For the ACGIH, perchloroethylene is classified as A3 (Animal Carcinogen), for the International Agency for Research on Cancer (IARC) it is listed as a 2A substance (probably carcinogenic to humans), and by the US National Toxicology Program (NTP) it is considered "reasonably

¹⁹ <http://www.eurochlor.org/solventemissionsdirective>

²⁰ http://eur-lex.europa.eu/LexUriServ/site/en/oj/1999/l_085/l_08519990329en00010022.pdf

²¹ <http://www.eurochlor.org/index.asp?page=377>

anticipated to be a human carcinogen". At EU level, perchloroethylene is classified as a Category 3 carcinogen.

Netherlands (MAC): 240 mg/m³ or 35 ppm.

Currently a new value is recommended (138 mg/m³). Also with Skin Notation.

United Kingdom (OEL): 345 mg/m³ or 50 ppm.

Switzerland (MAK-15): 170 mg/m³ or 25 ppm.

United Kingdom (STEL): 685 mg/m³ or 100 ppm.

For biological monitoring, the following BE indices are used :

Germany : 1 mg/l perchloroethylene in blood prior to next shift.

ACGIH : - 5 ppm perchloroethylene in expired air.

- 0.5 mg/l perchloroethylene in blood prior to last shift of workweek.

- 3.5 mg/l trichloroacetic acid in urine at the end of the workweek.

Beyond compliance

ECSC strongly recommends that perchloroethylene only be used in applications where all relevant workplace, disposal and other environmental regulatory requirements are met. In addition, many prudent operators have chosen to adopt practices and standards that go beyond the strict legal requirements for use, management and disposal of perchloroethylene and perchloroethylene-containing wastes. In addition to taking full responsibility for environmental protection, these operators help to avoid potential liability for any environmental contamination that can be traced to their solvent wastes - whether at their own plant or elsewhere - regardless of whether they have complied with the letter of the law. Such additional measures that go "beyond compliance" make good business sense because they minimise risks of liability.

Regulatory and other information for perchloroethylene

Chemical formula : C₂Cl₄

Molecular weight : 165.85

CAS-number : 127-18-4

EINECS-number : 204-825-9

Labelling : Xn, N, R40, (67/548/EEG) R51/53

Proposed labelling : X^o, N, R40, R38, R67, R51/53