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RISK REDUCTION MONOGRAPH NO. 2:

METHYLENE CHLORIDE

BACKGROUND AND NATIONAL EXPERIENCE WITH REDUCING RISK

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

Paris 1994

OECD Environment Monograph Series No. 101

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METHYLENE CHLORIDE

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Environment Directorate

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Also published in this series:

Risk Reduction Monograph No. 1: Lead

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RISK REDUCTION MONOGRAPHS

Risk Reduction Monograph No. 2: Methylene Chloride – Background and National Experience with Reducing Risk is the second in a series of OECD documents concerned with risk reduction activities for specific chemicals or groups of chemicals. The Risk Reduction Monographs contain sections on: the commercial life cycle; the environmental life cycle, including the sources of environmental releases, pathways, and estimations of exposure; risk reduction and control measures; and international and national positions on the perceived risk.

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FOREWORD

Background

In 1990, the Council of the OECD adopted a Decision-Recommendation on the Co-operative Investigation and Risk Reduction of Existing Chemicals [C(90) 163/Final]. This OECD Council Act is aimed at the reduction of risks from chemicals to the environment, and/or to the health of the general public or workers. It is based on the premise that international co-operation in risk reduction activities can enhance the technical and institutional aspects of risk management in Member countries through burden-sharing and a reduction of duplicative efforts. Furthermore, such activities can lead to a more effective use of the knowledge about risks that is being generated through, for example, national chemicals reviews and assessments; the OECD co-operative investigation of existing chemicals; and the work of other international organizations conducting hazard and risk evaluations, such as the United Nations' International Programme on Chemical Safety (IPCS).

International co-operation can provide a forum for the exchange of views on risk reduction strategies, thus increasing mutual understanding and facilitating the harmonization of programmes being undertaken at the national level. By means of this forum, technical barriers to trade can also be prevented.

The OECD's approach to risk reduction

The risk reduction process normally begins at the national level. However, the international character of the use and marketing of chemicals, and the mobility of certain chemicals in the environment, give risk reduction activities an international dimension.

The OECD's approach to risk reduction relies on the sharing and exchange of information on the management of specific chemicals. Readily available information concerning national risk reduction strategies can make comparative analyses possible. Where common interests emerge, the development and implementation of measured and consistent responses to unacceptable health and/or environmental risks can be facilitated.

In this context, risk reduction activities can take into account all stages of a chemical's commercial and environmental life cycles, beginning with the natural resources needed to produce it and extending through the chemical's uses to its eventual disposal. The chemical's health and environmental effects can be considered, together with exposure via all routes and media to different populations.

OECD work on methylene chloride risk reduction

OECD Member countries chose methylene chloride as one of the five chemicals (or groups of chemicals) to be included in an initial pilot project on co-operative risk reduction. An OECD Clearing House made up of lead countries for methylene chloride began initial information collection in support of this Risk Reduction Monograph in 1992. Within the Clearing House, all drafts of the document including this final version were developed by Sweden, with technical support from the other Clearing House countries: Germany, Switzerland and the United Kingdom.

The Joint Meeting of the Chemicals Group and the Management Committee of the Special Programme on the Control of Chemicals recommended that this document be derestricted. It is being made public under the authority of the Secretary-General.

EXECUTIVE SUMMARY

Chapter Summaries

1. Methylene Chloride Production, Use and Disposal

World production of methylene chloride (dichloromethane) in 1991 was estimated to be 437,000 tonnes. Usage in Western Europe decreased from 200,000 tonnes per year in the period 1975-1985 to 175,000 tonnes in 1989 and 165,000 tonnes in 1991.

Most applications of methylene chloride are based on its considerable solvent capacity. Other important properties are its volatility and stability. It is non-flammable.

The main uses of methylene chloride are:

- as a component of paint and varnish strippers, and of adhesive formulations;
- as a solvent in aerosol formulations;
- as an extractant solvent and as a process solvent in the food and pharmaceutical industries;
- as an extractant of fats and paraffins;
- as a process solvent in cellulose ester production, fibre and film forming, and polycarbonate production;
- as a blowing agent in the production of flexible polyurethane foam;
- in plastics processing, and metal and textile treatment;
- as a vapour degreasing solvent in the metalworking industries.

2. Environmental Fate, Transport and Occurrence

Methylene chloride is released to the environment as a result of its use by various industries, and as a result of the use of paint removers and aerosol products in the home. It is mainly released to the environment in air and, to a lesser extent, in water and soil. Based on the physical and chemical properties of methylene chloride, a Level I fugacity calculation according to Mackay and Paterson (1981) shows that more than 99 per cent will partition to the atmospheric compartment and less than 1 per cent to water. Due to its short atmospheric lifetime, there is little potential for methylene chloride to accumulate in the atmosphere.

The global warming potential of methylene chloride is small, quoted by the Intergovernmental Panel on Climate Change as 15, relative to carbon dioxide over 100 years, and 5 over 500 years. No significant impact on stratospheric ozone depletion is expected. However, due to the high emissions of methylene chloride to the atmosphere, it is not possible to exclude completely any danger to the ozone layer. Methylene chloride is not thought to contribute significantly to ground level ozone formation.

Methylene chloride is biodegradable under both aerobic and anaerobic conditions. It is not readily biodegradable as defined in the OECD Guidelines for Testing of Chemicals, but adapted sewage organisms will degrade it at a high rate. The low partitioning coefficient (Log P_{ow}=1.25) indicates a low potential for bioaccumulation.

In ambient air in rural and remote areas, mean background levels of methylene chloride range from 0.07 to 0.29 $\mu g/m^3$. The average concentrations in suburban and urban areas, respectively, are reported to be <2 $\mu g/m^3$ and <15 $\mu g/m^3$.

Methylene chloride is found in a variety of surface waters, with "typical" background concentrations of 0.05 µg/litre in fresh water and 0.5 µg/litre in urban areas. Background concentrations in the oceans are very low (not detectable, or a few ng/litre). Even in polluted areas, concentrations seldom exceed a few µg/litre. Higher concentrations are found locally, as an effect of discharges or in connection with accidental spills.

3. Exposure

The main route of human exposure is through vapour inhalation, sometimes accompanied by direct skin and eye contact. Human exposure occurs primarily through the use of methylene chloride, or methylene chloride-containing products, in occupational or consumer applications. Much lower levels of human exposure can occur through inhalation of methylene chloride in ambient air and through ingestion via drinking water, food and beverages.

Methylene chloride exposures vary substantially between different areas of use. The reported exposures within each area of use are also variable, depending on the risk reduction measures in effect, the methods used to take measurements, and the existing mandatory occupational exposure limits.

The exposures in occupational paint stripping are highly variable and greatly influenced by the size of the installation, the engineering controls in place, and work practices. Reported exposure levels on an 8-hour TWA basis range from a few ppm to above 500 ppm. The exposure levels in the furniture stripping industry (in which furniture is stripped by removing old paint and lacquer finishes prior to restoration and refinishing) are of special concern. Very high short-time exposures (1000-2000 ppm) have been reported from small-scale furniture stripping shops. However, exposure levels have been reduced to below 30 ppm in well controlled operations.

Methylene chloride is widely used as a process solvent in the manufacture of a variety of products. Most of the processes are carried out in closed systems. Exposure levels are normally low, but occasional high exposures (>100 ppm, 10-minute TWA) may occur during specific operations, e.g. filter change, charging and discharging. Some industrial processes involve somewhat higher exposure levels. The production of cellulose triacetate fibre can involve exposures above 500 ppm (8-hour TWA). Exposures from this process have been successfully reduced to below 100 ppm 8-hour TWA, using appropriate ventilation and enclosing the process equipment.

In non-occupational paint stripping the majority of the exposure estimates are below 500 ppm, although short-time exposures on the order of several thousand ppm have been reported. Exposure profiles are to a high degree dependent on the work situation. Lower exposures can be obtained by simple ventilation procedures. Consumer exposure to aerosol formulations may involve high peak exposures but, as the use of these products is generally very short in duration, the total exposure is considered to be low.

4. International and National Positions on the Risks from Methylene Chloride

This chapter presents an evaluation, from the International Programme on Chemical Safety (IPCS), of methylene chloride's human health risks and environmental effects.

Also presented in this chapter are statements, provided by OECD Member countries, in regard to national positions on the risks from methylene chloride. Essentially, these statements provide the rationale for any actions the country has taken to address effects associated with environmental or human exposures to methylene chloride. They are based on conclusions concerning the hazards of methylene chloride, and data from human health or environmental monitoring carried out to determine levels of exposure.

The national risk assessments and risk characterizations that have led countries to take action have a strong national character. Countries develop positions on the need for risk reduction activities only after they have analysed the hazard and significance of certain exposures, and have factored in local social, economic and political considerations. These positions are usually arrived at after considerable debate on the numerous factors involved, and thus are not expected to be consistent across Member countries.

5. Mechanisms for Risk Reduction

The methylene chloride risk reduction activities of 15 Member countries and the European Union are described in this chapter. The descriptions are based on information provided by countries. A summary of industry risk reduction activities, provided by the Business and Industry Advisory Committee to the OECD (BIAC), is also included.

Available information on risk reduction activities in Member countries is summarized in the tables in Annex A to this chapter. Information was taken either from detailed descriptions provided by countries, or from secondary sources or government publications.

The extent of risk reduction activities varies substantially among Member countries. Repeated requests for information on methylene chloride risk reduction activities were made to all Member countries in 1993 and 1994. Lack of information in this report on a particular country means either that no risk reduction activities have taken place in that country, or that the country has not responded to requests for information.

Possible alternative chemicals or methods in use are summarized in Appendix 1. The alternatives listed have not been evaluated from a toxicological or ecotoxicological point of view. The use of alternative chemicals or processes may pose other risks to human health or to the environment. It is therefore important to evaluate and compare risks carefully before making substitutions. It is also important to investigate in each case whether a particular substitute can be used, with regard to its technical efficacy.

EXPOSÉ DE SYNTHÈSE

Résumé des différents chapitres

1. Production, utilisation et élimination du chlorure de méthylène

D’après les évaluations, la production mondiale du chlorure de méthylène était en 1991 de 437 000 tonnes. En Europe occidentale, les quantités utilisées sont en diminution : elles sont passées de 200 000 tonnes par an, entre 1975 et 1985, à 175 000 tonnes en 1989 et à 165 000 tonnes en 1991.

La plupart des applications du chlorure de méthylène tiennent à son remarquable pouvoir solvant. Cette substance possède d’autres propriétés importantes : volatilité et stabilité. Elle est ininflammable.

Les principales utilisations du chlorure de méthylène sont les suivantes :

- ingrédient de décapants de peintures et vernis et de préparations adhésives ;
- solvant dans des aérosols ;
- agent d’extraction et solvant dans les industries alimentaires et pharmaceutiques ;
- agent d’extraction de corps gras et de paraffines ;
- solvant dans la production d’ester de cellulose et la fabrication de fibres et de films ainsi que dans la production de polycarbonate ;
- agent d’expansion dans les mousses souples de polyuréthanne ;
- fabrication de matières plastiques et traitement de métaux et de textiles ;
- solvant à l’état de vapeur pour le dégraissage dans les industries métallurgiques.

2. Devenir, transport et répartition dans l’environnement

Le chlorure de méthylène est émis dans l’environnement du fait de son utilisation par diverses industries et de l’emploi par les particuliers de décapants de peintures et de produits en aérosol. L’émission dans l’environnement se fait essentiellement dans le compartiment air et, dans une moindre mesure, dans l’eau et dans le sol. A cause de ses propriétés physiques et chimiques, le calcul de fugacité de niveau 1 d’après Mackay et Paterson (1981) donne comme résultat que plus de 99 pour cent du produit aboutiront dans le compartiment air et moins d’un pour cent dans l’eau. Puisque sa vie dans l’atmosphère est courte, le chlorure de méthylène a peu tendance à s’y accumuler.

La contribution que le chlorure de méthylène pourrait apporter au réchauffement mondial est faible : elle est de 15 par rapport à celle du dioxyde de carbone sur 100 ans et de 5 sur 500 ans, d’après le Groupe intergouvernemental d’experts sur l’évolution du climat. Le chlorure de méthylène ne devrait pas avoir d’effet notable sur la diminution de l’ozone stratosphérique. A cause de l'importance du volume émis, on ne peut cependant exclure ce danger complètement. En outre, on ne pense pas qu'il participe beaucoup à la formation d'ozone au niveau du sol.

Le chlorure de méthylène est biodégradable en conditions aussi bien aérobies qu'anaérobies. Il n'est pas facilement biodégradable au sens des Lignes directrices de l'OCDE pour les essais de produits chimiques, mais les organismes de traitement des eaux usées le dégradent rapidement après adaptation. Son faible coefficient de partage (Log P_{oe} = 1.25) montre qu'il est peu susceptible de bio-accumulation.

Dans l'air ambiant des zones rurales et reculées, les concentrations de fond moyennes du chlorure de méthylène vont de 0.07 à 0.29 $\mu g/m^3$. Les concentrations moyennes relevées dans les zones suburbaines et urbaines sont respectivement inférieures à 2 et à 15 $\mu g/m^3$.

On trouve du chlorure de méthylène dans diverses eaux de surface, avec des concentrations de fond caractéristiques de 0.05 µg/litre pour l'eau douce et de 0.5 µg/litre pour les zones urbaines. Les concentrations de fond dans les océans sont très faibles (en dessous du seuil de détection, ou de quelques ng/litre). Même dans les zones polluées, les concentrations dépassent rarement quelques µg/litre. Des concentrations plus élevées se rencontrent par endroits, du fait de déversements ou lors de rejets accidentels.

3. Exposition

La principale voie d'exposition de l'être humain est l'inhalation de vapeurs, parfois en même temps qu'un contact cutané et oculaire direct. Cette exposition tient surtout à l'utilisation de chlorure de méthylène ou de produits en contenant, lors d'activités professionnelles ou de travaux à la maison. Une exposition humaine beaucoup plus faible peut se produire par inhalation du chlorure de méthylène présent dans l'air ambiant et par ingestion d'eau potable, d'aliments et de boissons.

Les expositions au chlorure de méthylène varient sensiblement entre les différents lieux d'utilisation. Les expositions signalées dans chaque domaine d'utilisation varient également en fonction des dispositions en vigueur pour la réduction des risques, des méthodes de surveillance et des limites imposées pour l'exposition professionelle.

Les expositions lors du décapage professionnel de peintures sont extrêmement variables et dépendent dans une très grande mesure de la dimension des installations, des contrôles techniques en place et des méthodes de travail. Les niveaux d'exposition relevés en moyenne pondérée sur huit heures vont de quelques ppm à plus de 500 ppm. Les niveaux d'exposition dans le secteur du décapage de meubles (où les meubles sont décapés pour éliminer les anciennes couches de peinture et de laque avant restauration et nouvelle finition) sont particulièrement préoccupants. Des expositions très intenses de brève durée (1 000 à 2 000 ppm) ont été signalées dans des ateliers de petites dimensions où l'on décape des meubles. Cependant, lors d'opérations bien contrôlées, les niveaux d'exposition ont été ramenés en dessous de 30 ppm.

Le chlorure de méthylène est largement utilisé comme solvant industriel dans la fabrication de produits variés. La plupart des procédés se déroulent dans des systèmes clos. Les niveaux d'exposition sont normalement faibles, mais il peut y avoir des pics de temps à autre (>100 ppm, en moyenne pondérée sur 10 minutes) lors d'opérations spécifiques, telles que changement de filtre, chargement et déchargement. Quelques procédés industriels peuvent entraîner des niveaux d'exposition un peu plus élevés. La production de fibres de triacétate de cellulose peut donner lieu à des expositions supérieures à 500 ppm (moyenne pondérée sur 8 heures). Les expositions associées à ce procédé ont pu être ramenées en dessous de 100 ppm (moyenne pondérée sur 8 heures) en recourant à une ventilation appropriée et en confinant l'équipement utilisé.

Pour le décapage de peintures hors du contexte professionnel, la plupart des expositions évaluées se situent en dessous de 500 ppm, bien qu'on ait signalé des expositions de courte durée à des concentrations de l'ordre de plusieurs milliers de ppm. Les courbes d'exposition dépendent dans une très grande mesure des conditions de travail. Les expositions peuvent être atténuées par des méthodes simples de ventilation. L'exposition du consommateur à des aérosols peut atteindre de fortes pointes mais, comme l'utilisation de ces produits dure généralement très peu de temps, l'exposition est considérée dans l'ensemble comme faible.

4. Positions adoptées au niveau international et national quant aux risques liés au chlorure de méthylène

Ce chapitre présente une évaluation faite dans le cadre du Programme international sur la sécurité des substances chimiques (PISSC) des risques pour la santé humaine associés au chlorure de méthylène et de ses effets sur l'environnement.

On trouvera également dans ce chapitre des déclarations provenant de pays Membres relatifs à l'attitude adoptée par les divers pays vis-à-vis des risques liés à ce produit. Pour l'essentiel, ces déclarations donnent les raisons à la base de toute disposition prise par un pays donné pour faire face aux effets associés à l'exposition de l'environnement ou de l'être humain au chlorure de méthylène. Elles se fondent sur des conclusions relatives aux dangers présentés par le chlorure de méthylène et sur des données provenant d'enquêtes réalisées sur la santé humaine ou sur l'environnement afin de déterminer les niveaux d'exposition.

Les évaluations et les descriptions nationales des risques qui ont conduit les pays à prendre des mesures ont un caractère profondément national. Les pays n'ont défini leur position sur la nécessité de lancer des activités de réduction des risques qu'après avoir analysé le danger que présentaient certaines expositions, ainsi que leur ampleur, et avoir pris en compte des considérations locales d'ordre social, économique et politique. Comme ces positions sont habituellement établies après un débat approfondi sur les nombreux facteurs impliqués, il ne faut par conséquent pas s'attendre à ce qu'elles soient homogènes entre les différents pays Membres.

5. Mécanismes de réduction des risques

Ce chapitre décrit les activités de réduction des risques associés au chlorure de méthylène qui se déroulent dans 15 pays Membres et au sein de l'Union européenne. Cette description se fonde sur les informations fournies par des pays. On trouvera, en outre, un résumé fourni par le Comité consultatif économique et industriel auprès de l'OCDE (BIAC), des mesures prises par l'industrie pour réduire les risques.

Les informations disponibles sur les activités de réduction des risques poursuivies dans des pays Membres sont résumées dans les tableaux de l'Annexe A, à la fin du chapitre. Les informations résumées dans les tableaux proviennent de descriptions détaillées fournies par les pays, ou ont été extraites de sources secondaires ou de documents publiés par les pouvoirs publics.

Les activités de réduction des risques sont d'une ampleur extrêmement variable d'un pays Membre à l'autre. En 1993 et 1994, tous les pays Membres ont été invités à fournir des informations sur les activités de réduction des risques associés au chlorure de méthylène. Dans le présent rapport, l'absence d'informations relatives à un pays Membre donné signifie, soit que de telles activités n'ont pas eu lieu dans ce pays, soit que ce pays n'a pas répondu aux demandes d'informations.

Des produits de substitution possibles ou des méthodes de remplacement en usage sont énumérés à l'Appendice 1. Ces produits et méthodes n'ont pas été évalués du point de vue toxicologique ou écotoxicologique. L'utilisation de produits ou procédés de substitution pouvant présenter d'autres risques pour la santé humaine et l'environnement, il faut impérativement évaluer et comparer les risques avant de pratiquer des substitutions. Il est également important de vérifier que le produit de substitution a une efficacité suffisante permettant son utilisation.

CHAPTER 1

METHYLENE CHLORIDE PRODUCTION, USE AND DISPOSAL

1.1 Physical and chemical properties

Methylene chloride is a clear, highly volatile, non-flammable liquid with a penetrating, ether-like odour. Pure dry methylene chloride is a very stable compound. Other physical and chemical properties are shown in **Table 1.1**.

1.2 Production

Methylene chloride is mainly produced by the Stauffer process, using a two-stage reaction route. In the first stage, methanol is vaporized and reacted with gaseous hydrogen chloride to produce methyl chloride. The methyl chloride is dried and purified, then further reacted with gaseous chlorine to give methylene chloride and chloroform as prime co-products, with minor production of a small amount of carbon tetrachloride.

Liquid phase chlorination has been developed by Tokuyama Soda for the second phase of the production process. The ratio of methylene chloride to chloroform is variable, and controlled by varying the reaction conditions.

Reactions for the production of methylene chloride (non-stoichiometric) are:

Stage 1

$$CH_3OH + HCl \rightarrow \underset{\text{methyl chloride}}{CH_3Cl} + H_2O$$

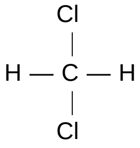
Stage 2

$$CH_3Cl + Cl_2 \rightarrow \underset{\text{methylene chloride}}{CH_2Cl_2} + \underset{\text{chloroform}}{CHCl_3} + \underset{\text{carbon tetrachloride}}{CCl_4}$$

Historically, the direct route to methylene chloride by chlorination of methane was used as well. This also produced the other three chloromethanes in varying proportions, depending on the conditions used (ICI pers. comm. 1992, CEC 1986).

Methylene chloride is one of the more stable of the chlorinated hydrocarbon solvents produced, but still requires the presence of a stabilizer prior to storage and use to guard against acidity and breakdown. The stabilizer is added immediately after product purification.

Table 1.1 Physical and Chemical Properties of Methylene Chloride

Substance name:	dichloromethane
IUPAC name:	dichloromethane
Synonyms:	methylene chloride
CAS No.:	75-09-2
EC No.:	602-004-00-3
EINECS No.:	200-838-9
Structural formula:	 $H-\overset{\overset{\displaystyle Cl}{\vert}}{\underset{\underset{\displaystyle Cl}{\vert}}{C}}-H$
Molecular formula:	CH_2Cl_2
Relative molecular mass:	84.933
Density [at 20°C (kg/m^3)]:	1315.7
Colour:	colourless
Boiling point (at 1013 hPa):	39-40.5°C
Solubility in water (at 20°C):	13-20 g/litre
Vapour pressure (at 20°C):	475.3 hPa
Flash point:	incombustible
Ignition temperature:	605°C
Explosion limits:	lower explosion limit 13% (v/v)* upper explosion limit 22% (v/v)*
Olfactory threshold:	883 mg/m^3
Conversion factors:	1 ppm = 3.47 mg/mg^3
	1 mg/m^3 = 0.288 ppm
Log P_{ow} (octanol/water):	1.25
Henry's Law constant, Pa.m^3/mol at 20°C:	380

* This is with a high energy source; these conditions are unlikely to arise in normal operations (source: IPCS 1994).

Vapour pressure, flash point, ignition temperature, olfactory threshold and log P_{ow} are the most relevant parameters for the risk assessment of methylene chloride.

The stabilizer most commonly used, on grounds of technical effectiveness, is amylene (2 methyl but-2-ene) at a level of approximately 50 ppm. Other stabilizers which may be used are methanol, ethanol, and cyclohexane at levels up to 400-500 ppm. Methanol or ethanol may be added at up to 1 per cent by weight. In certain applications where very arduous conditions may be encountered, a more complex blend of stabilizers may be used. The stabilizer system may be up to 6-7 per cent by weight in a typical formulation for use in metal degreasing.

1.3 End uses and world demand

1.3.1 Industrial uses

Most applications of methylene chloride are based on its considerable solvent capacity, especially for grease, plastics and various paint binding agents. Other important properties are its volatility and stability. Methylene chloride is also non-flammable.

Methylene chloride is mainly used (CEFIC 1983):

- as a component of paint and varnish strippers, and of adhesive formulations;
- as a solvent in aerosol formulations;
- as an extractant solvent and as a process solvent in the food and pharmaceutical industries;
- as an extractant of fats and paraffins;
- as a process solvent in cellulose ester production, fibre and film forming, and polycarbonate production;
- as a blowing agent in the production of flexible polyurethane foam;
- in plastics processing, and metal and textile treatment;
- as a vapour degreasing solvent in the metalworking industries.

Shown in **Table 1.2** are categories of methylene chloride use, based on a recent global analysis of sales.

The relative amounts in each use category can vary considerably from country to country, as well as with time (see **Figures 1.1 to 1.3**).

1.3.1.1 Paint removers

One of the most important applications of methylene chloride is its use in paint removers. The aircraft industry and the military are important users. Methylene chloride is the major component of nearly all solvent-based paint remover formulations, whether for industrial, professional, or consumer "do-it-yourself" (DIY) use. It is popular because of its low cost and high effectiveness. It can act on a wide range of paint substrates.

The paint remover is generally formulated with a number of other agents to increase its effectiveness: for example, alcohols, amines, ammonium hydroxide, etc.

Estimates of the market size in the United States for methylene chloride-based paint strippers vary from 41,000 tonnes (Wolf 1991) to 67,000 tonnes (CONSAD 1989), representing 25-35 per cent of the total methylene chloride market. This use is likely to decrease in the US with the advent of new federal and state regulatory controls (PTCN 1991).

The breakdown of paint remover use in the US varies. However, the following approximations are adequate:

- aircraft refurbishment (25 per cent);
- trade furniture stripping (17 per cent);
- retail (consumer use) (25 per cent);
- original equipment manufacture (10 per cent);
- military use (17 per cent);
- other (6 per cent).

In Europe, paint strippers represent approximately the same percentage of total methylene chloride use as in the United States, i.e. 25 per cent (ICI pers. comm. 1993). UK estimates again show paint stripping as 25-30 per cent of the total market, with approximately 50 per cent of paint strippers being used in the consumer/trade decorator field (ICI pers. comm. 1993). Paint remover use in Japan amounted to between 5000 and 6000 tonnes/year from 1986 to 1993 (about 6 per cent of total demand). The market size of this use of methylene chloride has continued at about the same level. Paint remover is mostly used in industrial sectors in Japan and not, as a prevailing practice, by consumers.

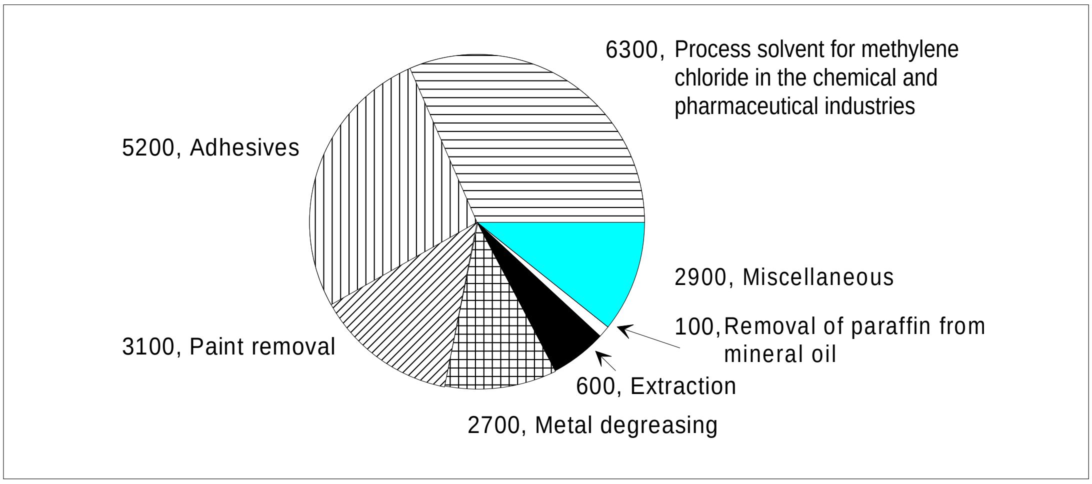
Estimates of global sales indicate that methylene chloride paint strippers make up approximately 16 per cent of the total methylene chloride market (see Table 1.2 below).

Table 1.2 Global Sales of Methylene Chloride by End Uses

End use	**%**
Aerosols	7.5
Food extraction	8.3
Paint stripping – industrial	8.3
Paint stripping – commercial	8.3
Pharmaceuticals	9.0
Polyurethanes	8.3
Polycarbonates	8.3
Vapour degreasing	8.3
Photo fabrication (cellulose triacetate)	8.3
Photoresist stripping	8.3
Other dispersive uses (adhesives)	8.3
Distributors (for onward sales)	8.3

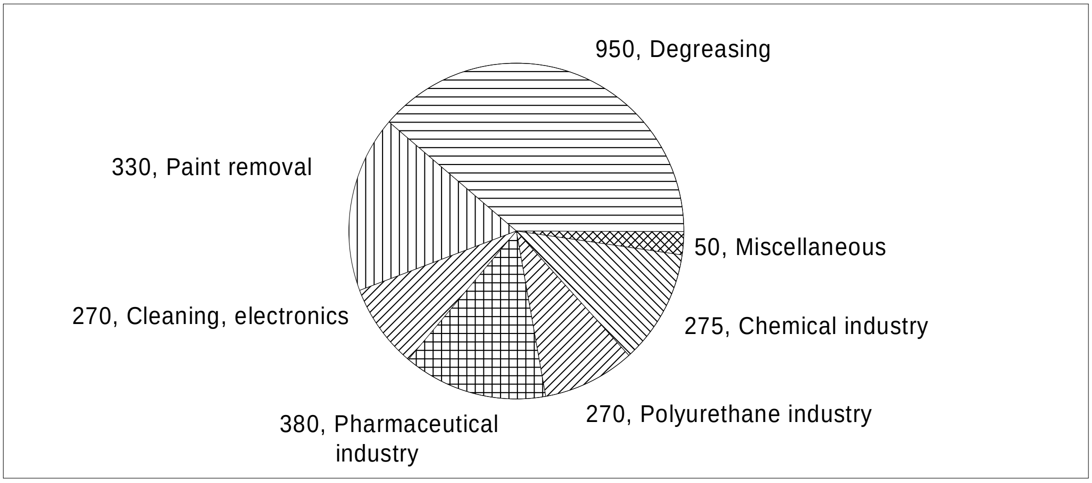
Source: Coopers and Lybrand 1992, commissioned by the global methylene chloride producers (draft)

Figure 1.1 National Estimation of Methylene Chloride Use in Germany 1992 (tonnes/year)



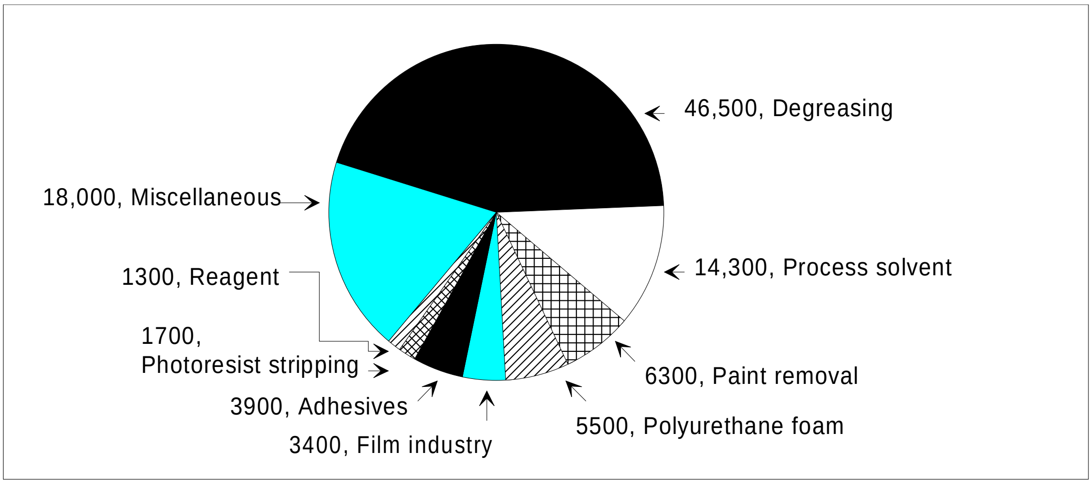
Source: Verband der chemishen Industrie, 1993

Figure 1.2 National Estimation of Methylene Chloride Use in Sweden 1988 (tonnes/year)



Source: National Chemicals Inspectorate, Sweden, 1990

Figure 1.3 National Estimation of Methylene Chloride Use in Japan 1993 (tonnes/year)



Source: Japan Association for Hygiene of Chlorinated Solvents, 1994

1.3.1.2 Extractant and process solvent use

There are several uses of methylene chloride in the chemical processing industries. In the chemical, pharmaceutical and food production industries, it is used as an extractant solvent and as a process solvent.

The main use of methylene chloride in the pharmaceutical industry at present is as a solvent for production and coating processes. Methylene chloride is used to extract certain natural products which are further processed for use as pharmaceuticals. This solvent is used as it gives very specific extraction of the desired product with high yields. Due to its low boiling point, methylene chloride is readily removed without causing thermal degradation of the extract. Methylene chloride, or blends with other solvents such as methanol or ethanol, are used in applying coatings to pills and tablets. Methylene chloride is also used as the reaction medium and process solvent in the production of many pharmaceutical products, including a wide range of antibiotics.

Methylene chloride is used as an extractant solvent in various areas of the food industries, notably as a caffeine remover, and also where the substances to be extracted are heat-sensitive, for example cocoa, edible fats, spices and hops. In the decaffeination process, caffeine is dissolved from the green coffee beans by an equilibrium water extract in a countercurrent series of percolators. The caffeine is then removed from the water extract by liquid-liquid extraction with methylene chloride (Kirk-Othmer 1992). Methylene chloride is also used to extract chlorophyll from grass and lucerne. It is considered to give the best profile of extracted material (ICI pers. comm. 1993).

In the chemical industry, methylene chloride is used as the process solvent in the production of polycarbonate plastic. The solubility of polycarbonate in methylene chloride is very high, and the solvent is readily removed from the plastic due to its low boiling point. It is also used in the production of cellulose triacetate flake, and the subsequent formation of textile fibres and photographic film from the flake. Methylene chloride is considered the only suitable solvent for these applications.

Methylene chloride is used in the polyurethane foam industry as a releasing agent in the moulding of polyurethane products, and for cleaning process equipment and purging spray guns. The trend in modern PU equipment, however, is towards high-pressure, self-cleaning dispensing machinery, reducing the need for clean-up and flushing. Methylene chloride is mainly used as the auxiliary blowing agent (ABA) in the production of slabstock flexible PU foam. The auxiliary blowing agent is used to achieve the desired foam densities and other favourable properties.

Slabstock or polyurethane foam is manufactured in a continual process by the reaction of toluene di-isocyanate (TDI) with polyether or polyester polyols in carefully controlled ratios. The reaction is modified by catalysts and surfactants. A certain amount of water is added, which generates foaming carbon dioxide by *in situ* reaction with the isocyanate. A wide range of foams are produced by manufacturers, with densities ranging from 10 kg/m^3 to more than 40 kg/m^3. Foam densities lower than 21-22 kg/m^3 can only be produced with the use of an auxiliary blowing agent. The auxiliary blowing agent is evaporated by the heat of reaction of the TDI and polyol. The generated gas expands the foam to the required density and modifies physical properties such as resilience and softness.

In the United States in 1985, approximately 605,000 tonnes of flexible polyurethane foam was produced using approximately 22,000 tonnes of auxiliary blowing agents (about 50 per cent CFC 11 and 50 per cent methylene chloride). In 1990, only 10 per cent of the auxiliary blowing agents used in this application was methylene chloride. The use of methylene chloride as an auxiliary blowing agent in the production of flexible polyurethane foam accounted for 10 per cent of US use of methylene chloride in 1985 (US EPA 1985). Methylene chloride may be used to replace CFC 11 in the production of low-density flexible PU foam. It is already used almost exclusively for flexible slabstock PU foam in the United Kingdom and the Netherlands (ICI pers. comm. 1992).

1.3.1.3 Cleaning and degreasing

In the metalworking industries, methylene chloride is used as a vapour degreasing solvent or, blended with petroleum and other hydrocarbons, as a dip-type cleaner. In the manufacture of metal products, cleaning is needed before painting, plating, plastic coating, etc. Degreasing in the sophisticated engineering industry is normally carried out with special equipment in which methylene chloride is used either in liquid or vapour phase. Methylene chloride is also used in the electronics industry in the production of circuit boards and as a stripper for photoresists. In some cleaning and degreasing operations, and in adhesive formulations, methylene chloride may replace 1,1,1-trichloroethane and CFC 113. In Japan, methylene chloride has been used increasingly as an alternative solvent to 1,1,1-trichloroethane in recent years.

1.3.1.4 Miscellaneous industrial uses

Other industrial uses of methylene chloride include:

- as a refrigerant;
- in oil dewaxing;
- as a dye and perfume intermediate;
- as a carrier in the textile and agrochemical industries;
- as a solvent and an extractant in research and laboratory work.

Methylene chloride is used in aerosols as a solvent and a vapour pressure modifier. Its use in this area may increase, as it can replace fluorocarbons in this role. Methylene chloride is similarly used as an alternative to ozone-depleting substances in other applications. It is estimated that 30 per cent of the worldwide consumption of 1,1,1-trichloroethane and 10 per cent of the consumption of CFC 113 may be replaced by methylene chloride (ICI pers. comm. 1993).

1.3.2 Use in consumer products

In consumer products, methylene chloride is used for many of the same purposes as in industrial uses. The main consumer use is in paint strippers. In the United States, 91 per cent of all consumer strippers are methylene chloride-based, versus 7 per cent hydrocarbon types and 2 per cent for all others. The market in the United Kingdom is also dominated by methylene chloride-based paint strippers, which account for over 90 per cent of consumer purchases (ICI pers. comm. 1993).

A survey of household solvent products in the United States found that 78 per cent of paint removers and 66 per cent of aerosol spray paints analysed contained methylene chloride (US EPA 1987a). In 1991, over 100 consumer products in Sweden contained methylene chloride (National Chemicals Inspectorate, Sweden, pers. comm.). In Norway the number of products is around 140, of which 45 are paint removers (Statens Forurensningstillsyn, Norway, pers. comm.).

In aerosol systems, methylene chloride acts as the solvent. The solvent in an aerosol has two functions: firstly as a solvent for the propellant gas, moderating its vapour pressure, and secondly as a solvent for the active ingredient which may typically be a hairspray resin, deodorant or paint formulation. Methylene chloride is used in concentrations of up to 35 per cent (w/w) in cosmetic products in the EU. It has not been used in cosmetic products (hairsprays) in the United States since 1987.

1.3.3 World demand

World production of methylene chloride shows a decline from 570,000 tonnes in 1980 (Edwards et al. 1982) to 437,000 tonnes in 1991 (Coopers and Lybrand 1992). Virtually all methylene chloride produced is used in the northern hemisphere: 424,000 tonnes, versus 12,000 tonnes in the southern hemisphere (Coopers and Lybrand 1992). The total global production capacity is approximately 670,000 tonnes. Most of the production capacity is within the OECD countries (630,000 tpa, compared with 40,000 tpa in non-OECD countries). Approximately 230,000 tonnes is produced in North America, 330,000 tonnes in continental

Western Europe, and 130,000 tonnes in the Far East. There is production capacity in the former USSR and the People's Republic of China, but it is thought to be less than 10 per cent of the above total, i.e. around 40,000 tonnes per year.

Table 1.3 shows the global distribution of methylene chloride sales in 1990-1991.

According to the European Chlorinated Solvents Association, there was a 40 per cent reduction in methylene chloride production in Western Europe in the period 1974-1990. A more recent production estimate (ICI pers. comm. 1992) is 306,000 tonnes in 1991. Usage in Western Europe shows a decrease from 200,000 tonnes per year in the period 1975-1985 (CEFIC 1986) to 175,000 tonnes in 1989 (Dow Chemical Company pers. comm.) and 165,000 tonnes in 1991 (ICI pers. comm. 1992).

Table 1.3 Global Distribution of Methylene Chloride Sales 1990-1991 (tonnes/year)

Region	1990	1991
North America	141,000	125,000
Europe	146,000	147,000
Far East	92,000	93,000
Rest of northern hemisphere	51,000	59,000
Rest of southern hemisphere	11,000	12,000

Source: Coopers and Lybrand 1992, commissioned by the global methylene chloride producers (draft)

CHAPTER 2

ENVIRONMENTAL FATE, TRANSPORT AND OCCURRENCE

2.1 Fate and transport of methylene chloride in the environment

Methylene chloride is released to the environment as a result of its use in various industries, and as a result of the use of paint removers and aerosol products in the home. It is mainly released to the environment in air and, to a lesser extent, in water and soil (IPCS 1994).

Based on the physical and chemical properties of methylene chloride, and a Level I fugacity calculation, Mackay and Paterson (1981) determined that more than 99 per cent will partition to the atmospheric compartment and less than 1 per cent to water. This strong tendency of methylene chloride to disperse to air is confirmed by monitoring data. It should be noted, however, that significant concentrations in surface waters can be found locally as an effect of discharges or accidental spills in effluent waters.

It has been estimated that 85 per cent of the total amount of methylene chloride produced in the United States is lost to the environment, of which 86 per cent is released to the atmosphere. Using data reported to US EPA for the 1988 Toxics Release Inventory, approximately 170,000 tonnes of the production volume in the United States for 1988 (230,000 tonnes) was lost to the atmosphere; of this, 60,000 tonnes resulted from industrial methylene chloride emissions and 110,000 tonnes from the use of consumer products and from other sources such as hazardous waste sites (IPCS 1994). Methylene chloride emissions from industrial and diffuse sources in the Netherlands are shown in **Table 2.1**.

2.1.1 Behaviour in the atmosphere

The atmospheric lifetime of methylene chloride, 5.8 months, is longer than the intrahemispheric mixing time of approximately one month. As a consequence, transport to regions within the hemisphere far removed from the emission source can occur.

The atmospheric lifetime is, however, fairly short relative to the inter-hemispheric transport time of one to one and a half years, resulting in higher concentrations of methylene chloride in the northern hemisphere, where most of the emissions presently occur (IPCS 1994). There is evidence suggesting that a natural source of methylene chloride may exist (Koppman 1993, Edwards et al. 1982). Compared with the halocarbons, which are implicated in the transport of chlorine to the stratosphere, methylene chloride is removed rapidly from the lower atmosphere.

Table 2.1 Methylene Chloride Emissions from Industrial and Diffuse Sources in the Netherlands

Activity	**Emissions (tonnes/year)**		
	Air	Water	Soil
Chemical industry	1317	15	
Pharmaceutical industry	1065	41	
Electrotechnical industry	385		
Plastic processing industry	341		
Paint industry	192		
Aerosol production	38		
Handling industry	42		
Miscellaneous industry	473	12	
Paint stripping (diffuse)	1890	10	100
Spray cans (diffuse)	1000		
Glue (diffuse)	20		
Total	**6763**	**78**	**100**

Source: Basisdocument 1984

Calculation methods for the impact of methylene chloride on stratospheric ozone depletion show only a very small effect. According to a simplified method for calculation (de Leeuw 1993), the Ozone Depletion Potential of methylene chloride can be calculated to 0.009. The study of Nimitz and Skaggs (1992) indicates an ozone depletion potential of less than 0.001 (i.e. non-zero). The difference in the two values, which is not a result of different lifetime estimates, is only a result of the uncertainties of both calculation methods. An earlier, more in-depth analysis by WMO on behalf of UNEP does not assign an ozone depletion potential to methylene chloride, on the grounds that ODP calculations are inappropriate for substances which do not have an assigned stratospheric lifetime. As a conclusion, no significant impact on stratospheric ozone depletion is expected from methylene chloride (WMO 1991b). However, due to the high emissions of methylene chloride to the atmosphere, it is not possible to exclude completely any danger to the ozone layer.

The principal process by which methylene chloride is scavenged from the atmosphere is by reaction with hydroxyl radicals (OH^*) in the troposphere, and in a series of reactions yielding CO, CO_2 and HCl, with some contribution to greenhouse gas. The contribution of methylene chloride breakdown products, when compared with those occurring from the combustion of fossil fuels, the breakdown of naturally occurring methyl chloride, and salt spray from the sea, is at least two orders of magnitude less (Edwards et al. 1982, Martin and Barber 1978, Gorkham 1958).

Due to its short atmospheric lifetime, there is little potential for methylene chloride to accumulate in the atmosphere. With global emissions in the region of 450,000 tonnes/year, the global background concentration is circa 35 ppt (0.1 µg/m^3) (WMO 1991c, 1991d). For this reason, its global warming potential is small, quoted by the Intergovernmental Panel on Climate Change as 15, relative to carbon dioxide over 100 years, and 5 over 500 years (Houghton et al. 1992).

Methylene chloride is not thought to contribute significantly to ground level ozone formation (US Fed Reg 1980, UK Department of the Environment 1990).

2.1.2 Degradability

Methylene chloride is hydrolytically stable, but is biodegradable under both aerobic and anaerobic conditions. It is not "readily biodegradable" as defined in the OECD Guidelines for the Testing of Chemicals (Japanese Ministry for Technology and Industry 1988), but adapted sewage organisms will degrade it at a high rate (Tabak et al. 1981, Klecka 1982, US EPA 1985). In Japan, according to tests by the government, the average degree of biodegradation (by activated sludge) is estimated to range from 5 to 26 per cent.

The low partitioning coefficient (Log P_{ow}=1.25) indicates a low potential for bioaccumulation. Methylene chloride has been confirmed to be non-accumulative or low-accumulative in tests on fish (Japanese Ministry for Technology and Industry 1988).

2.1.3 Behaviour in the hydrosphere

Methylene chloride enters the hydrosphere either directly, via aqueous effluents, or indirectly from the atmosphere by dissolution in seawater and in rainwater. Due to its high volatility and its low liquid film transfer coefficient, methylene chloride is rapidly transferred from the hydrosphere to the atmosphere. Assuming all rain that falls contains methylene chloride in equilibrium with atmospheric concentrations, annual global washout may be calculated at approximately 400 tpa.

Methylene chloride present in the soil is predicted to evaporate from the near surface layer into the atmosphere because of its high vapour pressure (IPCS 1994).

2.2 Methylene chloride in the atmosphere

Mean global background levels of methylene chloride are circa 0.1 µg/m^3 (National Academy of Sciences 1978, Zafiriou 1975). Measurements of latitudinal distributions of the atmospheric concentration of methylene chloride over the Atlantic between 45°N and 30°S showed that levels increased linearly between the Intertropical Convergence Zone and 45²N, with average mixing ratios of 36 ± 6ppt, and was almost constant in the southern hemisphere with an average of 18 ± 1 ppt (Koppmann 1993). In the ambient air of rural and remote areas, the mean background levels of methylene chloride range from 0.07 to 0.29 µg/m^3. The average concentrations in suburban and urban areas respectively are reported to be <2 µg/m^3 and <15 µg/m^3. Higher levels will be found in the vicinity of manufacturing and waste disposal facilities. Up to 43 µg/m^3 has been found in the vicinity of hazardous waste sites. Some reported levels of methylene chloride in the atmosphere are summarized in **Table 2.2**.

Mean atmospheric levels of methylene chloride at 22 locations across Canada (1991-1992) ranged from 0.5 µg/m^3 in the Longwoods Conservation Area, Ontario, to 9.9 µg/m^3 in Saint John, New Brunswick. The national mean value was approximately 1.7 µg/m^3, with an isolated maximum value of 311.3 µg/m^3 reported for Saint John, New Brunswick (Dann 1992).

Summer and winter levels of methylene chloride were compared for three urban sites in New Jersey by Harkov et al. (1984, as quoted by UK Department of the Environment 1993). Samples were taken 24 hours a day, seven days a week for six weeks in the summer of 1981 and winter of 1981-82. Methylene chloride was detected in 88-98 per cent of the samples. The geometric mean concentrations for the three sites were: summer, 1.2, 0.8, 2.5 µg/m^3; winter, 2.4, 3.1, 4.2 µg/m^3.

In Germany, it is assumed that approximately 85 per cent (22,500 tonnes) of used methylene chloride is emitted to the environment. Taking into account that 5200 tonnes of methylene chloride is primarily emitted to the hydrosphere (see Section 2.3), the discharge to the atmosphere is then estimated to be 17,300 tonnes. Environmental modelling (Mackay Fugacity Level III) gives a concentration of methylene chloride in ambient air of 0.4 µg/m^3.

2.3 Methylene chloride in water

2.3.1 Measured levels in water

Methylene chloride is found in a variety of surface waters, with "typical" background concentrations of 0.05 µg/litre in fresh water and 0.5 µg/litre in urban areas (**Table 2.3**). Background concentrations in the oceans are very low (not detectable or a few ng/litre). Even in polluted areas, concentrations seldom exceed a few µg/litre. Higher concentrations are only found locally in heavily polluted areas, or in connection with accidental spills.

Table 2.4 presents maximum concentrations measured in German rivers in 1988-1990. In 1991 and 1992, methylene chloride was not detected in the Rhine and its tributaries at a detection limit of 1 µg/litre. (Measurements in the Elbe and Weser rivers have not been carried out since 1988.)

Most studies on methylene chloride levels in groundwater have been carried out in the vicinity of industrial sites where it is used or disposed of. The results from a number of studies are presented in **Table 2.5**. These levels are often considerably higher than those found in surface water, and in some cases have persisted for some time after the last identified release. However, in two well-documented cases of accidental release it has been established that methylene chloride disappeared rapidly from groundwater channels, but not by drainage to deeper groundwater stocks. Methylene chloride was detected in only a small area of contamination and not beyond. In these two incidents (spills at Grenzach-Wylen and Heidelberg-Westadt), methylene chloride was detected only in small, narrowly defined pollution zones in concentrations of 802 mg/m^3 and 269,000 mg/m^3 respectively. In both cases, at well locations at a distance of 100 metres it was not possible to detect methylene chloride (Baldauf 1981, Leitfaden 1983, both as quoted by BUA 1986).

Methylene chloride enters the aquatic environment primarily through wastewater discharges. Wastewater from certain industries has been reported to contain methylene chloride at average concentrations in excess of 1000 µg/litre, these being coal mining, aluminium forming, photographic equipment and supplies, pharmaceutical manufacture, organic chemicals/plastics manufacture, paints and ink formulation, rubber processing, foundries and laundries (IPCS 1994).

In the US EPA STORET database on industrial effluents, 38.8 per cent of the samples recorded contained methylene chloride with a median concentration of 10,000 µg/litre (Staples et al. 1985, as quoted by IPCS 1994).

According to a survey of the Environment Agency, Japan, industrial effluents in that country contained methylene chloride at 48 factories in 13 industrial sectors, among 196 factories in 25 sectors, at a level of 0.01-9.0 mg/litre depending on the sector (Japanese Environment Agency, 1993).

Samples from the outfalls of four municipal treatment plants in southern California with both primary and secondary treatment contained <10 to 400 µg/litre methylene chloride (Young et al. 1983, as quoted by IPCS 1994).

2.3.2 Estimated levels in water

The exposure of the hydrosphere in Germany has been estimated as follows: In 1992, the total consumption of methylene chloride was 26,000 tonnes (this figure also includes approximately 2000 tonnes of recycled methylene chloride). It is assumed that 4200 tonnes (approximately 70 per cent of 6000 tonnes) from washing and cleansing agents, plus 1000 tonnes (approximately 5 per cent of 20,000 tonnes) from other uses, are discharged to the hydrosphere. Environmental modelling (Mackay Fugacity Model Level III) gives a concentration of 1.6 µg/litre.

The concentration in surface waters can be estimated on the basis of the wastewater regulation. According to this regulation, the discharge of certain industries must not exceed a maximum value of 0.1 mg/litre highly volatile chlorinated hydrocarbons. Assuming a worst-case scenario, the methylene chloride concentration in surface waters can be estimated to be 0.6 µg/litre.

Another starting point for estimating concentration in surface waters is to consider consumer products. Assuming that 25 per cent of methylene chloride in washing and cleaning agents is used in households, approximately 1050 tonnes will end up in municipal wastewater. The concentration of methylene chloride after passage through a wastewater treatment plant (elimination calculated according to SIMPLE TREAT) and dilution in surface waters is 4.1 µg/litre (Umweltbundesamt 1994).

Table 2.2 Levels of Methylene Chloride in the Atmosphere

Location	Concentration ($\mu g/m^3$)	Notes	Ref.
Wiltshire, UK	mean: 0.1	Dec/Jan 1974-5; 13 samples	a
Northern Italy	mean: <16 range: <5-100	samples from outside 14 houses and 1 office block	b
Netherlands	mean: 1.4-14 max: 8.5-42	3 sites: background, suburban, near sources; 1979-81	c
Arctic: clear air haze	mean: 0.08 mean: 0.11	spring 1984; 30 samples from aircraft	d
Norwegian Arctic (Spitzbergen)	mean: 0.26 mean: 0.29	July 1982 March 1983	e
California	mean: 7.2	mean of means, max. mean 20 $\mu g/m^3$	f
US: rural & remote urban & suburban source-dominated	median: 45 median: 630 median: 270	summary data 1970-80; 5 rural values, 718 sub/urban, 127 source-dominated	g
US landfills	mean: 3200 max: 42,000	survey of levels in gases from landfills	h
Japan: 1979 1980 1981	0.25-5.3 0.30-2.8 0.01-19.8	25 of 46 samples positive 47 of 135 samples positive 99 of 101 samples positive	i
Northern hemisphere Southern hemisphere	mean: 0.13 mean: 0.07	December 1981 December 1981	j

References:

a) Cox et al. (1976)
b) de Bertoli et al. (1984)
c) Guicherit and Schulting (1985)
d) Khalil and Rasmussen (1984)
e) Hov et al. (1984)
f) Hunt et al. (1986)
g) Brodzinsky and Singh (1983)
h) Vogt and Walsh (1985)
i) Japan OHS (1991)
j) Singh et al. (1983a)

Source: UK Department of the Environment 1993

Table 2.3 Levels of Methylene Chloride in Surface Waters

Location	Concentration (µg/l)	Reference
Rhine:		CEFIC (1986)
near Koblenz	5.35-171	
length profile	2-5	
at Lobith	1	
near Dutch border	5	
near Dutch border	1.0	
Rhine tributaries:		
Main at Kostheim	<1	
Ruhr at Mulheim	ND	
Ruhr at Duisberg	<1	
Mosel	1.5-2.0	
Neckar	0.6-1.0	
Elbe	0.7-2.1	
Rhine, Netherlands:		COST 64b (1984)
Maasluis, 1978	3-0	
Maasluis, 1979	3-10	
Lobith, 1978	10-30	
Lobith, 1979	3-10	
Niagara River	ND-0.045	Kaiser et al. (1983)
Lake Ontario: range	ND-4.6	
mean	0.57	

Source: UK Department of the Environment 1993

Table 2.4 Maximum Concentrations of Methylene Chloride in German Rivers 1988-1990 (µg/litre)

Location	**1988**	**1989**	**1990**
Weser (Nordenhan)	6		
Elbe (Schnackenburg)	11*		
Emscher (Mündung)	8.5	2.5	3.9
Lippe (Wesel)	5.5	<1	2.4*
Rhine (Kleve-Bimmen)	3.3	1.0	1.1*
Rhine (Götterswickerhamm)		1.0	3.9*
Wupper (Leverkusen)	2.3	21**	3.0

* *90th percentile value*
** *maximum value: the 90th percentile value was 13.6 µg/litre*

Source: Umweltbundesamt, 1994

Table 2.5 Levels of Methylene Chloride in Groundwater Near Industrial Sites

Location	(µg/litre)	Notes	Ref.
Below landfill site, Canada	4-60	6/37 samples + ve; site used until 1980, sampled in 1988	a
Below solvent recovery facility, Connecticut	100,000 7000 25 3900	on site, at WT (Water Table) on site, below WT 80 m downgrade, at WT 80 m downgrade, below WT	b
Below solvent recovery facility, Wisconsin	230,000 170,000 ND 20,000	on site, at WT on site, below WT 80 m downgrade, at WT 80 m downgrade, below WT	b
20 landfills, 2 dumps, US	64-1300 1.0-250 2.1-3.9	leachate, 4/6 samples + ve groundwater contamination expected, 7/13 samples + ve unknown/clean groundwater, 1/7 + ve	c
Groundwater wells near Tennessee waste site	1.5-160 median 45	detected in all samples; closed 1972, sampled 1978	d
Below metalworking plant, Hamburg	≤17,000		e
Sand pit, chemical and domestic waste dump, New Hampshire	≤299,000	Site use ended 1979, groundwater sampled 1982	f
Disposal site, Gloucester, Ontario	10,400 (mean 1081)		g
Disposal site, Toronto, Ontario	25,000,000	ruptured underground storage tank 1971, sampled 1987	h
Leachate from landfill site, Guelph, Ontario	131 1008	1988 1989	i

References: *ve = vapour extraction*

a) Lesage et al. (1990)
b) Cline and Viste (1985)
c) Sabel and Clark (1984)
d) Harris et al. (1984)
e) Weidner (1985)
f) McGarry and Lamarre (1985)
g) Jackson et al. (1985)
h) Ladanowski et al. (1993)
i) Lesage et al. (1989)

Source: UK Department of the Environment, Environment Canada 1993

2.4 Methylene chloride in soil and sediment

Background data on the contamination of groundwater by methylene chloride are limited. It is the sixth most frequently detected organic contaminant in groundwater at hazardous waste disposal sites in the CERCLA database (178 sites), with a detection frequency of 19 per cent. In contaminated groundwater in the state of Minnesota in the United States, up to 250 µg/litre methylene chloride has been detected. Levels of up to 110 µg/litre methylene chloride were found in percolation water from a waste disposal site in Germany. However, methylene chloride was not found in the groundwater below the site (IPCS 1994).

Data recorded in the US EPA STORET database revealed a median concentration of 13 µg/litre in 20 per cent of 335 sediment sampling data (IPCS 1994).

CHAPTER 3

EXPOSURE

3.1 Introduction

The main route of human exposure is through vapour inhalation, sometimes accompanied by direct skin and eye contact, primarily through methylene chloride or methylene chloride-containing products in occupational or consumer uses. Much lower levels of human exposure can occur through inhalation of methylene chloride in ambient air and through its ingestion via drinking water, food and beverages.

Some monitored levels of methylene chloride exposure in occupational and consumer uses are summarized in this chapter. Exposures from food, drinking water and beverages are summarized in Section 3.4 on exposure of the general population. Studies of levels of methylene chloride in ambient air have been reported in Chapter 2.

3.2 Occupational exposure

Almost all industrial activities in which methylene chloride is used present opportunities for exposure. Exposures range widely, depending on the particular operation, the risk reduction measures in use, and the existing mandatory occupational exposure limits. **Table 3.1** presents measured exposures by industry and activity. These figures are shown as 8-hour time weighted averages.

3.2.1 Production

The production of methylene chloride is normally carried out in closed system plants. A relatively small number of people are involved. Exposure arises primarily during filling and packing. Experience indicates that the application of sound and well recognized engineering control techniques will bring 8-hour TWA exposures well below 100 ppm (353 mg/m^3) (ICI 1984, 1992, UK HSE 1987, US NIOSH 1980).

3.2.2 Paint removal operations

Occupational exposures occur in the following industrial sectors: formulation of paint removers, original equipment manufacture, and maintenance and commercial furniture refinishing (US EPA 1990).

Formulators are exposed while transferring methylene chloride from storage tanks, and during mixing (blending) operations and packaging. The extent of exposure will depend on the control measures, work practices in force, and the occupational exposure limits. Exposures (8-hour TWA) range from a low of 0-5 ppm (0-186 mg/m^3) to over 500 ppm (1765 mg/m^3), yielding an average of 42 ppm (US EPA 1990).

Paint strippers are widely used in a number of original equipment manufacturing industries: automotive, rubber products, furniture and fixtures, plastics and electronics. Exposure to methylene chloride takes place during application, removal of the substrate soaked in methylene chloride, and disposal of the spent paint remover. Typical exposures range from 5 ppm (18 mg/m^3) to about 500 ppm (1765 mg/m^3), 8-hour TWA. Average direct exposure is an estimated 71 ppm (250 mg/m^3) (US EPA 1990).

In the maintenance sector, workers are exposed to methylene chloride during application, stripping, cleaning and drying. Exposure levels range from 0-5 (0-18 mg/m^3) to 500 ppm (1765 mg/m^3) TWA, the average level being 60 ppm (212 mg/m^3) (US EPA 1990). Activities such as loading, cleaning, waste disposal, and maintenance of dipping tanks present occasional high exposures. The application of vapour retarders reduces exposure.

Owing to problems of size and shape, removal of paint from aircraft and ships is difficult to control. Exposure levels are influenced by a number of factors, including the method of application, temperature, and work area.

Commercial furniture stripping involves either dipping the furniture into a tank containing a mixture of solvents including methylene chloride (typically 65 per cent) or coating it manually with a brush, both of which present ample opportunities for uptake by the dermal route. The solvent causes the paint layer to soften and blister. Normally, hand scrapers or hard brushes are used to remove the softened layers. With regard to methylene chloride exposure, furniture refinishing operations present a unique problem. Exposure levels are highly variable and greatly influenced by the size of the installation, the engineering controls in place, and work practices.

Some refinishers may operate on a part-time basis and/or from their homes. In some instances, concentrations over 2000 ppm (7000 mg/m^3) have been recorded, with an average exposure of 141 ppm (498 mg/m^3) on a TWA basis (US NIOSH, NEDB 1992, McCammon et al. 1991). This kind of exposure takes place in situations where the stripper is leaning over the tank and using a brush (causing agitation of the stripping liquor) to scrub the surface coating. However, exposure levels have been reduced to below 30 ppm (106 mg/m^3) (Fairfield and Beasley 1991) by using simple and well recognized techniques.

3.2.3 Aerosols

The assembling of aerosol cans basically consists of product filling, insertion of valve stem and valve, propellent charging, and sealing the product in the can. Exposure arises primarily during filling and packing. Levels observed are generally below 50 ppm (176 mg/m^3) (ECSA 1989). Exposure may also occur as a result of skin contact with liquid methylene chloride. Potential occupational exposure to methylene chloride as a result of the use of aerosol products varies, according to the use and the work undertaken (**Table 3.2**).

Table 3.1 Measured Occupational Exposure Levels of Methylene Chloride[1]

Industry	Activity	Exposure range (8-hr TWA) PPM (mg/m^3)	Reference	Comments
Production	Production activities	62-106 (219-374)	HSE (1987)	Maintenance activity with RPE
	Process plant	0.1-110 (0.35-389)	ICI (UK) (1984, 1992)	Communications to HSE (UK)
		5-25 (18-88)	NIOSH (1980)	Results obtained at one plant
Pharmaceutical	NA	2-1062 (7-3750)	Zahm et al. (1987)	NCI feasibility study
	Production work	0-5 ppm (0-18)	NEDB (UK)	Enclosed process
	NA	<35 (<123)	Astra, Sweden	Personal communication
	NA	0-17 (0-60)	JAHCS (1994)	Questionnaire survey
Glass Reinforced Plastic (GRP) manufacture	Cleaning and mould preparation	53-1896 (187-6693)	NEDB (UK)	Intermittent exposure, RPE may be worn; may not be representative of the industry
	Cleaning, mixing, etc.	0-100 (0-353)	Post et al. (1991)	Small factory units
Packaged products	Aerosol filling	27-178 (95-628)	ICI (UK) 1984	
Aircraft	Paint stripping	10-23 (35-81)	NEDB (UK)	RPE provided
	Paint stripping	10-82 (35-289)	Air Transport Association (US)	Submission to OSHA in 1987; RPE provided

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[1] For an explanation of the abbreviations used in Tables 3.1 and 3.2, see page 49.

Industry	Activity	Exposure range (8-hr TWA) PPM (mg/m^3)	Reference	Comments
Printing	NA	1-158 (3.5-558)	Zahm et al. (1987)	NCI feasibility study
Hairdressing salon	Hairspray application	1-19 (3.5-67)	Harris (1985)	Various types of products were tested
		<10 (<35)	NEDB (UK)	General ventilation
		1-2 (3.5-7)	Hoffman (1973)	
Decorative-industrial	Painting, maintenance	6-65 (21-229)	Chrostek and Levine (1981)	See IARC 41
	Paint stripping	5-500 (18-1765)	EPA (1990)	
	Used aerosol adhesives	<0-140 (0-494)	Fleeger and Lee (1988)	Some work areas are congested
Rubber products	Fabrication	59-86 (208-303)	NEDB (UK)	LEV
Triacetate fibre/ film manufacturing	Production	50-100 (176-353)	ECSA 1989 (CEFIC)	NCI feasibility study
		67-975 (236-344)	Zahm et al. (1987)	
		50-690 (176-2436)	Ott et al. (1983)	Products contain acetone
		20-67 (71-237)	JAHCS (1994)	Questionnaire survey

Industry	Activity	Exposure range (8-hr TWA) PPM (mg/m^3)	Reference	Comments
Furniture	Paint stripping	7-1080 (25-3812)	NEDB (UK)	Many without adequate controls
	Paint stripping	57-366 (201-1292)	McCammon et al. (1991)	Variable degrees of control
	Paint stripping	13-27 (46-95)	NIOSH (1991)	Well controlled with appropriate LEV
	Washing/refinishing	15-221 (53-780)	McCammon et al. (1991)	Variable degrees of control
	Spraying adhesive	62-422 (219-1490)	NEDB (UK)	Many without adequate controls
General manufacturing, cleaning and degreasing	Cleaning, degreasing, etc.	50-630 (176-2224)	Lee (1980)	See IARC 41
	Degreasing	15-40 (53-141)	Ruhe et al. (1981)	See IARC 41
		<0-130 (0-459)	Ruhe et al. (1982)	See IARC 41
		3-80 (11-282)	JAHCS (1994)	Questionnaire survey

Industry	Activity	Exposure range (8-hr TWA) PPM (mg/m^3)	Reference	Comments
Foam	Glue spraying	24-69 (85-243)	NEDB (UK)	LEV
	Moulding	25-310 (88-1094)	NEDB (UK)	High exposure due to insufficient/inadequate LEV
	NA	<70 (<247)	Jernelöv and Antonsson (1987)	In Swedish
	Various jobs	2-71 (7-251)	Zahm et al. (1987)	NCI feasibility study
	Polyurethane foam	5-165 (18-582)	Boeniger (1991)	High exposure experienced by sprayers
		3-30 (11-106)	JAHCS (1994)	Questionnaire survey
Motor vehicle manufacture	Spray painting, stripping	2-70 (7-247)	NEDB (UK)	LEV and RPE
Quarrying	Laboratory work-mineral processing	20-388 (71-1370)	NEDB (UK)	High exposure due to inadequate control
Metal treatment		2-224 (7-791)	Zahm et al.	NCI feasibility study
Food industry (nutrition)	Extraction	<0-30 (0-106)	Cohen et al. (1980)	See IARC 41

Table 3.2 Measured Consumer Exposure Levels of Methylene Chloride

Use	Activity	Peak exposure PPM	Average exposure PPM (mg/m^3)	Duration of average exposure	Reference	Comments
Aerosols	Hairdressing (salon, occ.)	6-30	1-5 (3.5-18)	8 hrs	CEC Scientific Comm. of Cosmetology	
	Hairdressing (home)	75	0.75 (2.6)	8 hrs		
	Hairdressing (salon, occ.)		22 (78)	8 hrs	ICI (pers. comm.)	Simulated worst-case exposures (heavy use)
	Hairdressing (salon, cons.)		30-75 (106-265)	10 min		
	Hairdressing (home)		100 (2) (353)	10 min (8 hrs)		Small unventilated room
	Hairdressing (salon, occ.)		1-19 (3.5-67)	8 hrs	Harris (1985)	Various types of products
	Hairdressing (salon, occ.)		<0 (0)	8 hrs	NEDB, HSE (UK)	General ventilation
	Hairdressing (salon, occ.)		1-2 (3.5-7)	8 hrs	Hoffman (1973)	
	Various aerosol products	500	102 (360)	10 min	Dow (1975)	Small, unvent. room, heavy use
	Paint spray aerosols	900	10 (35)	8 hrs	Dow (1978)	Unventilated room, heavy use
	Adhesive aerosols (occ.)		0-140 (0-494)	8 hrs	Fleeger and Lee (1988)	

Use	Activity	Peak exposure PPM	Average exposure PPM (mg/m^3)	Duration of average exposure	Reference	Comments
Paint strippers	Household solvent products	6000	5-500 (18-1765)	8 hrs	US EPA (1990)	A window or door open
	Indoor use	210-2025			Miljøstyrelsen (1988)	General ventilation
	Furniture stripping (consumer)	400	82 (289)	2 hrs	ICI (1988)	Through ventilation
	Consumer use	5000			ICI (1990)	No ventilation, simulated worst case
		<1000	53-64 (187-226)	5 hrs		With ventilation
		100-400				Room background during stripping
		20	45-75	1h 25 min		Room background after 5-6 min.
Painting, maintenance	Occupational exposure		6-65 (21-229)	8 hrs	Chrostek and Levine (1981)	See IARC 41

Abbreviations used in Tables 3.1 and 3.2:

CEFIC	European Chemical Industry Federation
Cons.	Consumer
ECSA	European Chlorinated Solvents Association
EPA	Environmental Protection Agency (US)
HSE	Health and Safety Executive (UK)
IARC 41	International Agency for Research on Cancer Monographs, No. 41 (1986)
ICI	Imperial Chemical Industries (UK)
JAHCS	Japanese Association for Hygiene of Chlorinated Solvents
LEV	Local Exhaust Ventilation
NA	Not Available
NCI	National Cancer Institute (US)
NEDB	National Exposure Database (Health and Safety Executive, UK)
NIOSH	National Institute for Occupational Safety and Health (US)
Occ.	Occupational
OSHA	Occupational Safety and Health Administration (US)
PPM	Parts Per Million
RPE	Respiratory Protective Equipment

3.2.4 Process solvent application

3.2.4.1 Cellulose triacetate fibre and film

Methylene chloride is widely used as a process solvent in the manufacture of a variety of products. Most of the processes are carried out in closed systems. Exposure levels are normally low, but occasional high exposures [>100 ppm (353 mg/m^3), 10-minute TWA] may occur during specific operations, such as filter change, charging and discharging. Some industrial processes involve somewhat higher exposure levels.

The manufacture of cellulose triacetate fibres and films can involve exposures of up to 100 ppm (353 mg/m^3) 8-hour TWA, even when good engineering controls are installed (ECSA 1989, Zahm et al. 1987, Ott et al. 1983). Without good engineering controls, exposure levels can reach about 500 ppm (1765 mg/m^3).

The process is often carried out in closed systems, so that occupational exposure during normal plant operations can be controlled within occupational exposure standards (ICI pers. comm.).

3.2.4.2 Pharmaceutical and food production industries

In the pharmaceutical industry, methylene chloride is used as a solvent and extraction medium. Sealed processes, high recovery rates and careful handling of discharges have helped to keep the exposures to around 30 ppm (106 mg/m^3). The solvent is recycled and occasionally distilled in a closed process. Residues are incinerated (incinerator for special waste) (Astra 1991, Zahm et al. 1987, NEDB 1992).

Methylene chloride is also used as an extraction medium in the food production industry. As in the pharmaceutical industry, the processes are sealed and exposure levels are generally low.

3.2.5 Polyurethane

When methylene chloride is used as an auxiliary blowing agent, it is vaporized by the heat of reaction. The gas generated expands the foam to the required density and modifies the physical properties, such as resilience and softness. Methylene chloride is therefore emitted continually throughout the foam production. Approximately 50 per cent is emitted between the start of the process and the cutting saw, which sections the continuously produced foam into blocks. Fifty per cent is emitted in the cure hall, where the foam is left for 24 hours in order to allow the reaction to be completed and the blowing agent to gas off.

The production line in a PU plant may be totally enclosed up to the cut-off saw and highly ventilated. Exposure to methylene chloride in the cure hall may be high. Exposures ranging from a few ppm to short-term exposures of over 500 ppm (1765 mg/m^3) have been reported (Jernelöv and Antonsson 1987, Boeniger 1991, NEDB 1992). Experience has shown that levels below 100 ppm (353 mg/m^3) 8-hour TWA are achievable (ICI pers. comm. 1993).

3.2.6 Cleaning and degreasing

The degree of exposure will be influenced by many factors, including the age of the equipment, type of engineering controls available, their maintenance, and the operational methods used. Open tanks without good ventilation can contribute to extremely high exposures and heavy losses of the solvent.

Modern equipment with cooling coils, mechanical handling and ventilation (with solvent recovery units) will help to reduce exposures and solvent loss substantially. In general, it is possible to reduce exposures to below 35 ppm (123 mg/m^3) (Swedish National Board of Occupational Safety and Health, pers. comm.).

3.2.7 Miscellaneous uses

Methylene chloride is used as a solvent in the formulation of rubber, "plastic" and moisture cure polyurethanes. Occupational exposures during the application of adhesives can be in excess of 100 ppm (353 mg/m^3), particularly in small companies (Fleeger and Lee 1988, NEDB 1992). The use of adhesives causes variable exposures. Simple control techniques similar to those used in occupational paint stripping applications will reduce exposures. Processes involving the formulation of adhesives are likely to be well controlled.

Methylene chloride is used as a solvent in the analysis of bitumen samples. The work is normally carried out in small laboratories, and exposure levels will be high unless adequate inexpensive measures are put into operation.

3.3 Consumer exposure

Consumer exposure to methylene chloride generally falls into two categories: exposure to aerosols, and exposure to paint strippers. For the purposes of this document, the term *consumer exposure* also includes the exposure of those in a work environment who use consumer products, for example personal care products in hair salons. Table 3.2 shows exposure readings for a variety of activities. Consumer use exposures are presented either as 8-hour or 10-minute time weighted averages. Consumer exposures are often short in duration. Therefore the 8-hour TWA exposure level may not always give relevant information on the exposure. No cases of volatile substance abuse involving methylene chloride-based consumer products appear to have been reported.

3.3.1 Aerosols

3.3.1.1 Personal care aerosols

In the Netherlands, peak concentrations in salons of 6-30 ppm (20-106 mg/m^3) have been measured, with an 8-hour TWA of 1-5 ppm (3-18 mg/m^3) (CEC Scientific Committee of Cosmetology). The same study measured a peak concentration of 75 ppm (265 mg/m^3) arising from home use of a hairdressing aerosol containing 35 per cent methylene chloride. This equates to a time weighted average of 0.75 ppm. Other studies that measured levels in salons have shown them to be of the same magnitude (Harris 1985, NEDB UK, Hoffman 1973).

Studies in the United Kingdom simulating consumer exposure during salon use showed figures well within the national Maximum Exposure Limit [100 ppm (353 mg/m^3) for an 8-hour TWA]. The hairdresser was exposed to 22 ppm (78 mg/m^3) on an 8-hour TWA despite what is seen as exceptionally heavy use, i.e. ten seconds of spray every 15 minutes during an eight-hour period. The customer exposure was measured at 30-75 ppm (106-265 mg/m^3), 10-minute TWA (ICI pers. comm.). The same study simulated home use of personal care aerosols containing methylene chloride. Even adverse conditions (small room, no ventilation) resulted in an exposure of 100 ppm (353 mg/m^3) on a 10-minute TWA, equating to 2 ppm (7 mg/m^3) on an 8-hour TWA (ICI pers. comm.). This work is characterized by low air changes, virtually no ventilation, and a more frequent rate of application than that determined by surveys of actual hairdressing work in salons.

Another study reported using three different aerosol products for over 15 minutes in a small, unventilated room. This study involved spraying with an air freshener, a deodorant and a hairspray aerosol, representing a worst-case scenario for these products. Peak methylene chloride concentrations of around 500 ppm (1765 mg/m^3) were measured, with an average 15-minute TWA of 102 ppm (360 mg/m^3) (Dow Chemical USA 1975).

Consumer exposures to aerosol formulations may involve high peak exposures. But as the use of these products is generally very short in duration, the total exposure is considered to be low.

3.3.1.2 Paint spray aerosols

The use of paint spray aerosols involves much longer spraying times, leading to higher exposures. Exposures have been measured following simulated heavy use by consumers of paint aerosols containing 30 per cent methylene chloride in a test room ventilated only after spraying (Stevenson et al. 1978). Peak methylene chloride concentrations of up to 900 ppm (3177 mg/m^3) were measured, equating to an 8-hour TWA of 10 ppm (35 mg/m^3).

3.3.2 Paint strippers

Paint strippers containing methylene chloride are used to refinish furniture and woodwork. Formulations are mainly available in liquid form, but also occasionally in an aerosol. Use conditions vary considerably. Most consumers leave a window or door open to the outside when using solvent-based products, but they rarely operate an exhaust fan (US EPA 1987). The mean time spent using paint strippers has been estimated at 125 minutes per occasion, although the frequency of use tends to be extremely low. It should be noted that paint strippers for consumer use are usually specially formulated with various evaporation retarders. These produce self-skinning surfaces, an effect which substantially reduces the rate of evaporation of the methylene chloride. It is of value to note, however, that a relatively short-term release (three to six minutes) of up to 1000 ppm of methylene chloride may be observed once the self-skinning surface is disturbed during removal of the stripper (ICI 1990, Girman and Hodgson 1986; also see **Figures 3.1 to 3.3**).

Exposures have been estimated on the basis of US investigations of household solvent products (US EPA 1990). The estimated levels ranged from less than 10 ppm (35 mg/m^3) to a few short-term exposures of 4000 to 6000 ppm (14,000-21,000 mg/m^3). The majority of the concentration estimates were below 500 ppm. A Danish study reported concentrations of methylene chloride in the breathing zone ranging from 210 ppm (741 mg/m^3) to 2025 ppm (7148 mg/m^3) when liquid paint strippers were used indoors (Miljøstyrelsen 1988).

In the United Kingdom, industry has carried out a number of experiments simulating paint stripping of furniture and household fittings (standard size doors) using methylene chloride-based strippers. Two series of experiments were made under different conditions of unassisted ventilation in a room of 63 m^2.

With no ventilation and the doors and windows closed, use of a paint stripper resulted in a rapid rise in methylene chloride concentration to 4000-5000 ppm (14,000-17,600 mg/m^3). No one should ever strip paint without proper ventilation (Figure 3.1). It is very rare that people would attempt to work under these conditions. Further experiments were carried out with the door and windows open following the paint stripper manufacturer’s instructions for use (Figure 3.2). Different types of formulations were tested with similar methods of use.

Personal exposure during each operation (1 h 25 min) was from 45 to 75 ppm TWA. Peak exposures varied from 300 ppm to 1000 ppm, but were of only a few minutes’ duration during application and scraping off. Personal exposure over five hours was 53-64 ppm TWA. The second series of experiments were carried out under conditions of natural ventilation, with internal wind speeds in the room of 0.1-0.6 m/s. Average personal exposures ranged from

45 to 66 ppm TWA for operations of from 38 to 52 minutes' duration (Figure 3.3) Peak exposures of 450-550 ppm over a few minutes were measured (ICI 1990).

No one should ever strip paint without proper ventilation (US Consumer Product Safety Commission pers. comm.)

3.4 Exposure of the general population

Studies of ambient air levels of methylene chloride have been referred to in Chapter 2.

In buildings where products containing methylene chloride are used, air levels much higher than those out of doors (>15 µg/m^3) may be found. Indoor air levels of methylene chloride measured in children's rooms in clear air regions and urban areas in 1991 in Germany ranged from 18 to 45 µg/m^3. Relatively high levels [mean 670 µg/m^3 (190 ppb), peak level 5000 µg/m^3] of methylene chloride have been found in the indoor air of residential houses (De Bertoli et al. 1988, as quoted by IPCS 1994). In a TEAM study conducted in Los Angeles in 1987, the 24-hour average exposure to methylene chloride of about 750 persons in six urban areas was 6 µg/m^3 (1.7 ppb).

Methylene chloride has been detected in drinking water supplies [estimations made before (1980) in numerous US cities (Dowty et al. 1975, Coleman et al. 1976, Kopfler et al. 1977, Kool et al. 1982), all as quoted by IPCS 1994]. The mean concentrations reported were generally less than 1 µg/litre (1 ppb). An average of 3-10 µg/litre and a maximum of 50 µg/litre were observed in a Canadian study of 30 potable water treatment facilities (Otson et al. 1982, as quoted by IPCS 1994).

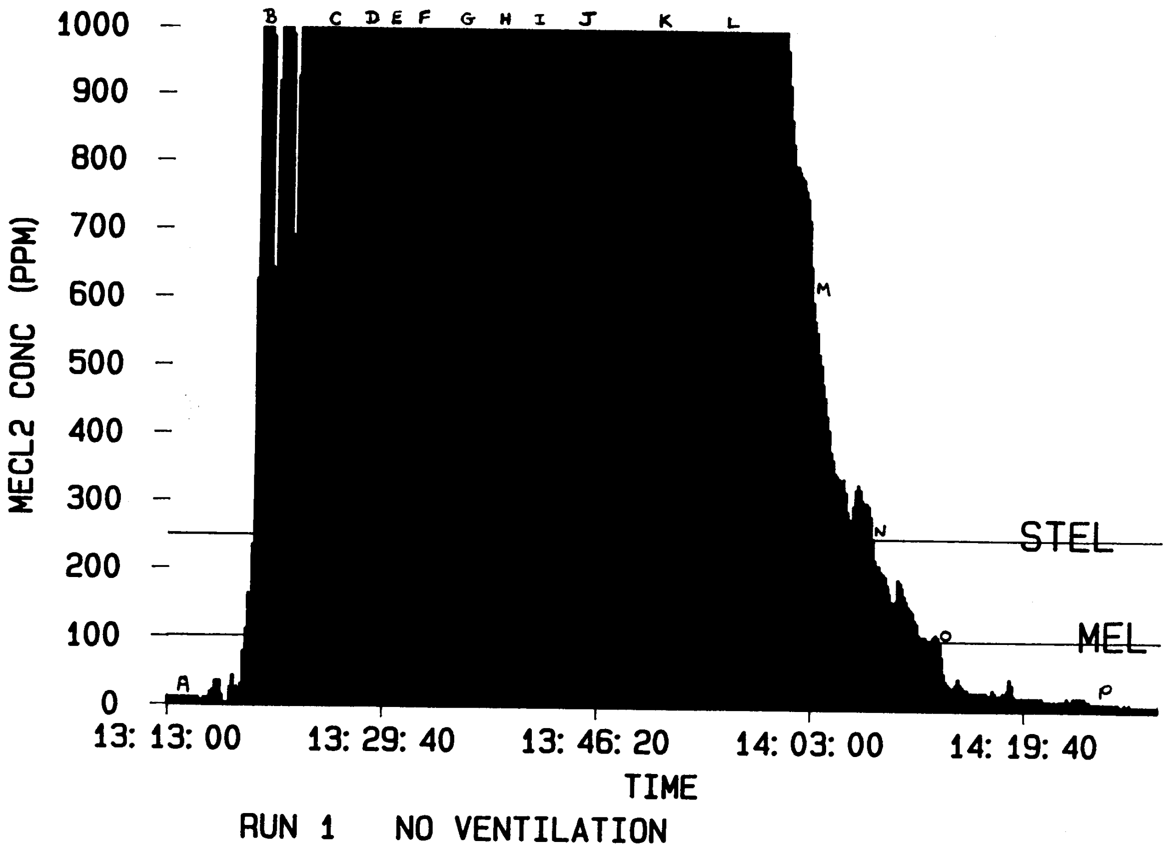
Samples from 128 US drinking water wells showed that 3.1 per cent of them had levels of 1-5 µg/litre (1-5 ppb) methylene chloride (Kelley 1985, as quoted by IPCS 1994).

Heikes (1987) has investigated levels of methylene chloride in table-ready foods, taken from the US Food and Drug Administration's Total Diet Study. Nineteen foods were examined, of which eight contained methylene chloride above the quantitization limit (not given). Detailed results for six of the foods are presented in **Table 3.3**.

No methylene chloride was detected in ice cream and yoghurt (Baner et al. 1981, as quoted by IPCS 1994).

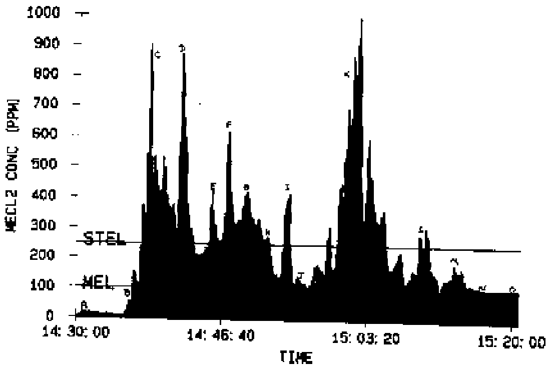
In seven types of decaffeinated ground coffee, the methylene chloride content ranged from <0.05 to 4.04 mg/kg. In eight instant coffee samples, <0.05-0.91 mg/kg methylene chloride was found (Page and Charbonneau 1984, as quoted by IPCS 1994).

Figure 3.1 Concentration of Methylene Chloride during Simulated Consumer Paint Stripping Operations, without Ventilation

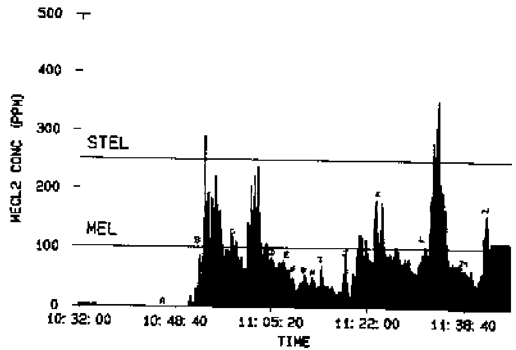


Source: ICI 1990

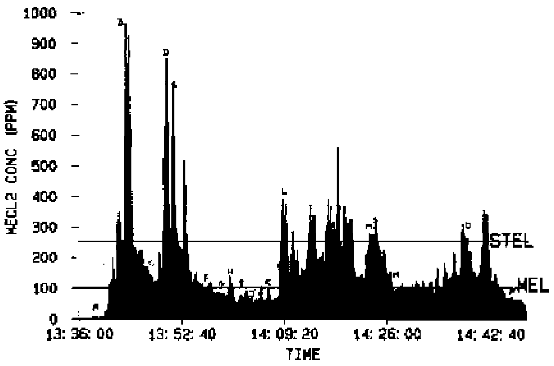
Figure 3.2 Concentration of Methylene Chloride during Simulated Consumer Paint Stripping Operations, with Doors and Windows Open



RUN 2 DOOR & WINDOWS OPEN



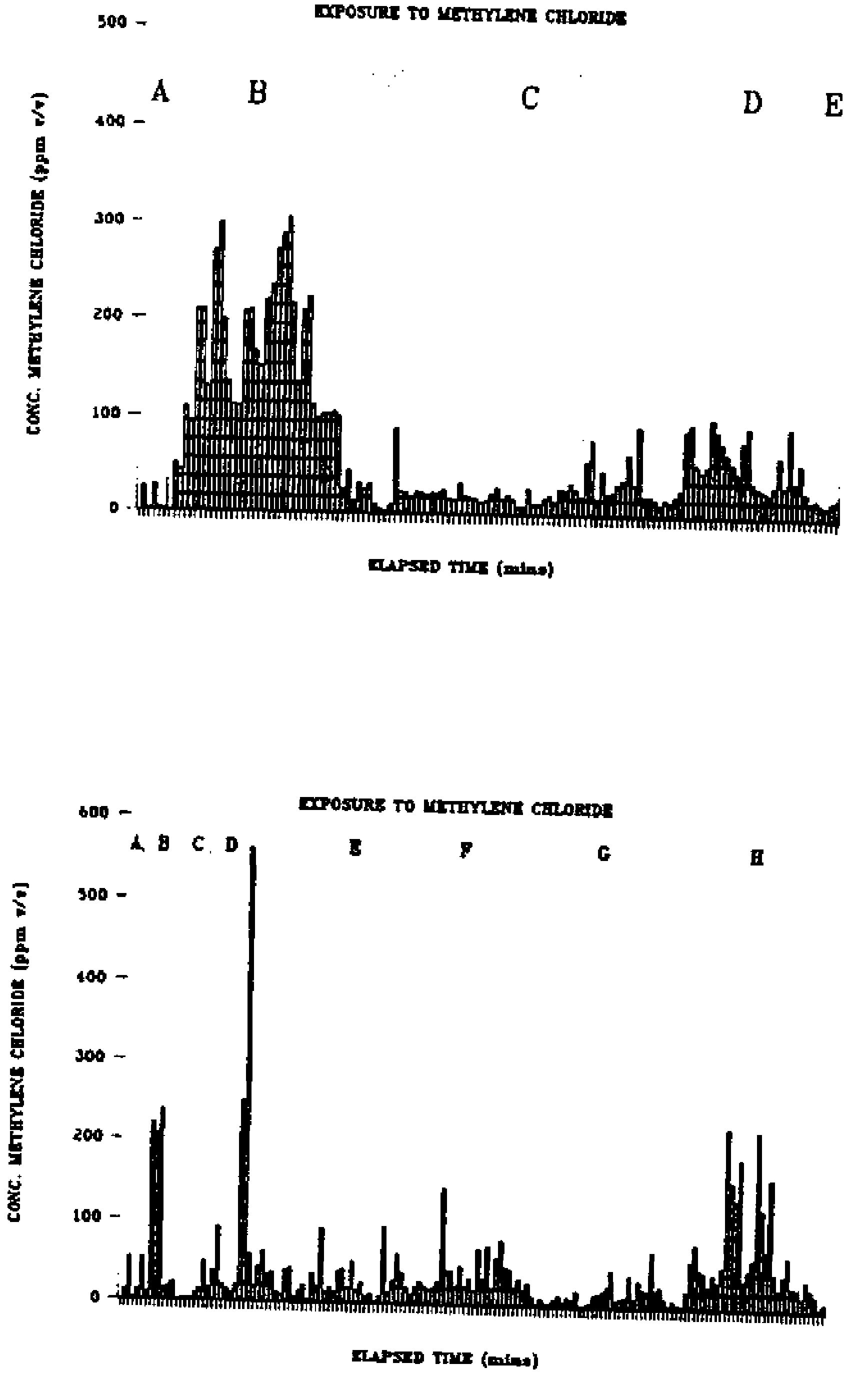
RUN 3 DOOR & WINDOWS OPEN WW



RUN 4 DOOR & WINDOWS OPEN WW

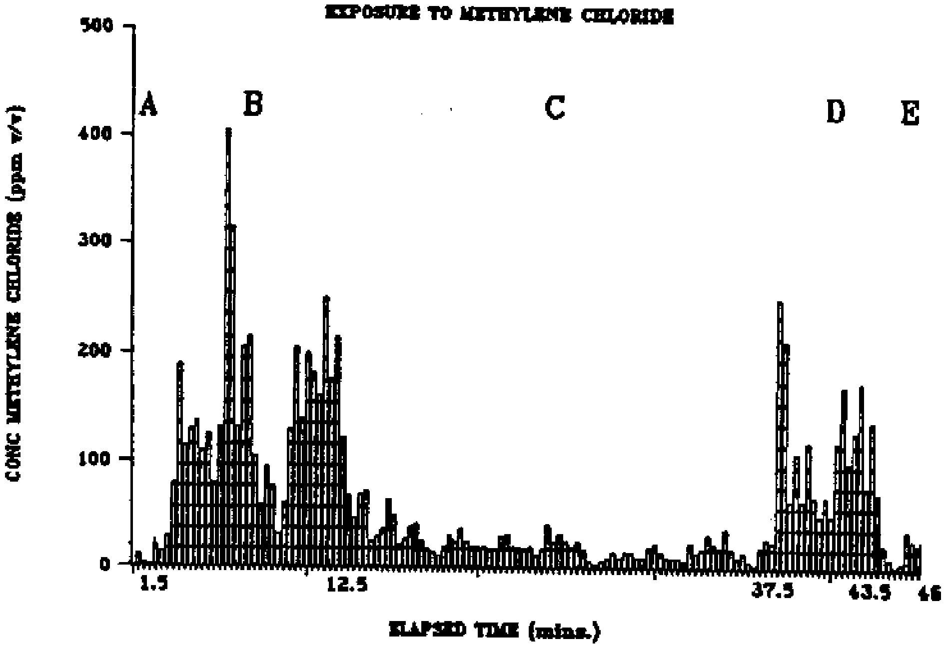
Source: ICI 1990

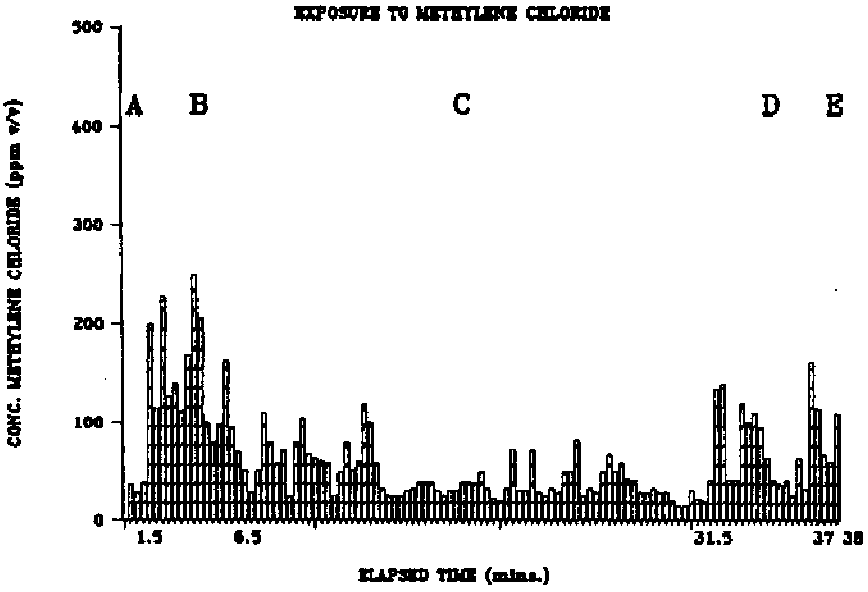
Figure 3.3 Concentration of Methylene Chloride during Simulated Consumer Paint Stripping Operations, with an Airflow of 0.1-0.4 m/s



Source: ICI 1990

Figure 3.3 (Continued)





Source: ICI 1990

Table 3.3 Methylene Chloride Content of Table-ready Foods

Food	**Number of samples**	**Number positive**	**Range of concentration (µg/kg)**
Butter	7	7	1.1-280
Margarine	7	7	1.2-81
Ready-to-eat cereal	11	10	1.6-300
Cheese	8	8	3.9-98
Peanut butter	7	4	26-49
Highly processed foods*	12	10	5-310

** For example, frozen chicken dinners, fish sticks, pot pies*

Source: Heikes 1987

CHAPTER 4

INTERNATIONAL AND NATIONAL POSITIONS ON THE RISKS FROM METHYLENE CHLORIDE

This chapter presents an evaluation, from the International Programme on Chemical Safety (IPCS), of methylene chloride's human health risks and environmental effects.

Also presented in this chapter are statements, provided by OECD Member countries, in regard to national positions on the risks from methylene chloride. Essentially, these statements provide the rationale for any actions the country has taken to address effects associated with environmental or human exposures to methylene chloride. They are based on conclusions concerning the hazards of methylene chloride, and data from human health or environmental monitoring carried out to determine levels of exposure.

The national risk assessments and risk characterizations that have led countries to take action have a strong national character. Countries develop positions on the need for risk reduction activities only after they have analysed the hazard and significance of certain exposures and have factored in local social, economic and political considerations. These positions are usually arrived at after considerable debate on the numerous factors involved. Thus they are not expected to be consistent across Member countries.

4.1 International position (IPCS)

The International Programme on Chemical Safety (IPCS) is a joint venture of the United Nations Environment Programme, the International Labour Organisation, and the World Health Organization. The main objective of the IPCS is to carry out and disseminate evaluations of the effects of chemicals on human health and the quality of the environment. The Environmental Health Criteria documents prepared by IPCS contain the collective views of an international group of experts and do not necessarily represent the decisions or the stated policy of the United Nations Environment Programme, the International Labour Organisation, or the World Health Organization.

The text below on "Evaluation of Human Health Risks" and "Evaluation of Effects on the Environment" is taken directly from the "Summary, Evaluation, Conclusions and Recommendations" in the International Programme on Chemical Safety (IPCS) Task Group-approved draft of the Environmental Health Criteria document on methylene chloride. Corrections may be made during editing of the draft document, including corrections to the figures quoted. However, any corrections made will not affect the conclusions given here.

EVALUATION OF HUMAN HEALTH RISKS

Human exposure to methylene chloride is mainly by inhalation of the vapour. Exposure of the general population to methylene chloride depends strongly on the indoor air concentration. Through the use of products containing methylene chloride, peak concentrations up to 4000 $\mu g/m^3$ have been reported. However, 24-h average exposures are in general below 50 $\mu g/m^3$.

Methylene chloride is rapidly absorbed through the lung and also from the gastro-intestinal tract. It is absorbed via the skin, but at a much slower rate than by the other routes. Once absorbed, methylene chloride is distributed throughout the body and will cross both the placenta and the blood-brain barrier. Methylene chloride is rapidly excreted, the majority being exhaled unchanged via the lungs. The remainder is metabolized to carbon monoxide, carbon dioxide and inorganic chloride. Two metabolic pathways have been identified, one involving cytochrome P-450 and the second involving glutathione-S-transferase. Clear species differences exist in the relative contributions of these two pathways. These differences have been used as a basis for a physiologically-based pharmacokinetic (PB-PK) model for methylene chloride which allows interspecies comparison of the concentrations of active metabolites at the target tissues, thus enhancing the value of results from animal studies in human health risk assessment. This approach has been used in assessing the human cancer risk associated with exposure to methylene chloride.

The acute toxicity of methylene chloride is low. The predominant effects in human beings are CNS depression and elevated blood carboxyhaemoglobin (CO-Hb) levels. These effects are reversible. Other target organs can be the liver and, occasionally, the kidney. Its odour threshold concentration is reported to be 540 mg/m^3 or greater. Mild CNS effects have been reported following exposure to concentrations as low as 694 mg/m^3 for 1.5 h (behavioural disturbances). More significant effects occur at concentrations in excess of 2000 mg/m^3. Narcosis has been reported to occur following 0.5-h exposure to 69,000 mg/m^3. Its metabolism to carbon monoxide leads to increases in blood CO-Hb levels following acute exposure to the vapour, a process which becomes saturable following exposures to high levels of methylene chloride. Exposure to either 100 or 530 mg/m^3 for 7.5 h leads to CO-Hb levels of 3.4% and 5.3% respectively in human volunteers. This effect forms the basis of most, if not all, published occupational exposure limits, where a level of 5.0% is judged to be acceptable.

The predominant effects following repeated or long-term exposure to methylene chloride are the same as for acute exposure. Reversible symptoms of CNS depression are seen in several species, including humans. The LOEL for this effect in all animal species is 7100 mg/m^3 by inhalation. No evidence of irreversible neurological damage was seen in rats exposed to methylene chloride by inhalation at concentrations up to 7100 mg/m^3 for 13 weeks. Additional target organs reported in various species chronically exposed to methylene chloride include the liver and, occasionally, the kidney. The NOAEL for chronic intermittent inhalation exposure was judged to be 710 mg/m^3 in rats. After continuous exposure, slight cytoplasmic vacuolisation in the liver of both mice and rats was observed at 88-350 mg/m^3.

A single study has reported the presence of methylene chloride in the placenta, foetus and breast milk of women following occupational exposure. The teratogenic potential of methylene chloride has been assessed in three animal studies. Small effects on either foetal or maternal body weights were reported but no evidence of an effect on the incidence of skeletal malformations or other developmental effects was seen. A well-conducted two-generation reproductive toxicity study in rats exposed to methylene chloride by inhalation at concentrations up to 5300 mg/m^3, 6 h/day, 5 days/week showed no evidence of an adverse effect on any reproductive parameter, neonatal survival or neonatal growth in either the F_0 or F_1 generations.

Under appropriate exposure conditions, methylene chloride is mutagenic in prokaryotic microorganisms with or without metabolic activation (*Salmonella* or *E. coli*). In eukaryotic systems it gave either negative or, in one case, weakly positive results. *In vitro* gene mutation assays and tests for unscheduled DNA synthesis (UDS) in mammalian cells were uniformly negative. *In vitro* assays for chromosomal aberrations using different cell types gave positive results, whereas negative or equivocal results were obtained in tests for sister chromatid exchange (SCE) induction. The majority of the *in vivo* studies reported have provided no evidence of mutagenicity of methylene chloride (e.g. chromosome aberration assay, micronucleus test or UDS assay). A very marginal increase in frequencies of SCEs, chromosomal aberrations and micronuclei in mice has been reported following inhalation exposure to high concentrations of methylene chloride. The significance of these results is questionable due to methodological deficiencies in the statistical analysis. There was no evidence of binding of methylene chloride to DNA or DNA damage in rats or mice given high doses.

Within the limitations of the short-term tests currently available, there is no conclusive evidence that methylene chloride is genotoxic *in vivo*.

Methylene chloride is carcinogenic in the mouse, causing both lung and liver tumours, following exposure to high concentrations (7100 and 14 100 mg/m^3) for their lifetime. These tumours were not seen in the rat nor the hamster.

Increased incidence of benign mammary tumours in female rats was observed in one study, and increased incidence and multiplicity were observed in two other rat studies. The increased incidence of these tumours was within historical controls; nevertheless there was a dose-response relationship within a study. It is considered that an increase in a tumour type which occurs with high and variable incidences in control animals, which does not progress to malignancy, and which may be related to changes in prolactin levels is of little importance in human hazard assessment.

In vitro and *in vivo* metabolism and biochemical studies, and mutagenicity assays in bacteria and B6C3F1 mice have provided a plausible explanation for the mechanism of action and the species differences in the carcinogenicity of methylene chloride to the lung and liver. This explanation is based on the existence of an isoenzyme of glutathione-S-transferase which specifically metabolizes methylene chloride to the reactive intermediates responsible for tumour induction in the mouse. Markedly lower levels of this enzyme in rats and hamsters are consistent with the fact that these tumours do not appear in these species. The levels of the enzyme in the liver are lower in humans than in rats or hamsters. The variability of the current estimates of this enzyme activity in human liver is low but the possibility of wider variation existing in subpopulations cannot be discounted. Although the currently available information on enzyme activity in human lung is limited, it is expected to be lower than in human liver. The carcinogenic potency of methylene chloride in man is expected to be low.

Mutagenicity studies on methylene chloride in bacteria and in the B6C3F1 mouse, which shows a very high level of activity of the isoenzyme, show positive effects, whereas mutagenicity has not been demonstrated in standard *in vivo* mutagenicity assays using other systems. These observations are consistent with the above hypothesis and provide a mechanistic basis for the induction of tumours in the mouse.

The role of the glutathione-S-transferase isoenzyme in the mediation of the demonstrated mutagenic effects and the correlation between the activity of this pathway and the species differences in carcinogenic response, has led to its use as the dose surrogate in physiologically based pharmacokinetic models used for human health risk assessment.

Overall, animal inhalation studies have shown effects on the liver from 710 mg/m^3 and on other organs from 1700 mg/m^3. However, these effects have not been observed in epidemiological studies. Effects on the CNS have been observed in both animals and humans and a threshold in humans has been defined, based on the level of the metabolite carbon monoxide in the blood, leading to exposure limits of the order of 177 mg/m^3.

EVALUATION OF EFFECTS ON THE ENVIRONMENT

Due to its high volatility methylene chloride released to the environment will end up in the atmosphere where it can be transported to regions far removed from the emission source. Methylene chloride is degraded in the troposphere by reaction with hydroxyl radicals giving carbon dioxide and hydrogen chloride as major breakdown products. Based on a lifetime in the troposphere of about 6 months it may be assumed that only a few percent, if any, of methylene chloride will reach the stratosphere. No significant impact on stratospheric ozone depletion is expected. Methylene chloride will also not contribute significantly to photochemical smog formation. In ambient air in rural and remote areas, background levels of 0.07-0.29 $\mu g/m^3$ have been measured. In suburban and urban areas levels up to 2 and 15 $\mu g/m^3$ methylene chloride have been found.

Concentrations of methylene chloride in the surface water of rivers in industrialized areas stay generally below 10 µg/litre. In industrial effluents, outfalls of municipal water treatment plants and leachates of landfill, concentrations of methylene chloride of up to 200 mg/litre have been measured.

In the aquatic environment, fish and amphibian embryos have been shown to be the most sensitive to methylene chloride with effects on hatching from 5.5 mg/litre; adult aquatic organisms are relatively insensitive even after prolonged exposure. There is no evidence to suggest that methylene chloride and/or its metabolites bioaccumulate in the environment. Given the concentrations observed in surface water (<10 µg/litre) and those in contaminated effluents (<200 mg/litre), no significant impact on the aquatic environment is expected.

Localized contamination of soils will not significantly disperse despite the mobility of methylene chloride; in ground waters and soils, biological degradation processes have been identified capable of mineralizing methylene chloride in a few days. From the limited information on soil organisms it may be assumed that contamination of soil has only a local and transient effect.

Apart from accidental spills, it is concluded that the present use of methylene chloride has no significant impact on the environment.

4.2 National positions

Austria

According to Maximal Workplace Concentration (MAK), methylene chloride is classified as potentially carcinogenic. Under the existing Chemicals Ordinance (208/89), it is classified as harmful with possible risk of irreversible effect.

Canada

Methylene chloride has been classified as a toxic substance under Canadian legislation dealing with occupational health and safety, foods, transportation, water and consumer protection. It is under review as a substance suspected to be hazardous to the environment.

The Priority Substances List, under the Canadian Environmental Protection Act (CEPA), lists methylene chloride as a priority substance. An assessment report describing the effects of methylene chloride on human health and the environment is in preparation.

Denmark

Methylene chloride has been on the list of carcinogenic substances made by the Danish Ministry of Labour since 1988.

Finland

Methylene chloride has been classified as a carcinogen in the third category.

Germany

In 1992 approximately 75,500 tonnes of methylene chloride was produced, of which 23,000 tonnes was used inside Germany. The chemical industry association (VCI, 21.4.93) has given a prognosis for the chlorinated solvent market in 1995. According to this reference, the solvent use will drop to 18,000 tonnes. The use patterns for methylene chloride are presented in Figure 1.1 (Chapter 1).

Because of its hazardous nature, methylene chloride requires caution in handling, use and transportation. Therefore it is subject to widespread regulations.

In accordance with the Ordinance on Hazardous Substances (GefStoffV, 1.11.93) methylene chloride is classified as "suspected of being carcinogenic".

Exposure

Maximum concentrations of methylene chloride in German rivers are presented in Table 2.4 (Chapter 2).

A comparison of methylene chloride concentrations in 1989 and 1990 shows an increase. In 1991 and 1992, methylene chloride was not detected in the Rhine and its tributaries at a detection limit of 1 µg/litre. (Measurements in the Elbe and Weser have not been carried out since 1988.)

Ecotoxicity

In an acute test, *Daphnia magna* was the most sensitive species with an EC50 (24h) of 13 mg/litre. A prolonged test with *Daphnia magna* is not available. In a validated embryo-larval test two fish and four amphibian species were tested with respect to the hatching rate, including teratogenic effects and the survival of larvae (four days post hatching). The results are shown in the table below. At concentrations between 0.8 and 5.5 mg/litre, teratogenic effects were also observed.

Species	**Test duration**	**LC50**	**Effect concentrations**
Salmo gairdneri	23d + 4d	13.1	LC8 = 0.042 mg/litre LC15 = 0.41
Pimephales promelas	5d + 4d	34.0	LC6 = 0.003 LC10 = 0.11
Rana temporaria	5d + 4d	16.9	LC5 = 0.18 LC11 = 0.65
Ambystoma gracile	5.5d + 4d	17.8	LC9 = 0.65
Xenopus laevis	2d + 4d	>29	LC9 = 0.65
Rana pipiens	5d + 4d	>48	LC9 = 1.17

References: Black et al. (1982), Knie (1988), Le Blanc (1980)

Environmental Impact and Fate

In the atmosphere methylene chloride is photochemically oxidative, degraded by OH radicals (t1/2 = 133 days). According to the classification criteria of the Federal Immission Control Act (TA Luft), methylene chloride is persistent. It can be assumed that part of the emitted methylene chloride will reach the stratosphere. An endangering of the already damaged ozone layer cannot be excluded, due to the high emissions of methylene chloride to the atmosphere.

Conclusion

From the available data, it cannot be excluded that methylene chloride causes a risk to the aquatic environment. It is strongly recommended to continue with regular measurements of methylene chloride at a detection limit below 1 μg/litre, and to phase out its use in consumer products.

Toxicology

In humans, the main effects of acute exposure are central nervous system depression and raised CO-haemoglobin level in the blood; these effects are, however, reversible. Tests for carcinogenic effects showed an increase in lung and liver tumours in mice after inhalation exposure. In rats, an increase in the incidence/frequency of benign mammary tumours occurred.

In one study, an increase in the incidence of sarcomas in the neck area was observed in male rats. After oral administration of methylene chloride to rats and mice, there were no clear indications of any carcinogenic effect. In hamsters, methylene chloride proved non-carcinogenic after inhalation exposure. On the basis of these results, methylene chloride is classified in the latest MAK values list as a substance for which there are grounds to suspect possible carcinogenicity.

Methylene chloride proved mutagenic in bacteria as well as genotoxic in yeasts. In drosophila, there were only slight indications of mutagenic effect. In mammalian cell cultures, there were some chromosome aberrations after exposure to methylene chloride, but no induction of unscheduled DNA synthesis and no point mutation. With regard to induction of sister chromated exchange, there are no clear results. Alkylation of DNA through methylene chloride could not be proved.

After exposure to methylene chloride *in vivo*, there was no induction of micronuclei in the bone marrow of mice, and no chromosome aberrations in the bone marrow of rats.

Results of cell transformation studies are not uniform.

In conclusion, it is clear that results for genotoxicity of methylene chloride are based almost exclusively on *in vitro* experiments. In existing *in vitro* tests on mammalia, however, methylene chloride proved not to be genotoxic.

Epidemiological studies showed no indication of carcinogenicity for humans.

Recommendations

Of primary importance in further investigations of human toxicity is an explanation of the difference between species in terms of carcinogenicity. There should be further pharmacokinetic experiments *in vivo*. It would also be useful to have further investigations of the effect mechanism, especially of the relative importance of the two metabolic processes in various exposure concentrations.

To explain conclusively a possible interaction (incorporation or covalent bond) of methylene chloride metabolites with DNA, a further *in vivo* study with radioactively labelled methylene chloride should be carried out.

Following the principles layed down in Directive 93/21/EEC, the following additional classification would be mandatory, which has been suggested by Germany to the European Union.

Classification

Dangerous to the environment

Labelling

R36	Eye irritant
R38	Skin irritant
R52	Harmful to aquatic organisms
R53	May cause long-term adverse effects in the aquatic environment
R63	Possible risk of harm to the unborn child
S61	Avoid release to the environment

Symbol

Xn

Japan

Methylene chloride is widely used for such purposes as metal cleaning, process solvent, photoresist stripping, fibre and film production, paint stripping, etc. in almost all industrial sectors except the food stuff industry. Its uses for consumer goods are limited.

Methylene chloride use in Japan increased from 80,200 tonnes in 1991 to 101,200 tonnes in 1993. Its use for photoresist stripping was reduced drastically between 1992 and 1993, but its use in metal cleaning as a substitute for 1,1,1-trichlorethane increased. Aqueous, semi-aqueous, hydrocarbon, alcohol and chlorinated solvent cleaners are also used as substitutes, depending on the object to be cleaned. However, among chlorinated solvents methylene chloride is widely preferred in Japan.

According to a questionnaire survey promoted by methylene chloride makers in 1994, generally good compliance with the standard 100 ppm specified by the Ministry of Labour, Japan, was indicated, with some difference in the level depending on the industrial sector. For 48 factories in 13 industrial sectors, out of 196 factories in 25 sectors, the effluents of methylene chloride were 0.01-9 mg/litre depending on the sector (Environment Agency, Japan, 1993).

The Netherlands

In 1984 approximately 19,780 tonnes of methylene chloride was imported and 15,000 tonnes was produced in the Netherlands. 27,260 tonnes was exported as methylene chloride (25,080 tpa), in products (2075 tpa) and in waste (105 tpa). 6763 tonnes was emitted to air, 78 tonnes to water and 100 tonnes to soil (see Table 2.1, Chapter 2). Fifty-seven per cent is due to industrial sources and 43 per cent to diffuse sources (Basisdocument 1990). 579 tpa is (bio)degraded.

According to available data, methylene chloride does not present a carcinogenic hazard to man (Basisdocument 1990). The Dutch Health Council confirmed that methylene chloride causes no mutagenic effects as a result of normal human exposure levels. Only as a result of relatively high exposure levels was methylene chloride found to be carcinogenic in experimental animal testing, probably due to other toxicological effects (tissue damage) occurring.

Norway

Methylene chloride is classified as harmful by inhalation, according to the Health Hazard Labelling Regulations. The substance is also classified as a low-potency carcinogen.

A criteria document for methylene chloride has been produced by the National Pollution Control Authorities and the Directorate of Labour Inspection’s Scientific Group for Identification of Carcinogens.

Sweden

Exposure to methylene chloride takes place primarily by inhalation. Absorption is rapid since the substance is soluble in both fat and water. Excretion of methylene chloride and its metabolites CO and CO_2 takes place almost entirely via the respiratory tract, on exhalation.

Exposure to methylene chloride raises the carboxy-haemoglobin content in the blood, which in turn reduces the oxygen-absorbing capacity of the haemoglobin. This anoxic effect and the general central nervous system depressing effect may result in symptoms such as dizziness, headache, fatigue and difficulties in concentrating. With high concentrations, pulmonary oedema may also arise. There are case reports describing coronary infarctions and ECG changes connected with heavy exposure to methylene chloride.

Methylene chloride is carcinogenic in rats and mice. In inhalation tests, the substance has produced tumours in rat mammary glands and mouse lungs and liver. Oral long-term administration of methylene chloride has induced lung tumours in mice. Genotoxic effects have been demonstrated in a number of test systems.

The National Chemicals Inspectorate has classified methylene chloride as a low-potency carcinogen.

The Institute for Environmental Medicine (IMM) at Karolinska Institutet has specified a low risk value of 100 ppb in ambient air, with reference to the carcinogenic and mutagenic effects of this substance.

In 1991 the Swedish Government decided that measures should be carried out in order to phase out the marketing and use of methylene chloride.

Switzerland

According to the Swiss Law for Toxic Substances, methylene chloride is classified in poison class 4 by virtue of its acute toxicity. In other countries and classification systems, methylene chloride is classified as a "possible carcinogen". The Swiss way of classification does not use this concept. Only substances clearly proven to be carcinogenic under conditions reflecting a possible human exposure will be classified as such. Due to the lack of such evidence, methylene chloride is not classified as a carcinogenic substance in Switzerland.

United Kingdom

The current view in the United Kingdom is that the compound does not present either a carcinogenic hazard to humans, or a hazard to the environment. It is for these reasons that the UK considers the use of methylene chloride in consumer products, paint stripper and aerosol cosmetics acceptable. Other, non-carcinogenic, adverse effects can occur at the higher, longer-term levels of exposure that may be found in the workplace, but these can be prevented by the enforcement of occupational health legislation, including an occupational exposure limit.

Methylene chloride has a wide span of applications. It has a unique range of properties, for example powerful solvency, non-flammability, stability and ready availability, which make it very adaptable within these applications.

Methylene chloride has been thoroughly studied to determine its potential health hazards to humans. It is a volatile solvent causing acute effects on the central nervous system which are fully reversible. In that respect it is like many other solvents, be they chlorinated alkanes, alcohols or aliphatic solvents.

A metabolite of methylene chloride is carbon monoxide, and concerns regarding the generation of carboxyhaemoglobin in blood are the critical toxicity consideration when setting occupational exposure limits.

Although there is some evidence that methylene chloride is mutagenic *in vitro*, negative results were consistently obtained *in vivo*. The compound is a carcinogen in the mouse, producing liver and lung tumours, but not in the rat. The tumours seen in the mouse do not arise from a genotoxic mechanism, but are believed to be secondary to toxic effects in the target tissue. Extensive data on metabolism indicate that the metabolic pathways that predominate in the mouse at high dose levels are not important in the rat or humans. It is these marked species differences that lead to the conclusion that methylene chloride is not a human carcinogen. This is borne out by epidemiology studies.

Methylene chloride does not pose any serious hazard to the environment. It is biodegradable, non-bioaccumulative, and has a low ozone depletion potential. It does not contribute to low-level ozone formation, and the global warming potential is effectively nil.

United States

United States agencies concerned with the health and environmental effects of methylene chloride (dichloromethane), including the US Environmental Protection Agency, the Agency for Toxic Substances and Disease Registry, the Occupational Safety and Health Administration, the National Institute for Occupational Safety and Health, the Food and Drug Administration, and the Consumer Product Safety Commission, have drawn a number of conclusions regarding exposure to methylene chloride.

The principal route of human exposure to methylene chloride is inhalation from use of consumer and industrial products containing methylene chloride. Methylene chloride is a solvent that is widely used for a variety of purposes. Workers involved in polyurethane foam blowing, spray painting, metal degreasing, paint stripping, aerosol packing and similar industrial activities involving the use of methylene chloride as a solvent have the highest potential exposure to methylene chloride (IARC 1986; OSHA 1986, 1991; Whitehead et al. 1984). The National Institute for Occupational Safety and Health (NIOSH) estimated that the number of workers potentially exposed to methylene chloride increased from about one million in the early 1970s to 1.4 million in the early 1980s (NIOSH 1986, NOES 1990). Because the production and use of methylene chloride has decreased since the mid-1980s, the number of workers exposed today is probably lower than the 1980s level. Paint strippers, adhesive removers, spray shoe polishes, adhesives, glues, paint thinners and many other household products containing methylene chloride as a solvent expose consumers to significant amounts of methylene chloride vapour, especially when the products are used indoors (CPSC 1987, 1990).

Due to the high volatility of methylene chloride, water and food concentrations of methylene chloride are low; therefore, inhalation is the predominant route of exposure for the general population. Exposures associated with inhalation during the use of methylene chloride-containing products are the most significant for the general population. Approximately 85 per cent of methylene chloride produced is lost directly to the atmosphere through dispersive uses leading to ubiquitous low level atmospheric concentrations (ATSDR 1991). The Toxics Release Inventory reports 42.5 million kg of methylene chloride were released to the atmosphere by manufacturers and processors of methylene chloride in the US in 1990 (TRI 1990). Concentrations of methylene chloride in drinking water are generally less than 1 µg/litre, which would lead to an average daily intake of 2 µg of methylene chloride (ATSDR 1991).

The central nervous system is a key target of methylene chloride toxicity. Human studies measuring visual-evoked potential reveal that the nervous system is an important target of methylene chloride toxicity. Methylene chloride results in liver toxicity to animals. Acute liver toxicity has not been observed in humans, although data suggest the liver may be affected by chronic exposure (EPA 1985, OSHA 1991). Acute effects appeared to be reversible; however, chronic exposures appeared to result in permanent damage (Haun et al. 1972, Burek et al. 1984, Nitsche et al. 1988, NTP 1986, OSHA 1991). There may be individuals, such as persons with compromised liver function, cardiac conditions (carbon monoxide is one of the metabolites of methylene chloride), or neurological disorders, who are particularly susceptible to the toxic effects of methylene chloride (ATSDR 1991). The EPA has set a Reference Dose (RfD) against which exposures can be evaluated. The RfD is an estimate of daily exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime (EPA 1985). The RfD for inhalation is 0.9 mg/kg/day, which corresponds to a reference concentration of 3 mg/m^3; the oral RfD is 0.06 mg/kg/day.

The EPA regards methylene chloride as a probable human carcinogen (Group B2). Inhalation of high levels of methylene chloride increases the incidence of liver and lung cancer in mice and benign mammary gland tumours in rats (NTP 1986). Although several epidemiological studies detected no excess risk of cancer in workers exposed up to levels of 475 ppm (Friedlander et al. 1978; Hearn et al. 1987, 1990; Ott et al. 1983), at least one study observed an excess of biliary cancer in a cohort of textile workers exposed to methylene chloride and other solvents in the production of cellulose triacetate fibre (Lanes et al. 1990). The quality of these studies and the uncertainties that exist regarding the mechanisms of carcinogenicity for methylene chloride do not permit the EPA to discount the positive findings in the bioassay (EPA 1987).

On the basis of carcinogenic and tumorigenic responses in rats and mice, NIOSH has recommended that methylene chloride be regarded as a "potential occupational carcinogen". Although the potential for methylene chloride-induced cancer in humans has not been determined, the probability of a population of exposed workers developing cancer could be decreased by reducing exposure. NIOSH recommends that occupational exposure to methylene chloride be controlled to the lowest feasible limit (NIOSH 1986). The United States Consumer Product Safety Commission regards methylene chloride as a possible human carcinogen.

The US EPA Office of Air and Radiation (OAR) is required under the US Clean Air Act to consider balancing of risks in examining uses of methylene chloride. The Significant New Alternative Policy does not permit substitution of any ozone-depleting substance with any substance determined to present adverse effects to human health or environment, where the Agency has identified an alternative, which reduces the overall risk and is currently or potentially available. Weighing methylene chloride in this way, the OAR has found that it compares favourably with its substitutes, in part because it is nonflammable and so poses less acute hazard. In rules issued under CAA, OAR has endorsed methylene chloride use in flexible foams (59CFR13083, March 18, 1994) and for solvent use (59CFR13091, March 18, 1994) as an alternative for CFCs.

The Agency for Toxic Substances and Disease Registry (ATSDR) has developed a toxicological profile for methylene chloride because it is a toxic substance commonly found at hazardous waste sites which are priorities for remediation under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980. In addition, ATSDR has determined Minimum Risk Levels (MRL) and set Environmental Media Evaluation Guides (EMEGs) for air, water and soil exposures. An MRL is an estimate of daily human dose levels of a chemical that is likely to be without appreciable risk of adverse non-cancerous health effects over a specified duration of exposure. An EMEG is an environmental concentration that corresponds to an MRL, that is, if an individual is exposed to a concentration at or below the EMEG, no harmful effects are expected to occur (ATSDR 1991).

Commission of the European Union

According to the Annex to Commission Directive 93/72/EEC of 1 September 1993 adapting to technical progress for the nineteenth time Council Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances, methylene chloride is classified as harmful and as a carcinogen in the third category. It is to be labelled as follows: R:40, S:(2-)23-24/25-36/37.

CHAPTER 5

MECHANISMS FOR RISK REDUCTION

The methylene chloride risk reduction activities of 15 OECD Member countries and the European Union are described in this chapter. Descriptions are based on information provided by countries. Country-specific risk management activities are summarized in **Table 5.1**. As shown in this table, the extent of these activities varies substantially among Member countries.

A summary of industry risk reduction activities, provided by the Business and Industry Advisory Committee to the OECD (BIAC), is also included in this chapter.

The tables in **Annex A** at the end of the chapter summarize available information on risk reduction activities in Member countries. Information in the summary tables was either taken from detailed descriptions provided by countries, or extracted from secondary sources or government publications.

Repeated requests for information on methylene chloride risk reduction activities were made to all Member countries in 1993 and 1994. Lack of information in this report on a particular country means either that no risk reduction activities have taken place in that country, or that the country has not responded to requests for information.

Possible alternative chemicals or methods in use are summarized in **Appendix 1**. The alternatives listed have not been evaluated from a toxicological or ecotoxicological point of view. The use of alternative chemicals or processes may pose other risks to human health or to the environment. It is therefore important to evaluate and compare risks carefully before making substitutions. It is also important to investigate in each case whether a particular substitute can be used, with regard to its technical efficacy.

Table 5.1 Areas in which Some Member Countries and the EU Have Developed Regulations and Standards for Methylene Chloride

(X = existing regulation/activity; P = proposed activity)

	Environmental media				Environmental sources			Products			Environ-mental health
	Drinking water	Surface waters	Ambient air	Soil	Air point sources	Water point sources	Foodstuffs or feed	Cosmetic products	Products for consumer use	Products for professional use	Occupational exposures
Australia			X						X		X
Austria	X								X	X	X
Belgium								X			X
Canada	X	X		X			X		X		X
Denmark			X					X	X		
Finland	X						X	X			X
France											X
Germany	X	X			X			X	P	X	X
Japan	X	X		X		X	X		X	X	X
Netherlands			X								X
Norway										P	X
Sweden			P		X	X	X	X	X	X	X
Switzerland	X	X	X		X	X	X	X	X	X	X
United Kingdom								X			X
United States	X	X	X	X	X	X	X	X	X	P	X
European Union							X	X			

Australia

In 1991, the exposure standard was reduced from 100 to 50 ppm (TWA), based on the documentation prepared by the ACGIH in 1986. The reason for lowering the Threshold Limit Value (TLV) for methylene chloride was to provide a wider margin of safety in preventing liver injury. The lower TLV also provides protection against the weak carcinogenic effects of methylene chloride. This standard has become a regulatory requirement in one State of Australia (Western Australia) and it is expected to become a regulatory requirement in several other States, and in workplaces which are under Commonwealth jurisdiction, in the near future.

Methylene chloride has been regulated as a Schedule 5 poisonous substance for at least 20 years in all States and Territories. Schedule 5 applies to poisons of a hazardous nature that are readily available to the public, but require caution in handling, storage and use. It is the lowest level of risk in the poisonous substances regulations. Pressurized spray packs that do not contain degreaser, decarbonizers, and paint strippers with more than 10 per cent methylene chloride are not included. However, those pressurized spray packs that are known to be publicly available are kept in Schedule 5, while those products for industrial use, to which occupational health controls apply, are exempted.

In the State of Victoria, the Environmental Protection Authority has established a Design ground level concentration (GLC) for methylene chloride of 24 mg/m^3. This GLC is used in conjunction with plume dispersion modelling to establish discharge emissions to the atmosphere.

Methylene chloride is classified as a dangerous good for transport by road and rail.

In 1991, Worksafe Australia published a Guidance Note for Determining and Classifying a Hazardous Substance. Methylene chloride will be defined as a hazardous substance by that procedure. This will mean that specific labelling requirements and training/education will become mandatory in the workplace when the guidance note becomes law.

Austria

The exposure limit amounts to 100 ppm (360 mg/m^3) in breathing air.

A ban on paints, coating materials, wood preservatives and removers which contain chlorinated hydrocarbons or benzene as solvents has been in practice since July 1, 1992. (Preparations containing less than 0.1 per cent of chlorinated hydrocarbons or benzene are deemed non-CHC or non-benzene containing preparations.) The use of chlorinated hydrocarbons in adhesives has been banned since January 1, 1994. The use of chlorinated hydrocarbons to inhibit flammability in foamed adhesives is permissible until December 31, 1995. The use of chlorinated hydrocarbons in coal tar pitch products and bituminous cold-bonding agents is permissible until December 31, 1994 and December 31, 1995, respectively. The use of chlorinated hydrocarbons in high-pressure packages to apply preparations (paints, lacquers, etc.) is permissible until December 31, 1994, to the extent that methylene chloride is required to reduce flame length. Preparations which do not comply with the requirements shall be exempt from the ban if the organic solvents are required for the intended application for technical reasons, and their substitution or the use of other methods is not possible at the current technological state-of-the-art (Federal Law Gazette no. 492/1991).

By ordinance BGBl.Nr. 776/1992, Austria regulated placing on the market and use of the ozone-depleting substances 1,1,1-trichloroethane and carbon tetrachloride. In order to reduce the use of hazardous chlorinated hydrocarbons as far as possible, one clause in this ordinance prohibits the substitution of trichloroethane by methylene chloride, trichloroethylene or tetrachloroethylene.

The sum of the concentrations of 14 different halogenated aliphatic hydrocarbons, including methylene chloride, must not exceed 30 µg/litre in drinking water.

Belgium

Methylene chloride is regulated by the EEC Directive on classification and labelling of dangerous substances.

According to the provisions for protection of employees against risks due to the exposure to chemical, physical and biological agents, methylene chloride is classified as a poison of hazardous nature that requires caution in handling, storage and use. The recommended occupational exposure limit is the Threshold limit Value (TLV) proposed by ACGIH (the American Conference of Governmental Industrial Hygienists) of 50 ppm.

Canada

Exposure in federally regulated workplaces to air containing methylene chloride, averaged over a full work shift, must not exceed 175 mg/m^3 or 50 ppm. The short-term exposure limit (STEL) is 1740 mg/m^3 or 500 ppm. The cited limits are prescribed in Part X "Hazardous Substances" of the *Canada Occupational Safety and Health (COSH) Regulations* issued pursuant to the *Canada Labour Code*. The regulations state that no employee shall be exposed to a concentration of an airborne chemical agent in excess of the value for that agent adopted by the American Conference of Governmental and Industrial Hygienists (ACGIH) in its publication entitled "Threshold Limit Values and Biological Exposure Indices for 1985-86". However, Part X is currently being reviewed and consideration is being given to referencing the current TLVs, as 174 mg/m^3 or 50 ppm.

Methylene chloride is included on the *Ingredient Disclosure List* (IDL), which is a part of the *Workplace Hazardous Materials Information System* (WHMIS), at a level of 0.1 per cent by weight. The IDL is published by the Minister of Health acting under the authority of the *Hazardous Products Act*, administered by the Department of Health Canada.

A comprehensive assessment of the risks posed by methylene chloride to health and the environment was recently completed as a part of the Priority Substance Assessment Program mandated under the Canadian Environmental Protection Act (CEPA). This program is designed to ascertain whether the Priority Substances in the environment pose a risk to the environment or the health of the Canadian general population (i.e. whether they are "toxic" as defined under CEPA) and then to take appropriate measures to control substances deemed "CEPA toxic". In this assessment, it was concluded that methylene chloride is "CEPA toxic", with respect to the fact that it enters the environment under conditions that are having or may have a harmful effect on the environment, and that it may constitute a danger to human life or health. Work is being done towards establishing options to further control risks from exposure to methylene chloride in the general environment.

The maximum acceptable concentration (MAC) for methylene chloride is 0.05 mg/litre in drinking water. This level is included in the Guidelines for Canadian Drinking Water Quality – 1989.

Methylene chloride is not directly regulated by the *Consumer Chemicals and Containers Regulations* under the *Hazardous Products Act*. Paint strippers are regulated when they contain specific regulated chemicals. Concern about consumer safety in the use of paint strippers containing methylene chloride led to the release of an information bulletin, "Health Hazard Posed by Paint Strippers and Spray Paints", in 1988 by Health Canada.

The use of methylene chloride as a food additive in spice extracts, as hop extract in malt liquor, and for decaffeination purposes is regulated in the FDR (Food and Drug Regulations). The regulations issue a permitted maximum residue; 30 ppm in spice extracts, 2.2 per cent in hop extracts, and 10 ppm in decaffeinated roasted coffee, decaffeinated instant coffee, decaffeinated tea leaves and instant tea.

Interim Water Quality Guidelines (March 1992) of 98 µg/litre and 50 µg/litre have been derived for the protection of freshwater aquatic life and as the recommended level for livestock water, respectively.

A document entitled "Interim Canadian Environmental Quality Criteria for Contaminated Sites" has been published as a part of the National Contaminated Sites Remediation Program. The criteria, expressed as concentrations which are not to be exceeded, are established for the assessment and remediation of water and soil. The following values apply to methylene chloride:

A Assessment Criteria:

Soil	0.1 µg/g dry weight
Water	0.1 µg/litre

B Remediation Criteria for Soil:

Agricultural	0.1 µg/g dry weight
Residential/Parkland	5 µg/g dry weight
Commercial/Industrial	50 µg/g dry weight

C Remediation Criteria for Water:

Freshwater Aquatic Life	No recommendation
Irrigation	No recommendation
Livestock Watering	No recommendation
Drinking Water	No recommendation

The transportation of methylene chloride is regulated by the *Transportation of Dangerous Goods Act*.

As a result of a national review of the pesticide registration system in Canada, a policy on formulant ingredients will be developed. In the interim, Agriculture Canada has adopted the following position on formulants/inserts:

1) On receipt of an application to amend a formulation or to register a new formulation, the applicant will be asked to find a substitute for or remove methylene chloride from their formulation. Methylene chloride is a United States Environmental Protection Agency (US EPA) List 1 inert.

2) If the registrant makes a case to keep methylene chloride, there must be the following statement on the label:

   "This product contains X per cent of methylene chloride which has been determined to be of toxicological concern."

3) Before agreeing to methylene chloride, Agriculture Canada may require additional toxicological studies on the inert and/or the formulation.

Denmark

The EEC Directive on classification and labelling of dangerous substances regulates methylene chloride. The EEC Directive on cosmetic products permits the use of methylene chloride in cosmetic aerosols in concentrations of up to 35 per cent v/v.

The Danish Ministry of Environment and the Confederation of Danish Industries are working on an agreement to reduce the total Danish emissions of VOC by 50 per cent. It is expected that special attention will be given to chlorinated solvents.

In 1989, the Danish National Agency of Environmental Protection agreed with the Danish Paint and Varnish Association that the content of VOC in household products, including methylene chloride and similar solvents in paint strippers, should be reduced to a minimum within three years.

Finland

The National Board of Labour Protection has established regulatory values for occupational exposure. The values for methylene chloride are 100 ppm (8 hours) and 250 ppm (15 minutes).

The domestic water (drinking water) must not contain more methylene chloride than 20 µg/litre.

The maximum residue levels of methylene chloride in food stuffs are: coffee 2 mg/kg, tea 5 mg/kg, and flavourings 0.02 mg/kg (implementation of EEC Directives 88/344 and 92/115).

The regulations concerning methylene chloride in cosmetic products are the same as in the EU.

Methylene chloride is classified as a carcinogen in the third category and should be labelled with Xn-R40-S(:2-)23-24/25-36/37.

France

The recommended occupational exposure limit is 100 ppm (or 360 mg/m^3) (8 hours) and 500 ppm (1800 mg/m^3) (10-15 minutes).

Germany

In 1992, approximately 75,500 tonnes of methylene chloride was produced, of which 23,000 tonnes was used inside Germany. Because of its hazardous nature, methylene chloride requires caution in handling, use and transportation. Therefore it is subject to widespread regulations.

Methylene chloride is included in section III B of the MAK list as a substance for which a well founded suspicion of carcinogenic potential exists. Whether methylene chloride possesses teratogenic effects has not been decided so far (group D of the MAK list). A value of 100 ppm or 360 mg/m^3 was established as a maximum permissible concentration at the workplace [MAK list (1993) of the Deutsche Forschungsgemeinschaft]. The biological workplace tolerance value (BAT-Wert) is defined by the CO-Hb level in blood, which may not exceed 100 µg/dl (Sicherheitsdaten von Roth, February 1990).

In accordance with the Ordinance on Hazardous Substances (GefStoffV. 26.10.93), methylene chloride is classified as suspected of being carcinogenic, and must therefore be labelled with R phrases 40 (irreversible damage possible) as well as with S phrases 23-24/25-36/37.

Under the First General Administrative Regulation implementing the Federal Immission Control Act (TA Luft, 6.11.92), which applies to installations subject to licensing, substances for which a well founded suspicion of carcinogenic potential exists are assigned to class 1. This means that the concentration in waste gas may not exceed 20 mg/m^3 at a mass flow of 0.1 kg/h. According to the Second Ordinance implementing the Federal Immission Control Act (2.BImSchV, 6.11.92), installations not subject to licensing must comply with a limit value of 50 mg/m^3 methylene chloride emissions, irrespective of the size of the plant.

This ordinance (2.BImSchV, 6.11.92), especially for plants for surface treatments, restricts the use of highly volatile halogenated hydrocarbons to closed systems. After treatment, the contents of the closed system can only be taken out if the concentration of highly volatile halogenated hydrocarbons inside the closed system is below 1 g/m^3.

If the solvent contains more than 50 per cent methylene chloride, the emission must not exceed a mass concentration of 50 mg/m^3. In undiluted exhaust, highly volatile halogenated hydrocarbons are restricted to no more than 20 mg/m^3. The extracted highly volatile halogenated hydrocarbons have to be recycled. The use of methylene chloride in dry cleaning is forbidden (TA Luft, 6.11.92).

Waste or residues containing methylene chloride are regulated on the basis of the Waste Act in the Ordinance on the Management of Used Halogenated Solvents (HKWAbfV, 23.10.89). Provisions include a ban on the mixing of such wastes or residues with other materials, as well as the obligation that distributors accept returned solvents. In view of the cessation of the burning of waste at sea, this ordinance ought to extend the utilization of used solvents.

Due to methylene chloride's mutagenicity and its mobility in soil, an increased danger for groundwater is indicated. The classification according to water-hazardous-categories aims to protect:

- surface water
- groundwater
- human health.

Methylene chloride is assigned to water-hazardous-category-2, as a substance hazardous to water (VwVwS, 9.3.90). The discharge of certain industries must not exceed a maximum concentration of 0.1 mg highly volatile chlorinated hydrocarbons/litre (Rahmen-Abwasser-VwV, 29.10.93).

Concerning drinking water in Germany, the following regulation exists: the sum total of methylene chloride, perchloroethylene, trichloroethene and 1,1,1-trichloroethane must not exceed 0.01 mg/litre (TrinkwV, 5.12.90). In a federal project group (Länderarbeitsgemeinschaft Wasser), recommendations for the assessment and remediation of damaged groundwater have been worked out in a draft. According to this draft, remediation is envisaged if the sum total of highly volatile chlorinated hydrocarbons is 20-50 µg/litre for groundwater or 5-25 mg/kg for soil.

Since 1986-1987, a voluntary agreement with the chemical industry exists to do without methylene chloride in cosmetic aerosols and washing agents. However, it remains questionable how far these voluntary agreements are effective. Formulated products such as washing/cleansing agents containing methylene chloride have to be notified according to the Washing/Cleansing Agents Act (WRMG, 19,1286); however, in August 1993, 169 formulated products containing methylene chloride were still on the market. This amounts to 6000 tonnes/year.

Surface treatment

Before substituting methylene chloride in metal degreasing, the most important parameters of the alternative system have to be determined.

Possible substitutes and alternative processes, with their advantages and disadvantages, are shown in **Table 5.2**. Tables A1 and A2 (in Appendix A) show the aqueous cleaners most commonly used in industry and an overview of aqueous cleaners in general, emphasizing the different tasks of the respective cleaners.

The combination of the cleansing contents in aqueous, inflammable and other solvents is very specific for the respective area of application. A lot of used substitutes and alternatives are given in the book by D. Minkwitz, *Substitutes to Chlorinated Hydrocarbons in the Degreasing and Cleaning in Industrial Processes* (in German, *Schriftenreihe der Bundesanstalt für Arbeitsschutz – Gefährliche Arbeitsstoffe GA38*, ISBN 3-89429-086-2).

The Technical Rules for Dangerous Substances (TRGS 612, Bundesarbeitsblatt 1993, 4, p54) give an overview of substitutes and alternatives for methylene chloride in paint stripping. This publication also recommends avoiding methylene chloride use in the private sector.

Nutrition industry

Alternative processes and chemical substitutes for methylene chloride in the nutrition industry are presented in **Table 5.3**. Fluid extraction and extraction with inflammable solvents are two possible alternatives. Further solvents can be obtained from Amtsblatt of the EC No. C312/7/8/9 (from 10th April 1990).

In Germany, hop extraction is mainly done with carbon dioxide (up to 80 per cent). The extraction of caffeine has switched over to carbon dioxide and water (up to 70 per cent). Otherwise, the extraction of other agricultural products such as seeds is done with hexane. Hexane itself poses a VOC problem which has to be met with recycling and waste gas reduction technology.

Presently a research project is taking place in Germany to investigate the "Replacement and Indispensable Use of Chlorinated Hydrocarbons". It will be completed by 31st January 1994. The OECD will be informed of the outcome of this research project.

Table 5.2 Possible Substitutes for Methylene Chloride in Germany

Alternative processes	Advantages in comparison with methylene chloride	Disadvantages in comparison with methylene chloride
aqueous cleaners in combination with: • spraying • vapour jet cleaning • electrolytic degreasing	• no emission of solvent • achievement of hydrophilic surfaces for subsequent aqueous processing • additional pre-treatment of surface possible (phosphatization) • good removal of pigment dirt and water-soluble salts	• not universally usable • high water consumption • sewage treatment necessary • danger of caustic injury • long soaking times • time-restricted use of bath • no recycling of cleaning chemicals • drying in capillaries is insufficient
inflammable solvents	• biological degradation	• danger of fire and explosion • high-safety plants necessary • drying of the workpiece necessary

cryogenic stripping (low-temperature treatment with liquid nitrogen)	• no environmental problems • no chemical change in the varnish material • optimal hygiene at the workplace	• not universally usable • stock of liquid nitrogen necessary • high energy consumption

Table 5.3 Possible Substitutes for Chlorinated Solvents in Food Extraction in Germany

Alternative method	Advantages in comparison with chlorinated solvents	Disadvantages in comparison with chlorinated solvents
Fluid extraction, e.g. carbon dioxide	• residue-free extracts • no toxicological doubts • high selectivity in the extraction process • unlimited availability of the extraction solvent	• taste shift • costly • high-pressure system necessary, which operates discontinuously and can only deal with small amounts
Extraction with inflammable solvents, e.g.: • hexane • ethanol • diethylether • ethylacetate • ethylmethylketone • acetone • low boiling point benzine	• in part, toxicologically favourable • lower environmental risk	• taste shift • danger of fire and explosion • plants must have high security standards

Japan

Under the Industrial Safety and Health Law, the environmental evaluation standard for workplaces has been set as 100 ppm. The level in the work environment should be monitored at least every six months by standard methods, and the records should be kept for three years. Industries have made voluntary efforts as follows: the editing and publishing of a "Manual for the Appropriate Use of Methylene Chloride", including the Material Safety Data Sheet (MSDS), in March 1993, and the holding of seminars at major cities using this manual.

In accordance with the "Food Sanitation Law" (Ministry of Health and Welfare), methylene chloride is not allowed to be used in the foodstuff industries even for indirect uses such as extractant or process solvent.

The transport of methylene chloride is regulated by the "Law Relating to the Prevention of Marine Pollution and Maritime Disaster", the "Ship Safety Law", and the "Civil Aeronautics Law", in accordance with United Nations recommendations on classification, etc.

Under the "Basic Environment Law", the Environmental Quality Standard for water, for methylene chloride, is issued as 0.02 mg/litre or less for human health (Environment Agency, Japan, March 1993). A regulation of maximum allowable limit of 0.2 mg/litre for effluents from industry and a detection level 0.002 mg/litre for prohibition of release to soil have been enforced under the "Water Pollution Control Law" (Environment Agency, Japan, February 1994). The Environmental Quality Standard for soil is issued as 0.02 mg/litre or less (Environment Agency, Japan, February 1994).

There is concern about exposure to methylene chloride via the atmosphere, due to its chemical and physical characteristics or the form of the emission to the environment. Therefore, we give priority to the examination of necessary measures on potential air pollution by methylene chloride, and the government is making efforts to research the actual conditions and to gather information.

There is also concern about the risk reduction of methylene chloride, because it is expected that its use as an alternative for trichloroethylene, tetrachloroethylene and 1,1,1-trichloroethane will increase. It is important to examine measures for the risk reduction of methylene chloride, with a due consideration of related similar substances which are used for the same purpose.

The Netherlands

In the Netherlands, the Occupational Exposure Limit has been reviewed and confirmed at 350 mg/m^3 (8-hour TWA) and 1750 mg/m^3 (15 minutes maximum). The Target Value for air is 20 μg/m^3, for soil 0.05 μg/kg, for surface water 0.5 μg/litre, and for groundwater 0.2 μg/litre. Potable water may not contain more than 1 mg/m^3.

In general, the concentrations of methylene chloride in the vicinity of industrial plants did not fluctuate in the last few years. However, at some locations the Target Value was exceeded. Emissions to air were reduced by 50 per cent from 1984 to 1988. In 1988 the Target Value was exceeded by 20 companies, in 1992 by five to ten companies. This reduction in discharges to air is (and will be) realized mainly by actions of industry. These actions are a result of the Hydrocarbons 2000 Action Programme [HAP 20(X)] and the Integrated Environmental Tasks (IET). The HAP 2000 implies the reduction of volatile organic carbons by 60 per cent in 2000 (since 1981). These VOCs include methylene chloride. In the IET, the emission reduction targets (since 1985) for industry are 80 per cent in 2000 and 90 per cent in 2010 in air.

As a result of replacing CFCs by methylene chloride as a propellant, the discharge of DCM from diffuse sources will be increased by 26 per cent. Because the current policy is primarily focused on industrial sources, the emission reduction for DCM will not be 80 per cent in 2000/2010 as stated in the National Environmental Policy Plan (NEPP, 1990-1994), but only 35 per cent in 2000. Additional actions on diffuse sources are therefore required, and policy is being made to achieve the reduction targets.

Short-term exposure concentrations during the use of spray cans in buildings and houses are sometimes relatively high. Levels of DCM can exceed the Occupational Exposure Limit during use of paint strippers containing DCM to refinish furniture and woodwork, and during activities in plastics processing.

The discharges of methylene chloride to water are very small (<3 per cent of the total discharge). The IET targets are 50 per cent reduction in 2000 and 2010 (since 1985). The emission of DCM to water was reduced by 50 per cent in the period 1984-1988. This is primarily a result of actions taken by industry. The emission reduction target for industry in 2000 and 2010 will be achieved. The Air Quality Standard is 20 μg/m^3.

Norway

The occupational exposure limit is 35 ppm.

The National Pollution Control Authorities are planning to require child-proof fastenings for containers of preparations with ≥ 1 per cent methylene chloride. This is an adaption to EEC Directive 91/442/EEC.

Sweden

The Swedish government has from January 1, 1993, banned the use of methylene chloride as such or in composite chemical products sold for consumer use. All occupational use of methylene chloride is to be prohibited from January 1, 1996. The prohibitions are entered in the Ordinance on Certain Chlorinated Solvents (Swedish Code of Statutes, SFS 1991:1289). Trichloroethylene is being phased out in parallel with methylene chloride.

The occupational exposure limit is 35 ppm, expressed as an 8-hour Time Weighted Average. Emissions from occupational use of methylene chloride are regulated by the Swedish Environmental Protection Act. Certain industrial activities must be reported or require a permit from the authorities. The permit and conditions of operation (including maximum allowable emissions of certain substances) are assessed in each individual case.

The Institute for Environmental Medicine (IMM) has proposed a medically based low risk level for methylene chloride of 100 ppb (350 $\mu g/m^3$) for ambient air.

According to the Code of Statutes issued by the National Food Administration, the maximum allowed residue of methylene chloride in decaffeinated coffee and tea is 5 mg/kg.

The imported amount of methylene chloride has decreased substantially the last few years, from approximately 2500 tonnes in 1988 to less than 1000 tonnes in 1991 (National Chemicals Inspectorate, Sweden). Methylene chloride is not produced in Sweden.

Non-halogenated solvents have been substituted for methylene chloride in products such as paints, adhesives, lubricants, anti-corrosive paint, cleaning agents, vulcanizing agents, etc.

In the manufacturing industry, methylene chloride is used for paint stripping and degreasing and cleaning applications. Methylene chloride for paint stripping is often replaced by alternative methods of stripping, e.g. blasting or freezing techniques. Methylene chloride in degreasing applications is replaced mainly by water-based cleaning systems (alkaline, neutral or acid).

In the pharmaceutical industry in Sweden, intensive efforts are under way to find substitutes for methylene chloride. In the production of pharmaceutical substances, methylene chloride will mainly be replaced by other non-halogenated organic solvents. In the coating of tablets, water- or alcohol-based systems will be used.

The phasing out of methylene chloride use in the polyurethane industry is in progress and will be accomplished within one to two years. Reported substitutes in use are dibasic esters and NMP for cleaning applications, and high solid agents for mould release applications

Switzerland

The Federal Office of Public Health has banned the use of chlorinated and brominated compounds as an ingredient in cosmetic products for skin and hair treatment.

In the Regulation on Constituents and Contaminants in Foodstuff (Fremd- und Inhaltsstoffverordnung) there are some residue values for methylene chloride. Decaffeinated coffee and tea may not contain more than 10 mg/kg methylene chloride (limit value); the limit value for extracts for decaffeinated coffee and tea is 5 mg/kg. The tolerance level for beer is 0.005 mg/kg.

Potable water may not contain more than 0.025 mg/kg of volatile halogenated compounds (tolerance level).

The occupational exposure limit of methylene chloride is 100 ppm, expressed as an 8-hour Time Weighted Average (Swiss MAK list 1992).

In the ordinance relating to Environmentally Hazardous Substances (Ordinance on Substances, Osubst), the use of methylene chloride for detergents and for cleaning agents which are discharged with wastewater is banned.

In the Clean Air Ordinance, methylene chloride is classified in the highest class 1. This means that the concentration in waste gas may not exceed 20 mg/m^3 at a mass flow of 100 g/h or more.

In the Ordinance for Waste Water Discharge, the limit value for effluents discharged into public sewers for chlorinated solvents is 0.1 mg/litre (measured as Cl). The water quality criteria for surface water flows and impounded river water is 0.005 mg/litre (measured as Cl).

In the Ordinance for Water Protection from Hazardous Liquids, methylene chloride is assigned to water hazard category 1. This category includes liquid substances which affect the water quality in small quantities.

Switzerland would like to strengthen control over the use of chlorinated solvents in general. For this reason, a revision of the Ordinance on Substances will be proposed which will force the suppliers of chlorinated solvents to take back these solvents after use in order to guarantee a controlled discharge or recycling. In addition, mixing of chlorinated solvents after use will be prohibited.

United Kingdom

The current view in the United Kingdom is that the compound does not present either a carcinogenic hazard to humans, or a hazard to the environment. It is for these reasons that the UK considers the use of methylene chloride in consumer products, paint stripper and aerosol cosmetics acceptable. Other, non-carcinogenic, adverse effects can occur at the higher, longer-term levels of exposure that may be found in the workplace, but these can be prevented by the enforcement of occupational health legislation, including an occupational exposure limit.

Methylene chloride does not pose any serious hazard to the environment. It is biodegradable, non-bioaccumulative, and has a low ozone depletion potential. It does not contribute to low-level ozone formation, and the global warming potential is effectively nil.

The UK Occupational Exposure Limit has been set at 100 ppm (8-hour Time Weighted Average) and 300 ppm (short-term exposure, 15-minute reference period). In consumer products, methylene chloride is allowed at concentrations up to 35 per cent for use in aerosols of cosmetic products under the terms of the EC Cosmetics Directive (76/768/EEC).

Most of the substitutes suggested have major problems associated with them. Many are flammable, and some have a demonstrably greater environmental impact than methylene chloride, for example hydrocarbons that contribute to low-level ozone formation. Others have poorly understood toxicity or environmental effects compared with methylene chloride. The use of blasting techniques in paint stripping can result in heavy metal dusts, while caustic soda in consumer products presents well known health and safety hazards. The UK also notes that concern has been expressed over the irritant properties of NMP. In the semiconductor industry, chronic eye irritation and headaches were reported in workers exposed to 0.7-1.5 ppm NMP(Beaulieu and Schmerber 1991). Severe dermatitis can occur in workers following prolonged or repeated skin contact to NMP (Leira et al. 1992).

United States

In order to help reduce environmental and occupational exposures to methylene chloride, a number of US government agencies and industry groups have taken regulatory actions and/or voluntary measures in an effort to promote public health. A brief summary of these activities is as follows:

Worker Exposure. The Occupational Safety and Health Administration (OSHA) has established a number of standards for workers covering a range of exposure intervals. A permissible exposure level-time weighted average (PEL-TWA) of 500 ppm was established in 1971. The PEL-TWA is an allowable exposure level in workplace air averaged over an 8-hour shift. OSHA also established a ceiling value (not to be exceeded in the workplace) of 1000 ppm. In 1991, OSHA proposed more stringent standards for methylene chloride, a PEL-TWA of 25 ppm, and a short-term exposure limit (STEL) of 125 ppm (FR 56:57036-57141 (1991). An STEL is not to be exceeded in any 15-minute sampling period (OSHA 1991). Other, non-binding guidelines for worker protection have been issued by the American Conference of Governmental Industrial Hygienists (ACGIH) and the National Institute for

Occupational Safety and Health (NIOSH). The ACGIH advises that 8-hour time-weighted exposures not exceed 50 ppm (ACGIH 1990). NIOSH has established a level immediately dangerous to life or health (IDLH) at 5000 ppm and recommended the lowest feasible level obtainable as the recommended exposure limit (REL) (NIOSH 1985, 1986). The IDLH is defined as the maximum environmental concentration of a contaminant from which one could escape within 30 minutes without any escape-impairing symptoms or irreversible health effects (ATSDR 1991).

The Environmental Protection Agency (EPA) considers methylene chloride a toxic substance and regulates its discharge to surface water. EPA established Ambient Water Quality Criteria that set acceptable concentrations of methylene chloride in water for various purposes. These are 0.19 μg/litre for water and fish and 1.6 μg/litre for fish only. Drinking water regulations set a goal that there be no methylene chloride in drinking water – Maximum Contaminant Level Goal (MCLG) is 0 mg/litre. The maximum tolerated level, Maximum Contaminant Level (MCL) is as reported 0.005 mg/litre (EPA 1992). Under the Comprehensive Environmental Response, Compensation and Liability Act, persons are required to report to EPA any spill or discharge of methylene chloride which equals or exceeds 1.000 lbs. The 1990 Clean Air Act Amendments designated methylene chloride as a hazardous air pollutant requiring EPA to promulgate emission standards for its release to air. Several states have already established acceptable ambient air concentrations for methylene chloride. EPA's Office of Pollution Prevention and Toxics, in co-operation with the Consumer Product Safety Commission (CPSC), is currently assessing the hazards of substances used as paint strippers, including methylene chloride and its substitutes, in order to pursue risk reduction throughout the paint stripping industry by identifying the relative risks of paint stripping chemicals and by providing improved information on safe use practices.

The Food and Drug Administration (FDA) is responsible for regulating the chemical substances permitted in food additives, drugs and cosmetics. FDA banned the use of methylene chloride in cosmetic products, particularly hair sprays, in 1989 (54 FR 27328). FDA set limits for residual methylene chloride in foods in 1967 (32 FR 12605) for instances in which methylene chloride may be used as an extraction solvent to produce hops, spices and decaffeinated coffee (ATTSDR 1991). Residual methylene chloride is limited to a level not to exceed 10 parts per million (ppm) in decaffeinated roasted coffee and in decaffeinated soluble coffee extract (instant coffee) [21 CFR 173.255(c)].

The Consumer Product Safety Commission (CPSC) regulates hazards in consumer products. CPSC issued a statement of interpretation and enforcement policy in 1987 advising manufacturers that products which expose consumers to a significant amount of methylene chloride vapour must bear a label advising of the potential risk of cancer, explaining factors that control the degree of risk, and stating the precautions to be taken.

CPSC is working with EPA to gather exposure and toxicity information that will be used to assess the relative health hazards of methylene chloride and substitute chemicals used in paint strippers and adhesive removers. A CPSC report on consumer behaviour in paint stripper use, prior to and following placement of cautionary labelling on methylene chloride paint strippers, mentions a change in behaviour in between 8 and 13 per cent of consumers as a response to labelling (Pollack-Nelson 1992). CPSC is also developing recommendations to enhance the potential for labels to bring about proper ventilation practices and to revise existing consumer education materials on paint strippers.

The US EPA is conducting an assessment of the risks of chemicals currently used as paint strippers in the consumer and small commercial shop market. This investigation is called Consumer/Small Shop Paint Stripping Use Cluster. One goal of this assessment is the preparation of a report identifying and comparing the relative risks of each chemical, and describing ways to reduce the risks associated with the use of each chemical. A second goal of this investigation is the implementation by industry of voluntary, readily achievable risk reduction measures, including: (1) glove testing to determine the efficacy of protective equipment against actual paint stripping formulations (which often contain multiple solvents acting in concert); and (2) improved labelling identifying hazards and providing easy-to-follow instructions for safe use.

In response to information indicating that the use of NMP as a substitute for methylene chloride in paint strippers could present a significant risk of reproductive and developmental harm to humans, EPA initiated a risk assessment of NMP in 1992. The final version of the Lifecycle Analysis and Pollution Prevention Assessment for NMP in Paint Stripping was released to the public on 10 September 1993. EPA concluded that dermal exposure to NMP in paint strippers does present a risk of reproductive or developmental harm, but also concluded that the identification and use of impervious gloves could significantly reduce that risk. Accordingly, EPA is pursuing voluntary action by industry in conjunction with the overall activity of the Paint Stripping Use Cluster. EPA has also entered into a consent order with industry to provide for additional testing of NMP to determine other possible health effects.

Commission of the European Union

The EEC Directive on classification and labelling of dangerous substances regulates methylene chloride. Directive 76/768 EEC on cosmetic products restricts the use of methylene chloride in cosmetic aerosols. The maximum authorized concentration in the finished product in 35 per cent w/w.

According to a proposal for the 13th amendment of Directive 76/769/EEC (concerning restrictions on the marketing and use of certain dangerous substances and preparations), the Commission will examine the use of methylene chloride in consumer products three years after the Directive has come into force.

The European regulations on classification, packaging and marking of dangerous substances list methylene chloride as a carcinogen in the third category. It should be marked Xn-R40 (possibility or irreversible effects)-S:(-2)23-24/25-36/37.

Directive 88/344/EEC (with amendment 92/115/EEC) regulates the use of extraction solvents in preparation of foodstuffs. The Directive issues a list of solvents that Member States must permit, to the exclusion of all others. In addition, the Directive issues maximum residue limits in the extracted foodstuff of, among others, methylene chloride. Maximum residue limits of methylene chloride in decaffeination of or removal of irritants and bitterings from coffee is 2 mg/kg in roasted coffee and 5 mg/kg in tea. In the preparation of flavourings from natural flavouring materials, the maximum residue limit of methylene chloride is 0.02 mg/kg.

Industry Risk Reduction Initiatives

The Business and Industry Advisory Committee to the OECD (BIAC) has reported that all producers of methylene chloride in Member countries subscribe to the Responsible Care Programme of Action of the Chemical Industry.

Responsible Care is the Chemical Industry's commitment to continuous improvement in all aspects of health safety and environmental protection.

Membership of a National Chemical Industry Association is conditional upon a signed commitment to the Guiding Principles of the Responsible Care programme by the chemical producer.

The Guiding Principles require a pledge that companies will make health safety and environmental performance an integral part of overall business policy and that both employees and contractors to the company will be made aware of this.

The Guiding Principles require companies

- to conform to statutory regulations
- to operate to the best practices of the industry
- to assess the actual and potential health, safety and environmental impact of their activities and products
- to work closely with the authorities and the community in achieving the required levels of performance
- to be open about activities and give relevant information to interested parties.

Codes of practice and guidance notes based on industry experience are made available to member companies which cover all relevant factors of the industry.

Amongst these factors are customer use, waste management and disposal and Product Stewardship. Product Stewardship is practised by individual companies. Many activities of Product Stewardship are also carried out by the trade organisations ECSA, European Chlorinated Solvents Association, HSIA, Halogenated Solvents Industry Alliance, and JAHCS, Japan Association for Hygiene of Chlorinated Solvents.

Product Stewardship involves assessing all the information on the health and environmental aspects of a product and providing guidelines on the steps required to protect those who use the product, the general public and the environment.

In the case of methylene chloride, specific help is available from producer companies in the following:

Distribution – in ensuring that mode of transport and packaging is that which meets national and international requirements (ADR/RID,[1] IMO, UN) to enable safe transport of methylene chloride.

Storage – in providing expertise in the detailed requirements to ensure methylene chloride is received and stored by the customer in an appropriate and soundly engineered manner.

Handling – in providing guidance with respect to appropriate safety and protective equipment, in measuring and monitoring personal exposure in use, measurement of emissions into the environment, safety in use, in recycling techniques, emission reduction techniques and correct waste disposal. Most companies now have arrangements to recycle solvent from small tonnage users who are unable to afford their own recovery equipment, via approved solvent recoverers. Waste disposal is arranged via approved disposal companies whose modus operandi meets national regulatory requirements.

Practical research

Producer companies have a long track record of carrying out experiments simulating consumer use in order to determine patterns of use and exposure regimes, and potential hazards and risks. Research covers not just industrial use of methylene chloride but also consumer use, in particular use in paint strippers and aerosols. The result of this work has been either published or made available to those who would benefit from this additional knowledge.

Examples are:

Review of aerosol propellants and solvents (ICI, August 1963)

Methylene chloride in aerosol use (DOW, May 1975 and March 1976)

Methylene chloride in paint strippers (ICI, 1990 and 1993)

There are many other examples similar to the above.

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[1] European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR), and Regulations concerning the International Carriage of Dangerous Goods by Rail (RID).

Toxicological research

Producer companies have been involved for over 20 years with researching and using test animals to determine the effects on human health. Work includes study on uptake and excretion by inhalation and skin permeation, central nervous system effects and carboxyhaemoglobin formation. The health of exposed workers has also been investigated and reported.

Industrial users have produced and continually updated epidemiological studies (Eastman-Kodak and Celanese Corp) covering almost 40 years of methylene chloride's use as a production solvent.

Long-term animal studies

A joint industry group led by Dow Chemical USA, including Vulcan, Diamond Shamrock, LCP and ICI, sponsored chronic inhalation studies in the rat and hamster (Burek et al. 1980, Nitsche et al. 1982). A methylene chloride users trade association sponsored studies (chronic ingestion of methylene chloride in drinking water) in the rat and mouse (National Coffee Association 1982). Investigation of response to methylene chloride in different species has been carried out by both Dow in the US (Reitz 1986 et seq.) and ECETOC (European Ecology and Toxicology Centre, Akzo, Atochem, Hoechts, Huls, ICI Solvay). A further study to identify how the glutathione route in the mouse is responsible for carcinogenicity in this species is being funded jointly by all methylene chloride producers in OECD countries (members of Halogenated Solvent Industry Alliance, Japan Association of Hygiene of Chlorinated Solvents, and European Chlorinated Solvent Association).

The total expenditure on all the above research to date exceeds US$ 10,000,000.

Industry uses data derived from the above research to ensure chemicals are used appropriately in their various end uses and that the appropriate chemicals are chosen in fulfilling various needs both within industry and by consumers.

Alternative chemicals and methods for risk reduction in use

Paint stripping

A large number of chemicals are available for use as an alternative to methylene chloride for paint stripping applications. These are listed in Appendix A. However, the chemicals have both advantages and disadvantages in comparison with the use of methylene chloride.

Caustic-based strippers (sodium hydroxide, calcium hydroxide) are available in paste form or in powder form which the consumer can make into a paste. These strippers are non-flammable, can remove multiple layers of paint, and do not expose the user to lead pigments. However, these substances are corrosive and can cause burns and potential permanent damage to soft and mucous tissue. They can damage substrates, especially wood (raises grain, darkens some woods). They are not effective on all types of paints. The caustic-based strippers may also make heavy metals present in the paints, soluble. Disposal of the waste therefore increases the availability of e.g. lead in the environment.

N-methyl pyrrolidone (NMP) is a non-chlorinated organic stripper in use. NMP offers a long open time for working, it can strip multiple paint layers and there is no risk of resolving lead-based pigments. NMP is most effective on water-based paints and acrylics. NMP is however less effective on alkyds, PU paints and varnishes. It may cause harmful health effects (by skin penetration). There is some evidence of teratogenicity.

Di-basic esters can strip multiple layers but works slowly. They may cause CNS effects and have an unknown chronic toxicity.

Non-chlorinated solvent-based strippers (toluene, xylene, acetone, ketone mixtures) will work faster than NMP or dibasic esters on certain paints. However, these solvents are flammable and are not effective on certain types of paint. There are known adverse acute CNS effects. These substances also tend to have a higher photochemical ozone creation potential than methylene chloride.

Hot air strippers are easy to use and involve no chemical hazards to handle. They are effective on many types of paint. The use may, however, in some cases damage the substrate and the hot air method is not effective on metal substrates.

Blow torches enable the removal of multiple coats and involve no chemical hazards in handling. However, there is a risk of fire, damage to substrate and it may be less effective on certain paints. There is also a danger of exposure to lead pigment and decomposition fumes.

Manual and mechanical abrasion techniques are cheap but labour intensive. The method may involve damage to substrate and exposure to dust.

The same alternative chemicals and methods as in consumer paint stripping are used in industrial paint stripping. In addition, the following methods may be mentioned.

The use of *particle blasting* (plastic, natural or inorganic particulate matter) enables relatively rapid stripping of all types of paint without leaving a chemical residue. The method requires a high capital cost as special equipment is needed. Dust is generated and the substrate may be damaged.

Cryogenic stripping involves the use of liquid nitrogen to thermally loosen paint bonded to the substrate. There is no chemical waste and it works on most paints. The capital cost and running costs are however high. The thermal shock may cause damage to the substrate.

Exposure reduction to methylene chloride in PU foam production:

Exposure reduction is achievable in cleaning operations by

a) minimizing the amount of solvent being used in cleaning.

b) using closed containers to handle fresh and used solvent.

c) ensuring adequate ventilation and carrying out atmospheric measurements to ensure correct working practices.

Exposure reduction in foam production may be achieved by

a) ensuring the production line as far as the cut-off saw is enclosed and the ventilation rate is adequate to meet the OEL (occupational exposure limit) for the isocyanate. This will ensure the methylene chloride exposure is minimal.

b) ensuring adequate ventilation in the cure hall to achieve the OEL for methylene chloride where manual or fork lift truck handling of the blocks is carried out.

c) A number of companies have installed remotely operated overhead cranes to handle foam blocks straight off the production line thus removing the operators further from the source of emission.

PU foam blowing

PU foam may be produced without the use of an ABA (auxiliairy blowing agent). The foam may be produced relying on in-situ generated CO_2. There are technical limits on the maximum amount of water which may be added to the formulation, which limits the lowest density to 21-22 kg/m^3.

The advantage of this technique is that no blowing agent is needed. One disadvantage is that there may be a risk of spontaneous combustion of the foam. (The ABA also has a cooling action which lowers the maximum exotherm generated.)

PU foam may be produced by AB technology. AB technology uses the reaction of formic acid with the isocyanate to generate in-situ carbon monoxide. With this method it is possible to produce lower density foam (17 kg/m^3). However, carbon monoxide is highly toxic and has a cumulative effect during exposure.

Acetone as the auxiliary blowing agent has been developed for use in the flexible block foam PU industry. Formulation changes are required to make allowance for the higher boiling point of acetone. The use of acetone requires the production plant to be suitable for flammable solvent vapours.

Additional CO_2 may be used as the auxiliary blowing agent. The production rate may however be slower.

Pharmaceutical industry

Methylene chloride is used in the pharmaceutical industry as an extraction medium, in tablet/pill coating and as a process solvent. It is recycled in closed processes.

Other solvents such as alcohols, hydrocarbons or ketones may be used as alternative extraction solvents in specific cases. Water or alcohol may be used as alternatives to methylene chloride in the tablet coating process. Other organic solvents or mictures of solvent may be used in certain cases as alternatives to methylene chloride use as a process solvent. The changing of a process solvent requires a relicensing of the production route. This may be a lengthy process.

Cellulose triacetate industry

There are no technically or commercially viable alternatives to methylene chloride or methylene chloride/methanol blends in the cellulose triacetate industry.

Polycarbonate production

There are no technically or commercially viable alternatives to methylene chloride in polycarbonate production. The process is carried out in closed systems so occupational exposure during normal plant operations is low and well within occupational exposure standards.

Alternative metal cleaning and degreasing processes

The *aqueous cleaning* process is very contamination specific in that the cleaning solution is normally formulated for a particular soil being removed from a component with a particular material of construction. High pressure sprays are normally required for parts with small blind holes and complex openings to ensure penetration. Process control is very important with aqueous solutions to ensure good cleaning. Care must be taken with parts after cleaning to ensure water residue does not lead to corrosion of the parts. For this reason, drying is important and usually consists of air knives and hot air.

Pre-treatment of water may be necessary (softening and de-ionization) to prevent clogging of spray jets and to avoid stains and ionic residue.

The management of waste water must be considered very carefully with the aqueous cleaning process. The soils (solids, grease, fats, etc.) must be separated from the effluent water stream. This can require ultrafiltration.

The *alcohols* mainly used for cleaning have flashpoints between -9 and 14^{o}C, which make them all highly flammable. This means that the equipment must meet electrical classification regulations and the work place must comply with existing regulations.

Hydrocarbons with a flashpoint higher than 55^{o}C used in cold dip process can be used without special equipment. However, the liquid will have very long drying times and it may be necessary to remove them from the workpiece with water. In some systems the hydrocarbon is removed by hot air drying. In this case, because the fluid is taken above its flashpoint, the hydrocarbon vapour-air mixture has to be kept well below the low explosion limit.

Annex A (TO CHAPTER 5)

Methylene Chloride Risk Reduction Activities: Summary Tables

ENVIRONMENTAL MEDIA
SOURCE: DRINKING WATER

COUNTRY	ACTIONS
Australia	
Austria	The sum of the concentrations of 14 different halogenated aliphatic hydrocarbons, including methylene chloride, must not exceed 30 micrograms/litre in drinking water.
Belgium	
Canada	The drinking water quality guideline is 50 µg/litre. For water used for livestock, the interim agricultural water quality guideline for methylene chloride is also 50 µg/litre.
Finland	Methylene chloride in domestic water must not exceed 20 µg/litre.
Denmark	
France	
Germany	The sum total of methylene chloride, perchloroethylene, 1,1,1-trichloroethane must not exceed 0.01 mg/litre.
Greece	
Iceland	
Ireland	
Italy	
Japan	Maximum acceptable concentration in drinking water is 0.02 mg/litre.
Luxembourg	
Mexico	
Netherlands	Potable water may not contain more than 1 mg/m^3.
New Zealand	
Norway	
Portugal	
Spain	
Sweden	
Switzerland	Potable water may not contain more than 0.025 mg/kg of volatile halogenated compounds (tolerance level).
Turkey	
United Kingdom	
United States	Ambient Water Quality Criteria set acceptable concentrations of methylene chloride in water for various purposes and established a maximum contaminant level of 0.005 mg/litre for drinking water.
European Union	

	ENVIRONMENTAL MEDIA SOURCE: SURFACE WATERS
COUNTRY	**ACTIONS**
Australia	
Austria	
Belgium	
Canada	Interim Water Quality Guidelines 98 µg/litre and 50 µg/litre.
Finland	
Denmark	
France	
Germany	Methylene chloride is assigned to water-hazardous-category-2, as a substance hazardous to water.
Greece	
Iceland	
Ireland	
Italy	
Japan	Environmental Quality Standard for water is 0.02 mg/litre or less.
Luxembourg	
Mexico	
Netherlands	
New Zealand	
Norway	
Portugal	
Spain	
Sweden	
Switzerland	The water quality criteria for surface water flows and impounded river water is 0.005 mg/litre (measured as Cl). The limit value for effluents discharged into public sewers and surface waters for chlorinated solvents is 0.1 mg/litre (measured as Cl).
Turkey	
United Kingdom	
United States	Spill or discharge of methylene chloride which equals or exceeds 1000 lbs must be reported to EPA.
European Union	

ENVIRONMENTAL MEDIA
SOURCE: AMBIENT AIR

COUNTRY	ACTIONS
Australia	The Environmental Protection Authority has established a maximum ground level concentration for methylene chloride of 24 mg/m^3.
Austria	
Belgium	
Canada	
Finland	
Denmark	Agreement to reduce total Danish emissions of VOC by 50%.
France	
Germany	For installations subject to licensing, concentration in waste gas may not exceed 20 mg/m^3 at a mass flow of 0.1 kg/h. For installations not subject to licensing, a maximum of 50 mg/m^3.
Greece	
Iceland	
Ireland	
Italy	
Japan	
Luxembourg	
Mexico	
Netherlands	The air quality standard is 20 μg/m^3.
New Zealand	
Norway	
Portugal	
Spain	
Sweden	Maximum allowable emissions are assessed in each individual case.
Switzerland	The concentration of methylene chloride in the waste gas may not exceed 20 mg/m^3 at a mass flow of 100g/h or more.
Turkey	
United Kingdom	
United States	The 1990 Clean Air Act Amendments designated methylene chloride as a hazardous air pollutant requiring EPA to promulgate emission standards for its release to air. Several states have already established acceptable ambient air concentrations for methylene chloride.
European Union	

ENVIRONMENTAL SOURCES
SOURCE: FOODSTUFFS

COUNTRY	ACTIONS
Australia	
Austria	
Belgium	
Canada	Permitted maximum residues are: 30 ppm in spice extracts, 2.2% in hop extracts and 10 ppm in decaffeinated roasted coffee, decaffeinated instant coffee, decaffeinated tea leaves and instant tea.
Finland	Permitted maximum residues are: 2 mg/kg in coffee, 5 mg/kg in tea and 0.02 mg/kg in flavourings.
Denmark	
France	
Germany	
Greece	
Iceland	
Ireland	
Italy	
Japan	In accordance with the "Food Sanitation Law" (Ministry of Health and Welfare), methylene chloride is not allowed to be used in the foodstuff industries even for indirect uses such as extractant or process solvent.
Luxembourg	
Mexico	
Netherlands	
New Zealand	
Norway	
Portugal	
Spain	
Sweden	Maximum allowed residue of methylene chloride in decaffeinated coffee and tea is 5 mg/kg.
Switzerland	Maximum residue values for methylene chloride are: decaffeinated coffee and tea, 10 mg/kg; extracts for decaffeinated coffee and tea, 5 mg/kg. The tolerance level for beer is 0.005 mg/kg.
Turkey	
United Kingdom	
United States	Residual methylene chloride is limited to a level not to exceed 10 ppm in decaffeinated roasted coffee and in decaffeinated soluble coffee extract (instant coffee).
European Union	Methylene chloride is on a list of permitted extraction solvents. Maximum residue limits issued are 2 mg/kg in roasted coffee and 5 mg/kg in tea. In the preparation of flavourings from natural flavouring materials, the maximum residue limit of methylene chloride is 0.02 mg/kg.

ENVIRONMENTAL SOURCES
SOURCE: MISCELLANEOUS

COUNTRY	ACTIONS
Australia	Methylene chloride is classified as a dangerous good for transportation by road and rail.
Austria	
Belgium	
Canada	Transportation regulated by the "Transportation of Dangerous Goods Act". Pesticides containing methylene chloride must be labelled. Organohalogen compounds are on the List of Prohibited Substances for Ocean Dumping, 1988. Environmental Quality Criteria for contaminated sites.
Finland	
Denmark	
France	
Germany	A ban on mixing of wastes or residues of methylene chloride with other materials. Obligation that distributors accept returned solvents.
Greece	
Iceland	
Ireland	
Italy	
Japan	
Luxembourg	
Mexico	
Netherlands	
New Zealand	
Norway	
Portugal	
Spain	
Sweden	
Switzerland	Guide for the disposal of waste water, solid waste and used air with solvent cleaning plants for textiles (1987). Guide for water baths for the removal of grease: substitutes for solvents, treatment and disposal of waste water and solid waste (1992), published by the Swiss Federal Office of Environment, Forests and Landscape.
Turkey	
United Kingdom	
United States	
European Union	

	PRODUCTS SOURCE: CONSUMER PRODUCTS
COUNTRY	ACTIONS
Australia	Pressurized spray packs available for consumer use, regulated as Schedule 5 poisonous substance – requires caution in storage, handling and use.
Austria	
Belgium	
Canada	Information bulletin, "Health Hazard Posed by Paint Strippers and Spray Paints".
Finland	Regulations concerning cosmetic products are the same as in the EU.
Denmark	Content of VOC in household products (paint strippers) should be reduced to a minimum within three years.
France	
Germany	A voluntary agreement between the administration and the chemical industry not to use methylene chloride in cosmetic products. Preparing ordinance which provides for prohibition and limitation of various aliphatic chc's, including methylene chloride. The ordinance puts a ban on consumer use. As an exemption, the draft allows the professional use of methylene chloride and its preparations to remove certain paints for which no alternative methods are available.
Greece	
Iceland	
Ireland	
Italy	
Japan	
Luxembourg	
Mexico	
Netherlands	
New Zealand	
Norway	Plans to require child-proof fastenings for containers of preparations with >1% methylene chloride.
Portugal	
Spain	
Sweden	The use of methylene chloride as such, or in composite chemical products sold for consumer use, is banned from 1 January 1993.
Switzerland	The use of chlorinated and brominated compounds as ingredients in cosmetic products for skin and hair treatment is banned.
Turkey	
United Kingdom	
United States	Products for consumer use containing 1% or more of methylene chloride must be labelled with information regarding the potential risk of cancer, factors that can control the degree of risk, and the precautions to be taken. The use of methylene chloride in cosmetic products, particularly hair sprays, was banned in 1989.
European Union	The maximum authorized concentration in cosmetic aerosols in the finished product is 35% w/w.

	PRODUCTS SOURCE: OTHER CHEMICAL PRODUCTS
COUNTRY	ACTIONS
Australia	
Austria	A ban on paints, coating materials, wood preservatives and removers which contain chlorinated hydrocarbons.
Belgium	
Canada	Included on the ingredient disclosure list at a level 0.1% by weight as a part of the Work Place Hazardous Materials Information System.
Finland	
Denmark	
France	
Germany	
Greece	
Iceland	
Ireland	
Italy	
Japan	Products containing 5% or more methylene chloride must bear a label for notice of handling and use according to the "Industrial Safety and Health Law."
Luxembourg	
Mexico	
Netherlands	
New Zealand	
Norway	
Portugal	
Spain	
Sweden	All occupational use of methylene chloride is to be prohibited from January 1, 1996.
Switzerland	The use of methylene chloride for detergents and for cleaning agents which are discharged with wastewater is banned.
Turkey	
United Kingdom	
United States	
European Union	

ENVIRONMENTAL HEALTH
SOURCE: OCCUPATIONAL EXPOSURE

COUNTRY	ACTIONS
Australia	The OEL is 50 ppm (8-hour TWA).
Austria	The OEL is 100 ppm (8-hour TWA).
Belgium	The recommended OEL is 50 ppm (8-hour TWA).
Canada	TWA over a full work shift must not exceed 50 ppm. The short-term exposure limit (STEL) is 500 ppm.
Finland	The OEL is 100 ppm (8-hour TWA) and 250 ppm (15-minute TWA).
Denmark	
France	The recommended OEL is 100 ppm (8-hour TWA) and 500 ppm (10- to 15-minute TWA).
Germany	The OEL is 100 ppm (8-hour TWA). The biological workplace tolerance value (BAT-Wert) is defined by the CO-Hb level in blood which may not exceed 100 µg/dl.
Greece	
Iceland	
Ireland	
Italy	
Japan	The environmental evaluation standard for workplaces is 100 ppm.
Luxembourg	
Mexico	
Netherlands	The OEL is 100 ppm (8-hour TWA) and 500 ppm (15-minute maximum).
New Zealand	
Norway	The OEL is 35 ppm (8-hour TWA).
Portugal	
Spain	
Sweden	The OEL is 35 ppm (8-hour TWA).
Switzerland	The OEL is 100 ppm (8-hour TWA).
Turkey	
United Kingdom	The OEL is 100 ppm (8-hour TWA) and 300 ppm (short-term exposure, 15-minute reference period).
United States	OSHA has established a permissible exposure level of 500 ppm (8-hour TWA). The exposure level of 1000 ppm must not be exceeded (ceiling value). OSHA has proposed more stringent standards, a PEL-TWA of 25 ppm, and a short-term exposure limit (STEL) of 125 ppm. The ACGIH advises an 8-hour TWA exposure not to exceed 50 ppm. NIOSH has established a level immediately dangerous to life or health (IDLH) at 5000 ppm and recommended the lowest feasible level obtainable as the recommended exposure level (REL).
European Union	

APPENDIX 1

Alternative Chemicals or Processes in Use

The possible alternatives listed below have not been evaluated from a toxicological or ecotoxicological point of view. The use of alternative chemicals or processes may pose other risks to human health or to the environment. It is therefore important to evaluate and compare risks carefully before making substitutions. It is also important to investigate in each case whether a particular substitute can be used, with regard to its technical efficacy.

Tables A1 and A2 show the aqueous cleaners most commonly used in industry, and an overview of aqueous cleaners in general, emphasizing the different tasks of the respective cleaners.

Paint stripping

Alternative chemicals

- Aqeous solutions of sodium hydroxide, potassium hydroxide or inorganic hydroxides
- N-methyl pyrrolidone (NMP)
- Dibasic esters (DBE)
- Toluene
- Xylene
- Acetone
- Ketone mixtures
- Furfuryl alcohol

Alternative processes

- Cryogenic stripping (low temperature treatment with liquid nitrogen)
- Abrasive blasting technology [dry (plastic, natural or inorganic particulate) or liquid blasting media]
- Use of decals instead of paint for ornamentation or identification
- Use of removable floors and wall coverings
- Burning-off in special furnaces
- Hot air guns or blow torches
- Oxidative degradation in mineral acids or molten salt

Pharmaceutical industry

Alternative chemicals

- Non-halogenated solvents
- Water-based solutions

Nutrition industry

Alternative chemicals

- Alcohols (ethanol or methanol)
- Diethylether
- Ethylacetate
- Ethylmethylketone
- Acetone
- Low boiling hydrocarbons
- Water-based solutions

Alternative processes

- Fluid extraction (e.g. carbon dioxide)
- Pressing process

Polyurethane industry

Alternative chemicals

- Alcohols (ethanol or isopropanol)
- High solid (wax dispersed in a silicone or paraffin oil)
- Carbon dioxide

Metal cleaning and degreasing

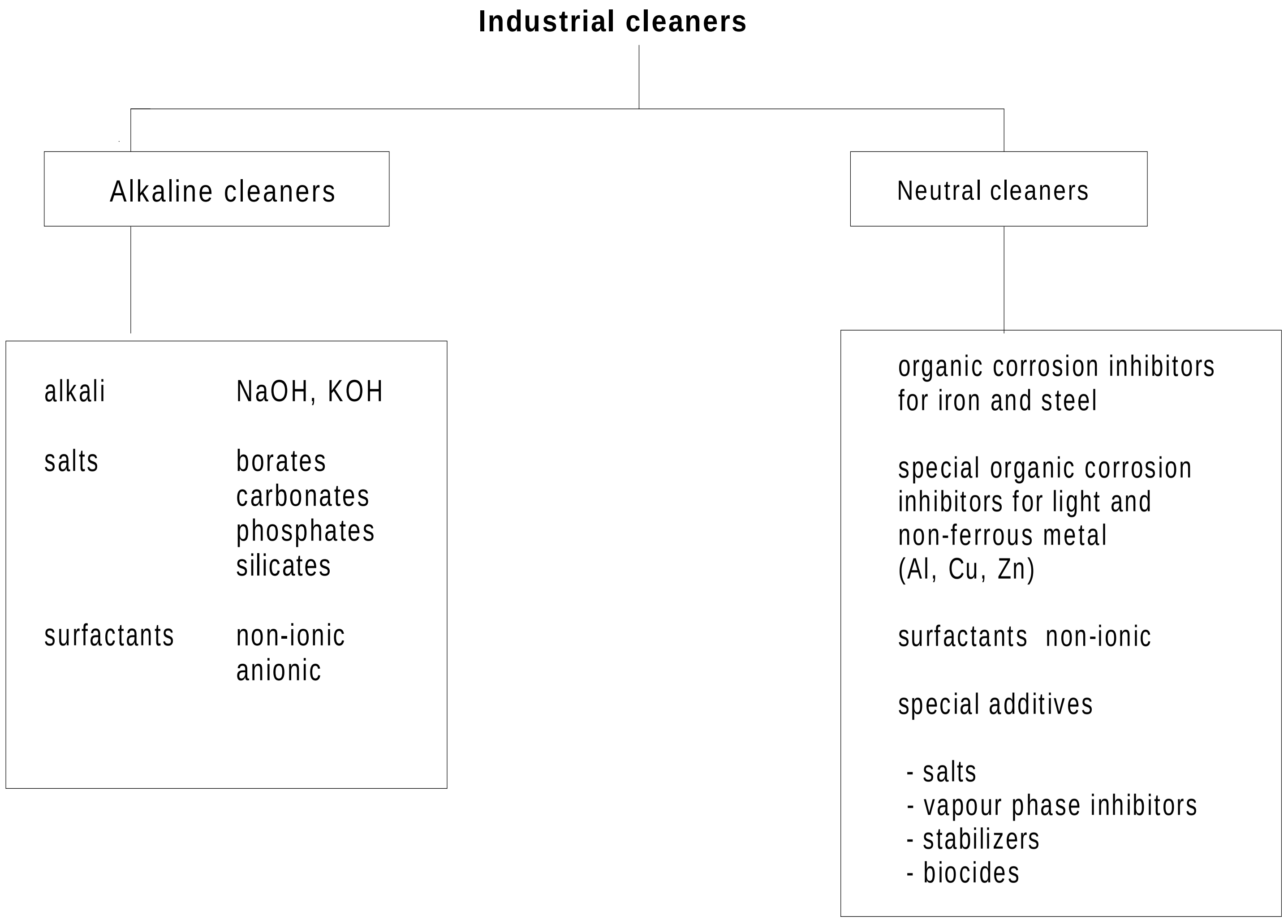
Alternative chemicals

- Alkaline cleaning systems (water, alkali, complexing agents and surfactants)
- Alcohols (ethanol and isopropanol often combined with mechanical processing and/or ultrasound)
- Petroleum products
- Ketones
- Esters
- Limonen and other terpenes

Alternative processes

- Ultrasound technique

Table A1 Industrial Cleaners



Source: Umweltbundesamt 1993

Table A2 Types of Aqueous Cleaners

pH	Type of cleaner	Basis	Task
14 ↑	strong alkaline	caustic soda/silicates soda/phosphates/surfactants	degreasing, varnish removal
	alkaline	silicates/phosphates/surfactants	degreasing of iron
	neutral cleaners	alkanolamines/emulgators phosphates/surfactants	intermediate cleaning, passivation
7			
	acidic cleaners	acidic salts/surfactants	cleaning and phosphatization of steel and alkali-sensitive workpieces
	iron phosphatization and degreasing	acidic alkaliphosphates/ surfactants/activators	pre-treatment of iron/zinc before varnishing
0 ↓	pickling solution	hydrochloric, sulphuric, phosphoric acid	derusting/removal of paint

Source: Umweltbundesamt 1993

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