Methylene chloride: Advantages and Drawbacks of Possible Market Restrictions in the EU

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Authors: Dr. A. Tukker and Ir. L. Ph. Simons TNO-STB P.O. Box 6030 2600 JA Delft the Netherlands + 31 15 269 54 50 + 31 15 269 54 60 e-mail Tukker @stb.tno.nl

Summary

Introduction

This study contains an analysis of the risks of exposure to Dichloromethane (DCM). It also expounds the selection of several priority applications of DCM enabling restrictions on marketing and use to be considered as one of the means of reducing risks. An analysis of the socio-economic consequences of such restrictions of marketing and use are presented.

Risk assessment

Noteworthy is that this six-month risk assessment project can in no way be compared with the in-depth, multi-year assessments currently in progress under the Existing Substances Programme of the EU. What we did was mainly re-evaluate a number of existing extensive risk assessments on DCM (e.g. IPCS, Environmental Health Criteria 164, 1996; RIVM, Integrated Criteria Document Dichloromethane by Slooff and Ros, 1988; and ECETOC, technical reports nos. 26, 32, 34). Based on these documents, we arrived at criteria for the evaluation of short-term and long-term exposure of humans to DCM reflected in Table 0.1. The table includes data derived - as far as possible - in line with the EU Technical Guidance Document for Evaluation of Substances, and also lists the ranges of current occupational health standards applicable in EU countries.

We confronted the criteria in Table 0.1 with exposure data found in various literature sources for about ten exposure situations. The magnitude by which the NOAEL exceeds the estimated exposure has been assessed. From a pragmatic point of view and taking into account factors such as the human population to which the

Population	Short-term	Long-term
General public Inhalation 	700 mg/m ³ (LOAEL, humans: 1-few hours) ^a	125-700 mg/m ^{3 b} (NOAEL, liver toxicity, rat)
 Ingestion 	N/A	6 mg/kg b.w./day (NOAEL, liver toxicity, rat)
Workers (occupational exposure)	250-2500 mg/m ³ (15-min STEL) [°]	120-350 mg/m ³ (8 hr. TWA in EU countries) ^c

Table 0.1: The basis for a toxicological evaluation of exposure to DCM

a. Based on protection against mild, reversible CNS-effects. The traditional safety factor approach would require a margin of safety of 100 for correction for the use of a LOAEL rather than a NOAEL and to include intraspecies variation. This would result in a standard of 7 mg/m³. For shorter time frames (e.g. 15 minutes), a factor 4 to 10 higher might be justified.

b. The traditional safety factor approach would require a margin of safety of 100 for interspecies and intraspecies extrapolation, resulting in standards of 60 ug/kg b.w./day for oral intake and 1.25-7.0 mg/m³ for inhalation. The last-mentioned value is well in line with the Air Quality Guideline of 3 mg/m³ derived by the WHO based on a maximum increase in CO-Hb levels of 0.1 % in the general population by indirect exposure to DCM.

c. Range of occupational health standards in different countries. In most cases based on a maximum increase of 5 % in CO-Hb levels.

exposure applies, the uncertainty arising from the variability in the experimental data, and intraspecies and interspecies variation, one of the following qualifications was indicated as applicable:

- (i) there is a need for further information and/or testing;
- (ii) there is at present no need for further information and/or testing and no need for risk reduction measures beyond those already being applied;
- (iii) there is a need for limiting the risks taking into account those risk reduction measures which are already being applied.

Indirect exposure of humans to DCM via the environment appears to present no clear reason for concern. Also, concentrations in the environment seem to be generally regarded as being below the levels at which effects on organisms can be expected, though we obtained one comment claiming that the PNEC applied should be at a much lower than used in most existing assessments. The results of the analysis pertaining to direct exposure to humans is summarised in Table 0.2. We used the following criteria for evaluation in accordance with the data in Table 0.1:

- Short-term exposure of workers:
 - (i) between 250 mg/m³ (lowest STEL in EU member states) and 700 mg/m³ (LOAEL for short-term exposure);
 - (ii) below 250 mg/m³ (lowest STEL in EU member states);
 - (iii) above 700 mg/m³ (LOAEL for short-term exposure).
- Long-term exposure of workers:
 - between 120 mg/m³ (lowest Occupational Exposure Limit (OEL) in EU member states; Margin of Safety (MOS) of a factor 4-5 with the NOAEL) and 350 mg/m³ (highest OEL in EU member states, MOS of a factor of 2 with the NOAEL);
 - (ii) below 120 mg/m³ (lowest OEL in EU member states);
 - (iii) above 350 mg/m^3 (highest OEL in EU member states; MOS of a factor of 2 with the NOAEL).
- Short-term exposure of consumers/general public:
 - between 7 mg/m³ (MOS of 100 with the LOAEL) and 250 mg/m³
 (lowest STEL in the EU for workers; MOS of 2-3 with the LOAEL);
 - (ii) below 7 mg/m³ (MOS > 100 with the LOAEL);
 - (iii) above 250 mg/m^3 (lowest STEL in the EU for workers, MOS of 2-3 with the LOAEL).
- Long-term exposure of consumers/general public:
 - (ii) below 1.25-7 mg/m³ (MOS of 100 with the NOAEL);

(i) or (iii): above 7 mg/m³, depending on MOS (irrelevant in practice).

Note, many subjective elements are at stake in such an analysis. For instance, a main argument with regard to consumer exposure of paint remover and adhesives is that individuals are only very infrequently exposed. Hence, we evaluated the risks of short-term exposure only. As stated in Table 0.1, for this purpose a LOAEL for a mild, reversible CNS-effect during short-term exposure was used. Just how important protection of the general population against such low-frequent,

reversible CNS-effects is however debatable. Furthermore, occupational health is generally regulated by specific legislative structures. Table 0.1 indicates that there is a MOS of two between many of the occupational health standards in EU member states and the least stringent NOAEL based on liver toxicity in rats for long-term exposure. Though this MOS is small in view of the possible interspecies and intraspecies variation, the fact that the exposure situation is not fully comparable (e.g. life time exposure versus exposure during (a part of) a professional career) is noteworthy. In this respect, a rather fundamental question is at stake. The EU Technical Guidance Document demands the evaluation of worker's exposure to DCM, but one could also argue that this evaluation should be entirely left to the existing (national) structures in which OELs are set.

Exposure category	(ii) no need for information or risk reduction	(i) need for further information and/or testing	(iii) there is a need for limiting risks
Production of DCM	Х		
Paint stripping			
 Consumer (unventilated) 			Х
 Consumer (ventilated) 		Х	Х
 Occupational 		Х	Х
Adhesives			
Consumer		Х	
 Occupational 	Х	Х	
Aerosols			
Consumer		Х	Х
 Occupational 	Х	Х	
Pharmaceutical industry	Х		
Other chemical industry			
Other industries	Х		
 Foam industry 		Х	Х
Degreasing		Х	Х
Coatings, textiles,	Х		
detergents, food extraction			
Others	N/A	N/A	N/A
Indirect exposure	Х		

Table 0.2: A review of risk characterisation of different exposure situations to DCM.

Note: Consumer exposure evaluation based on short-term exposure

Table 0.2 shows that in most regular industrial plants using DCM, where closed technology can be applied, exposure levels appeared to be acceptable. For applications like degreasing and application in the foam industry, the most logical approach seems to be exposure reduction of workers, where needed, rather than imposing market restrictions. For a number of inherently 'open' DCM applications the above evaluation framework suggests a need for further information and testing, or limiting the risks. Hence, we concentrated the analysis of the advantages and drawbacks of marketing restrictions on those applications only, for which such restrictions form one of the possible policy approaches. Of the total 147,500 tpa DCM used in the EU in 1995 it concerns:

- The use of paint remover (some 30,000 tpa DCM in Europe);
- The use of adhesives (some 15,000 tpa DCM in Europe);
- The use of aerosols (estimates between 1,500 and 15,000 tpa DCM in Europe).

Socio-economic consequences

In all these cases, an analysis was included of the socio-economic consequences of the reduction of marketing and use for consumer, professional and industrial applications. However, it should be stressed that particularly for professional and industrial applications regular occupational exposure reduction measures rather than market restrictions could well be sufficient. Assessing which measure is preferable was not part of this study. The socio-economic consequences of market restrictions can however affect the following actors:

- the formulators of paint remover, adhesives, and aerosols;
- the users of these products (consumers, professionals and industrial users);
- the producers of DCM and the related chlor-chemicals industry.

As for **paint removers**, restrictions on marketing and use of DCM may have some implications for formulators since professional users may move in part to mechanical methods. For the other part, they will not be much affected since they produce both the alternative as the DCM-related product and the technology is similar and needs no major investment. The main point is that the basic chemicals for the alternative paint remover, particularly NMP, are up to a factor 4 more expensive than DCM. Since retailers have a rather powerful position in the production-consumption chain, assistance from third parties might be needed to convince retailers that charging the additional costs is reasonable.

Consumers and professionals will have to count on much longer stripping times, and especially because the alternative chemicals are more expensive, it will mean additional costs of some 125 to 325 Million Euro per annum in the EU. Regulation at EU level will have little effect on competition. Only aeroplane stripping is an activity where competition could be influenced from outside the EU, but here the companies (at least the larger ones) who have already switched to alternatives feel rather comfortable about their competitive strength. Worth mentioning is that alternatives often have the disadvantage of longer stripping times. For alternatives like NMP, whether or not the toxicological database is sufficiently strong to ensure absence of danger is topic of debate.

The total production of **adhesives** in the EU is around 1.6 Million tonnes per annum, amounting to some 3,000 Million Euro. Probably 1-2 % of this turnover, and approximately 300 to 600 jobs, is related to DCM-based adhesives. Formulators are generally involved in the production of DCM-based adhesives and alternatives. However, some alternatives may need different production equipment, e.g. in relation to the use of more flammable materials.

Consumer and professional use of DCM-based adhesives does not seem to amount to much, hence in such applications market restrictions will go unnoticed. The need for market restrictions mainly depends on the whether or not one wants to protect humans against reversible CNS effects during short-term exposure. Industrial users include foam product manufacturing and the furniture industry, where spray applications in particular may lead to the most problematic exposure situations. Hotmelts and water-based adhesives are promising potential alternatives that are already in use by several producers. However, there may be some dedicated applications where DCM is used for its nonflammability or compatibility with certain plastics or resin compounds; properties not easily achieved with other solvents. Furthermore, a switch to alternatives may invoke the need for investing in new spray technologies, for example. This could prove problematical for particularly the smaller users. In sum, there is scope for reducing the use of DCMbased adhesives without major socio-economic consequences. However, we believe that a short-term, outright ban might have consequences that could not be foreseen and analysed in full within the confines of this report. If the EU were to strive for restriction of marketing and use of DCM in these industrial applications, our suggestion would lean toward finding a way for a gradual reduction of use, e.g. via the method of the 'bubble concept' proposed by Environment Canada.

As for **aerosols**, the indications of how much DCM is used in the EU market vary greatly: between 15,000 tpa (ECSA data), and less than 1,500 tpa (several national inquiries and information from formulators). An explanation could be that DCM-based formulations are largely exported. This corresponds with 71 or 7.1 Million DCM-containing aerosol units, or some 1.7 or 0.17 % of the total EU market, some 500 or 50 jobs, and some 150 Million or 15 Million Euro turnover. Any socio-economic effects will mainly be of relevance to the formulators. Consumers, professionals and industrial users are unlikely to be confronted with major effects if the alternative is technically feasible.

For the formulators, effects on employment and turnover will be minimal since the same firms produce DCM-containing aerosols and DCM-free aerosols. Some initial investment costs may be needed to cover research on new formulations and investment in equipment to deal with drawbacks like the flammability and hygroscopy of some alternatives. The estimated costs can amount to a maximum of roughly 30 % of the current turnover. With regard to the bulk of the eighties-relevant DCM aerosol applications including personal care products like hairsprays, all companies interviewed have already made the switch. Hence, it is obvious that restrictions on marketing and use of DCM will not have any socio-economic effects on these applications. Some special applications like insecticide sprays and paints also seem to have enough leeway for a switch. However, our analysis did not have the level of detail to ensure the absence of any possible formulation technical problems. We therefore feel that some prudence is required when pursuing outright bans without leaving sufficient slack for a transition.

The impact on producers of DCM and related firms in the chlor-chemical industry is clear. At worst a very stringent market reduction policy of the EU (banning DCM in paint remover for professional and consumer use and in aerosols, and reducing DCM use in adhesives by 70 %) would cause a decline in the DCM market of 45,000 tpa (some 33 % of the current EU market). Indirectly some 32,000 tpa less chlorine would have to be produced (some 0.3 % of the current EU market). Approximately 110 direct staff and 30 Million Euro of turnover in the DCM and chlorine production could be affected. Since the production of DCM is related inevitably in chemical terms to other solvents (e.g. chloroform), a knock-on effect of a factor 2 or 3 could occur because the economic basis of production of other solvents could also be affected. The same would apply to the chlorine production if the solvent production linked to captive use of chlorine produced onsite. Drastic reductions of the DCM market could be a driver for rearrangement of the chlorinated solvent and chlorine production structure which may lead to closure of a major chlor-chemical production location, and thus socio-economic consequences at local level. Since the EU production of DCM is much larger than the EU market (250 versus 150 ktpa), further reduction of the domestic market may lead to adaptation of the production structure to above the EU level. Obviously, a positive effect outside the chlor-chemical industry will be an increased demand for alternative solvents or chemicals.

Overall conclusion

In sum, the main problems with a drastic reduction of marketing and use of DCM will be probably occur in the chlor-chemical industry. It will lead to the typical effects related to a transition in industry: negative effects on employment, turnover and the competitiveness of producers of DCM, and benefits for producers of the alternatives. Generally, very disruptive effects related to such a transition can be reduced if a reasonable time horizon for arranging the transition is allowed. This would imply that if the EU were to embark on a stringent reduction programme for the use of DCM, a reasonable period for its implementation should be allowed. However, the need for such a policy depends on the following discussion points:

- 1 For consumer applications of DCM (particularly those leading to a rather infrequent exposure, like paint remover and adhesives): the desirability and need to protect consumers against short-term, reversible CNS-effects;
- 2 For professional/industrial applications of DCM: the extent to which the EU should leave standard setting and policy making to the existing (national) evaluation structures for occupational health, and the extent to which other measures than market restrictions would be appropriate and/or preferable.

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- 1 A review of animal test data and human case studies on acute effects (1a) and skin and eye effects (1b)
- 2 A review of animal test data and human case studies on repeated dose/chronic effects
- 3 A review of animal test data and human case studies on chronic/carcinogenic effects
- 4 Classification and standards for DCM in different countries
- 5 List of persons and institutes contacted within the framework of this study

1. Introduction

For over a decade there has been an ongoing and thorough societal discussion on chlorinated substances as industry and environmentalists struggle with each other worldwide. Environmentalists argue that the list of chlorinated substances with proven problems (like PCBs, DDT, etc.) is extensive, that chlorinated substances tend to exhibit undesirable properties like persistence and bioaccumulation, and that a substance-by-substance risk assessment approach is too slow and gives too uncertain results to ensure the absence of danger (e.g. IJC, 1993). From the environmentalist's viewpoint the use of reactive chlorine in production processes may lead to unwanted by-products and emissions that are not covered by regular emission inventories. They also emphasise the fact that some 80 to 90 % of the organochlorine found in nature (fish fat, sediment) has not yet been identified and that new classes of globally distributed persistent organochlorines are still discovered in nature. Hence, the environmentalists believe that the current chlorine chemistry could still be contributing to a global distribution of persistent organochlorines. From a precautionary viewpoint and finding this mere chance unacceptable, they come to their frequently heard claim that chlorine - including substances like DCM - must be phased out.

Industry, on the other hand, feels that the risks related to chlorine are manageable. Chlorinated substances are among the most thoroughly researched. Classical risk assessments have revealed problems for only a limited number of chlorinated substances, and most of these have already been contained by stringent risk reduction measures. As industry continuously tries to improve its performance it believes that the problem of unknown by-products and related emissions is rather small in terms of volume. According to the industry historical burdens and naturally produced organochlorine constitute the most likely explanation for the unidentified organochlorine in nature. Hence, from industry's viewpoint, there is no need to treat the chlorine industry differently than the other chemical industry.

Within the context of this debate, chlorinated substances appear on the political agenda on a regular basis in a number of EU member states. Issues that often are subject of debate are PVC, and chlorinated solvents such as methylene chloride (or Dichloromethane, DCM), leading to formal or informal measures against chlorinated substances in several EU member states. Such measures on national level can lead to trade barriers (e.g. Coleman, 1993). Similar discussions are at stake with chlorinated solvents. An EU policy on the marketing and use of chlorinated solvents is desirable to avoid differences in national policies that could hamper the proper functioning of the internal market.

The Commission made a commitment to examine the case for limitations on the marketing of certain chlorinated solvents to consumers. The chlorinated solvents trichloroethylene and perchloroethylene are currently subject to an extensive risk assessment within the Existing Substances Programme of the EU. As this programme does not yet include DCM, Directorate-General III (DG III) of the Commission commissioned a separate study into the risks to human health and environment posed by DCM and of the advantages and drawbacks of possible restrictions on its marketing and use. TNO was asked to perform this research.

The study basically consisted of a market analysis of the uses of DCM in Europe, an assessment of risks related to DCM in various applications, and an analysis of the socio-economic consequences of market restrictions of priority applications. The market survey was mainly based on data supplied by representative organisations of industry, cross-checked with a large amount of more detailed (governmental) studies made in EU member states. As for the risk assessment, the brief of the study stated that, where possible, the Technical Guidance Document in support of Commission Directive (further called 'Technical Guidance Document')¹ was to be followed. Yet, there are two remarks that must be made here:

- 1. The study on DCM was commissioned as a six-month contract that included elements other than risk assessment work alone, in contrast to regular risk assessments under the Existing Substances Programme which normally take several years to complete on incomparable budgets. This study therefore cannot be compared to such regular risk assessments. We merely used a number of existing risk reviews on DCM and (re-) evaluated them making use of the framework given by the Technical Guidance Document.
- 2. As indicated in the first paragraph, the core of the controversy on chlorine between environmentalists and industry is about how to evaluate risks. Environmentalists basically argue that classical risk assessments leave many of the (uncertain) risks related to chlorine uncovered. Thus, they will probably argue that an analysis of risks of DCM strictly according to the principles of the Technical Guidance Document will be insufficient. But, as the Terms of Reference of the study asked us to stay as close as possible to these principles it would mean that the risk assessment part of the study may be incapable of solving the controversy at stake.

¹ Technical Guidance Document in Support of Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances and Commission Regulation (EC) No 1488/94 on Risk Assessment for Existing Substances, Part 1, 1996.

The risk assessment part indicated priority DCM applications for which restrictions of marketing and use could be one of the policy options to reduce risks. As for the socio-economic consequences of such market restrictions, our analysis was based on interviews and statistical information if:

- 1. alternatives for the application were available;
- 2. they had drawbacks in terms of employment and usage costs;
- 3. a switch to such alternatives would result in major transition costs for capital equipment;
- 4. no alternatives were available yet for specific essential applications.

Given this study approach, the structure of the report is as follows:

- *Chapter 2* reviews an inventory of the DCM market in Europe. It also gives an assessment of the possible exposure to DCM by application: short-term exposure to consumers, exposure to workers, and long-term exposure of the general public via indirect exposure routes.
- *Chapter 3* gives a dose-response assessment of DCM.
- *Chapter 4* gives a risk characterisation related to the use of DCM in general and in different applications. It ends with a list of priority DCM applications for which risk reduction seems to be appropriate, and for which restrictions of marketing and use could be one of the options to achieve this;
- *Chapter 5* discusses the socio-economic consequences of such restrictions for producers, formulators and users of DCM-containing products.
- *Chapter 6* ends with conclusions.

2. Use, emissions and exposure in the EU

2.1 Introduction

The formula of DCM and some of identification numbers are presented in Figure 2.1 and Table 2.1. It is a clear, colourless, non-flammable, volatile liquid with a penetrating ether-like odour. It is slightly soluble in water, alcohol, phenols, aldehydes, ketones and organic liquids and miscible with chlorinated solvents, diethyl ether and ethanol. It will form an explosive mixture in an atmosphere with a high oxygen content, or in the presence of liquid oxygen, nitrite, potassium, or sodium. When heated to decomposition, it emits highly toxic fumes of phosgene.

п

Figure 2.1: The molecular formula of DCM

2.1: Identification of descriptions of DCM

Compound identification	Description
CAS number	75-09-2
EINECS number	200-838-9:
EEC number	602-004-00-3
IUPAC name	Dichloromethane

DCM is currently the most important chlorinated solvent used in terms of volume. Because of its considerable solvent capacity, its volatility and stability and nonflammable characteristics, DCM is used in a range of applications. These include:

- paint stripping;
- adhesives;
- applications in the pharmaceutical industry (process solvent and tablet coating);
- as solvent or auxiliary agent in processes in the chemical industry, for example:
 - foam blowing (e.g. polyurethane);
 - polycarbonate production;
 - triacetate production;

- aerosols;
- degreasing agent in the mechanical and electrical engineering industry;
- coatings;
- textiles;
- detergents/dry cleaning;
- extraction processes in the food industry;
- others.

In this chapter we will discuss the European market distribution for DCM, comparing in section 2 the market data from different sources on EU and member state level. Furthermore, we will discuss per application which fraction of the use ends up as emission to the atmosphere, in the water and as waste, indicating - based on generic studies - in which range direct exposure of consumers and/or workers takes place in these applications. A summary of this information follows in a final section together with the indirect exposure of man and environment, and the exposure routes considered to be most important.

2.2 The DCM market in the EU

The use of DCM has declined gradually over the years. In the period 1974-1984, an average of some 200 ktpa was used in the EU gradually declining from the mideighties to some 140 ktpa in 1994. The small growth in use since then might have to do with the fact that in some applications DCM can be applied as an alternative to solvents and components that were banned in 1996 under the Montreal protocol on ozone-depleting substances, such as 1,1,1- Trichloroethane. Figure 2.2 reviews these developments. Noteworthy is that the production of DCM in the EU is much higher than its use. According to the European Chlorinated Solvent Association (ECSA, 1999) about 100 kton DCM is exported annually from the EU.



Figure 2.2: Consumption of DCM in Europe from 1974-1998.

Several sources give a distribution of DCM over the different market applications. The most aggregated data come from the ECSA, the trade organisation of the European chlorinated solvent producers. Furthermore, various studies provide insight into uses on the level of individual EU member states. ECSA data are the most recent and the most useful for this study, since this study covers the whole EU. A problem with the data at individual member state level is, that the use structure in these individual states can vary greatly (e.g. the structure of a national chemical industry). Furthermore, such data may not be up-to-date. It is likely that the rather large decline of DCM use over the years was not equally distributed over different sectors, so that market distributions of some years ago may be invalid for the current situation.

Table 2.2 reviews ECSA market breakdown data for 1995 for DCM. In addition, data are given for 1990 in Netherlands (Tukker et al., 1995), 1994 and 1997 in Germany (UNR, 1999, and ECSA, 1999), 1988 in Sweden (KemI, 1991), the UK (HSE, 1998) and Denmark (Danish EPA, 1999)². It is apparent that there are some deviations between these individual country market structures on one hand and the ECSA data on the other. Most of these deviations do not seem to be too worrying. First, it is likely that there are important differences in the market structures between EU member states. For instance, Sweden applied a rather stringent occupational health standard back in 1988, which may have led to discouragement of consumer and 'open' workshop applications. It may well be that the imports of various applications not produced in Sweden (adhesives, aerosols) have not been included in full in the KemI study³.

² IPCS (1996) gives also a market breakdown for the US and Europe, but that one is not included in the table. The breakdown was for 1984 and 1985. IPCS stated that 'data apply to the situation approximately 10 years ago and may have changed since. Reliable reports on present trends are not available'. For this reason, we felt including such dated data not appropriate. Chlorine mass flow analyses for Europe of Ayres and Aryes (1996) and Kleijn and van der Voet (1998) give similar total DCM uses for Europe as given by ECSA, but do not specify it further to application type. Hence, for this study we do not use their work further.

³ It has to be noted that Sweden restricted the use of DCM considerably since 1988.

Finally, one has to acknowledge that such market data suffer inherently from elements such as definition problems⁴. For instance, there is significant difference between the ECSA estimate for use in aerosols and the data on national level. If, for instance, the national studies counted paint remover and adhesive aerosols as paint remover and adhesive, this could be an explanation. All and all, we feel it is best to work with the data obtained from ECSA. They are the most recent and most useful for this study on EU level. Furthermore, apart from aerosols maybe, the cross-check with national data gives no clear reason to question the ECSA data, other than for what seems to be an inherent uncertainty related to such market surveys.

⁴ For instance, even ECSA discovered that their early market studies over-estimated the use in paint stripping.

Table 2.2: DCM markets by application in the EU and some EU member states from various sources (in ton)

Applications	EU, 1995 (ECSA, 1999)		Germany, 1997 (ECSA, 1999)		Germany, 1994 (UNR, 1999)		Denm undat (Danis 1999)	Denmark, undated (Danish EPA, 1999)		Netherlands, 1990 (Tukker et al, 1995)		Sweden, 1988 (Keml, 1991)		UK (HSE, 1998)	
	%	Total	%	Total	%	Total	%	Total	%	Total	%	Total	%	Total	
Paint stripping	19.7	29100	25	3780	30.78	5540	20.5	100	23.5	2000	14.7	370	25	7500	
Adhesives	10.2	15089	12	1793	18.18	3272	2.6	12.5	1.2	100	0.6	15	10	3000	
Aerosols	9.8	14473		0	1.62	292	0.0	0	2.4	200	0.4	10	2	600	
Pharmaceutical	31.7	46806	20	3112	31.74	5713	6.1	30	11,8	1004,5	15.0	380	25	7500	
process solvent															
tablet coating															
Degreasing			1	200	2.46	443	14.3	70	7.1	607	44,3	1120			
cold	4.6	6775													
vapour	3.2	4773													
Coatings, textiles, food extraction			12	1848											
coatings	1.1	1694													
textiles	0.8	1232													
food extraction	0.7	1078			4.14	745			0.5	45			2	600	
cleaning agents	0.4	616					0.8	4	0.5	40					
Other chemical			11	1737					47.1	4000	10.9	275	25	7500	
polycarbonate	1.3	1848													
triacetate production	0.5	770													
foam blowing	6.5	9546									11.1	280			
Others			18	2757			55.6	271.5	5.9	503,5	3	75	11	3300	
mould release	0.1	154			1.62	292									
laboratory use	0.8	1232													
sales to other distributors															
exports															
others	8.4	12317			9.46	1703									
Total	100	147500	100	15227	100	18000	100	488	100	8500	100	2525	100	30000	

Note: For Germany, UNR the chemical industry is included in the pharmaceutical industry

2.3 Emissions and direct exposure by application

2.3.1 Introduction

This section deals with the emissions from each application and the direct exposure of consumers and workers to DCM. We divided the chain of production and consumption into the following elements:

- 1. production of DCM (pure solvent);
- 2. formulation of DCM (in a specific product group);
- 3. use of DCM (in a specific product group), making a distinction into:
 - a) occupational exposure situations, divided into:
 - industrial applications (e.g. the use as a solvent in a reactor);
 - professional applications (e.g. use as degreasing bath in small workshops, use of DCM-containing products by painters, etc.);
 - b) consumer exposure situations.

Data from both emissions and exposure can diverge per application. We took emission factors from various studies (e.g. Tukker et al., 1995; Kleijn and v.d. Voet, 1998; HSE, 1998 and IPCS, 1996) and chose a reasonable average emission factor. As for exposure, we relied on various literature sources and review documents (e.g. IPCS, 1996 and Slooff and Ros, 1988) for an indication of direct exposure data. Below is a description of the production of DCM and formulation of DCM-containing products, followed by a discussion of the formulation and use of each DCM-containing product group in the sequence as indicated in Table 2.2.

2.3.2 Production of DCM

Description

A common way of producing DCM is by chlorinating methyl chloride. In a first step, methanol and a return flow of HCl react to this basic compound. Then, by chlorinating the methyl chloride, dichloromethane (DCM) and chloroform can be obtained with HCl as by-product. The pure individual compounds are obtained by distillation.

Emission factors

Confidential data obtained during the research of Tukker *et al.* (1995) show that the emission factor of DCM to air and water are very low compared to the use of DCM (e.g. for air: well below 1% in 1995). Hence, we ignore this emission in this report as any steps to make necessary reductions to protect the general public must be taken in the use phase.

Direct exposure (industry)

The occupational exposure during DCM production seems to be rather low (HSE, 1998). Over 90 % of the eight-hour TWAs were below 10 ppm (35 mg/m³); geometric mean exposure that were reported to HSE (1998) were below 1 ppm (3.5 mg/m³) for plant and packing personnel. Higher values were measured for distribution personnel, i.e. tanker drivers delivering to customer sites (18 ppm or 63

 mg/m^3 as a mean eight-hour TWA). Hence, the main focus would not seem to be the production plants themselves, but the transport and distribution stage. The OECD report mentions exposure levels between 219 and 374 mg/m^3 during maintenance activities (data of HSE, as cited in OECD, 1994:43).

2.3.3 Formulation of DCM containing products

Description

Most of the products described below involve a formulation step in which the DCM is blended with other materials to form the final product. These formulation and blending activities usually take place in an industrial environment, where emissions and exposure can be fairly well controlled.

Emission factors

The emissions of the formulation of DCM-containing products are also relatively low compared to those in the use stage. We therefore ignore this emission in this report as any reductions deemed necessary to protect the general public need to be made in the use phase.

Direct industrial occupational exposure

Occupational exposure during the production and formulation of DCM-containing products should be rather controllable. For instance, occupational exposure to aerosols mainly takes place during filling and packing. Here too, control measures and working practices determine the level of exposure but levels seem to be generally below 180 mg/m³ (HSE, 1998).

2.3.4 Paint stripping

Description

There are three variations of paint stripping: industrial applications, professional applications and consumer applications. Paint strippers are widely used in industries such as the automotive, furniture, plastic, electronic and rubber product industries, both as hand stripping and other stripping forms (e.g. submersion and spray stripping). In the Netherlands, about 25 % of the paint market is a consumer market (KPMG, 1992), suggesting that some 25 % of the paint strippers may be used by do-it-yourself consumers. This fits well with data from the UK where 50 % is reported to be used for hand stripping (do-it-yourself and professional), and 50 % for other professional applications (HSE, 1998). In Sweden, consumer applications of paint remover in 1988 were more limited: data given in KemI (1991) suggest that some 40 out of 370 tpa (or 10 %) was used in the consumer market. This may reflect the rather discouraging approach of Swedish authorities towards the use of chlorinated solvents, particularly in the consumer sector.

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Emission factors

Tukker *et al.* (1995), basing themselves on Verhage (1991), used an emission factor of 85 % to air and 15 % to waste. These data were cross-checked with the Dutch emission record system and the Dutch hazardous waste notification system plus data on average compositions of chlorinated waste (v.d. Steen, 1991). There may be a small emission to water, which is not included here. UBA (1991) mentions for 'Oberflächebehandlung', which probably includes paint stripping, similar data: 90 % to air and 10 % to waste.

Direct exposure – consumer use

Various tests have been done on consumer applications from DCM-containing paint stripper. An IPCS (1996) review mentions the following data. US EPA (1990) has estimated the consumer exposure based on an investigation of household solvent products. Estimated exposure levels ranged from 35 mg/m^3 to a few short-term exposures of over 14,100 mg/m³. The majority of the concentrations were below 1770 mg/m^3 . ICI, a solvent producer, communicated to the IPCS results of a test series on a number of paint stripper formulations used under varying conditions in a small room. In one test with through ventilation, a twohour time-weighted average (TWA) exposure of 289 mg/m³ were measured. Peak exposure occurred during application (460 mg/m^3) and during scrap-off (between 710-1410 mg/m³, and never above 3530 mg/m³. When no ventilation was applied, worst-case exposure could be over 14 g/m^3 , under which concentrations the work of an average do-it-yourself consumer would be impeded. Good ventilation, as recommended by the suppliers, would result in an eight-hour TWA of 187-226 mg/m^3 (personal communication of ICI, as reported in IPCS, 1996). HSE (1998:24) refers to authors who found one-hour TWAs of 840-2765 mg/m³ (240 to 790 ppm) in an unventilated room and 129.5-948 mg/m³ (37 to 270 ppm) with the door open. If this exposure is recalculated to eight-hour TWAs this would result in the somewhat lower values as reported by ICI. However, Slooff and Ros (1988) refer to Otson et al. (1981), who give much higher figures for eight-hour TWAs: 460- $2,980 \text{ mg/m}^3$ in unventilated rooms and $60-400 \text{ mg/m}^3$ in ventilated rooms.

Direct professional occupational exposure

There is probably be no fundamental difference between the application of paint removers by professional painters and consumers. Hence, the test situations and data described above are assumed valid for occupational exposure during professional use as well.

Direct industrial occupational exposure

As for the industrial applications, DCM is used in situations that in most cases are more manageable with regard to exposure than consumer and professional use. Usual techniques for paint removal are manual coating, tank dipping or spray application. It is perfectly obvious that the extent of exposure will greatly depend on the control measures taken and work practices adopted.

Hence, it is difficult to give generic values for occupational exposure. A study of US EPA (1990) showed a range for an eight-hour TWA from 18 mg/m³ to 1770 mg/m^3 or more (IPCS, 1996). HSE (1998) reported for immersion stripping of wood higher values for the period between 1980 and 1994 (eight-hour TWAs ranging from 38.5 to 7000 mg/m³, with about 700 mg/m³ as a mean value), but somewhat lower values for the period between 1990 and 1994 (35 to about 2100 mg/m^3 , with an average of 350 to 420 mg/m³). The last-mentioned values may reflect improved health and safety measures. Yet, HSE reported that caution is appropriate when suggesting that these lower exposure data are significant, due to the low number of samples, etc. Exposure in the lower range is feasible when protection measures such as LEV⁵ are applied; without LEV and/or under poor ventilation conditions this can be a factor 4 or more (HSE, 1998:21). Also for immersion stripping of metal objects exposure can be held below 100 ppm (or 350 mg/m^3) if appropriate protection measures are implemented. Paint removal from aircraft involves a spray process, leading to an exposure of 29 to 95 ppm eight-hour TWA (mean 62 ppm or 210 mg/m³). Peak levels could be up to 1600 ppm or 5400mg/m³ (HSE, 1998:23). In the paint stripping industry for furniture without adequate control measures, exposure levels found were between 258 and 3812 mg/m^3 (EPA, 1990).

2.3.5 Adhesives

Description and emission factors

DCM is used in adhesives because it is highly solvent, highly volatile and nonflammable. Our data does not show for certain whether or not consumer and professional applications are still of importance.

Emission factors

Based on a mass balance study, Tukker et al. (1995) calculated for the Dutch use of DCM as adhesives, an emission of 100% to air.

Direct consumer and professional/industrial occupational exposure

The use of DCM as solvent in adhesives can, during the use phase, lead to an occupational exposure of short-term levels of more than 350 mg/m³ (IPCS, 1996). HSE (1998) concentrated on spray applications as it was thought likely that this type of application could give rise to the highest exposure. HSE's database showed no significant diminishing of exposure data before and after 1990; the mean eighthour TWA was about 200 mg/m³ (52-58 ppm), ranging from 3.5 to over 1500 mg/m³. The mean short-term exposure can turn out to be a factor 8 higher than given here. It is probably difficult to make a sharp distinction between professional and industrial exposure. Spray applications may be used by professionals as well as in workshops. As for consumer exposure, no data are available. For the time being, we will assume as a worst-case that the same exposure levels for workers might be applicable, albeit at a much lower frequency.

⁵ This LEV is either a slot extraction at the rear of the immersion bath, or one or two axial fans on the wall a the rear of the tank.

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2.3.6 Aerosols

Description and emission factors

In the past, important applications of aerosols were hairspray aerosols and other personal care products. However, during the research for this study we found that particularly in hairspray aerosols the use of DCM has become negligible within the EU. The only reported applications of DCM in spray cans are those in which DCM fulfils another function. Examples include its use as formulating agent in insecticide spray cans and solvent in aerosol paints. It must be assumed that virtually 100 % of the DCM used in such applications will be emitted to the air.

Direct consumer exposure

A recent IPCS review (IPCS, 1996) has summarised various studies into exposure of workers and/or consumers to DCM used in spray cans. Also the company ICI simulated various conditions. Most of these studies concentrate on personal care aerosols, which in the mean time are not or hardly in use anymore. We assumed that the results are to a certain extent applicable to other aerosol products as well.

Under unfavourable conditions, such as the absence of ventilation and a small room, an exposure from personal care aerosols of 353 mg/m^3 was measured as a 10-minute TWA. Assuming that exposure only takes place during this period, ICI indicated this implied 7 mg/m^3 for an eight-hour TWA (IPCS, 1996). A Dutch study reported in IPCS (1996) had reported a peak exposure during home use of 265 mg/m^3 , equivalent to a TWA of 2.65 mg/m^{36} . Consumer exposure during salon use was found to be 106-205 mg/m³. Another Dutch study (Slooff and Ros, 1988: 36) concentrated on short-term exposure. When a hair spray was used around the head for about 10 seconds, average concentrations near the mouth were 800 mg/m^3 for a period of 5 minutes. When it was used only at the back and the sides of the head, this concentration was 90 mg/m³. With extreme ventilation (doors and windows open, ventilator in the room) the 5 minute averages were 100 mg/m^3 and 20 mg/m³ respectively. A simulated worst-case scenario was when three different aerosols products were used in a small, unventilated room resulting in a peak concentration of 1765 mg/m³ (Dow chemical USA, 1975). Obviously, these conditions are rather irrelevant for insect repellent use, since this is usually not applied near or on the head. However, it is also clear that there was no ventilation during the use of insect repellent. The extent to which ventilation was applied after use is unclear, and the exposure time to the residual concentration might have been relatively long in some case (e.g. when a room had been sprayed before going to sleep).

⁶ The source gives no indication if this is a 8 hr. TWA.

Direct professional occupational exposure

As for professional use, the ICI study showed that a rather heavy salon use of about one 10-second spray every 15 minutes, leads to a hairdresser exposure of 77,7 mg/m^3 for an eight-hour TWA. This seems to be reasonably in line with the values of Slooff and Ros (1988) reported above. The Dutch study that is cited by IPCS (1996) resulted in somewhat lower values: peak concentrations of 21-106 mg/m³, and a 3.5 to 17.7 mg/m³ eight-hour TWA (IPCS, 1996:64).

2.3.7 Pharmaceutical applications

Description

DCM is applied in two forms in the pharmaceutical industry: as a process solvent and as a tablet-coating agent. Internal recycling by distillation is common in this industry. In the pharmaceutical industry, process changes (including solvent changes) may require re-approval of a product and process within the framework of regulatory and quality standards for medical products.

Emission factors

Outputs are DCM with distillation residue (waste), emissions to air and emissions to water. Tukker et al. (1995) calculated for Dutch plants 55 % emission to air, 44% discharge with waste, and 1% emission to water.

Direct industrial occupational exposure

Consumer exposure is irrelevant in this case. The IPCS (1996) review reports that in the pharmaceutical industry, sealed processes, high recovery rates and careful handling of discharges can bring exposure rates to around 106 mg/m³. The UK HSE's (1998) occupational exposure database showed that for process operators in pharmacy the values can in practice be much lower, in the range of 3.5 to 10 mg/m³ (or 1 to 2.9 ppm; eight-hour TWA). According to a feasibility study, workers in production facilities without adequate control measurements could be exposed to levels between 7 and 3750 mg/m³ (Zahm et al., 1987).

2.3.8 Other chemical industry

Description

DCM is applied in a variety of processes in the chemical industry. Well-known uses include solvent in the polycarbonate production, blowing agent in PUR production, etc.

Emission factors

On the basis of a mass balance study, Tukker et al. (1995) calculated for the Dutch chemical industry an emission of 0.2 % to water, 64.8 % to air and 35 % to waste.

Direct industrial occupational exposure

When solvents like DCM are used in closed systems, occupational exposure is low. A review of HSE (1998) showed that the mean exposure at most was 23 mg/m³ (eight-hour TWA) for most closed industrial applications. However, when specific operations such as filter changing, charging and discharging, etc. are at stake, 10-minute TWAs could be 350 mg/m³ (IPCS, 1996). Several specific processes may lead to relatively high exposure levels. For instance, according to IPCS (1996 exposure up to 350 mg/m³ (eight-hour TWA) may occur) during cellulose triacetate production even when good control systems are installed. Sampling of one plant in 1978 showed exposure levels ranging from 177 to 2436 mg/m³ in the processing area and from 18 to 1341 mg/m³ in the preparation area (Ott et al., 1983). Yet, these data are much higher than reported by HSE (1998), which were some 20 mg/m³ (eight-hour TWA) on average with a range of 0 to 160 mg/m³.

DCM is also used in the foam industry as cleaning agent or auxiliary blowing agent. It is also used as releasing agent in the moulding of PUR products. Exposures range from a few to over 1770 mg/ m³ (IPCS, 1996). HSE indicates for the use as blowing agent a range of 13 to 570 mg/m³ for eight-hour TWAs (HSE, 1998). For other tasks in PUR production this exposure may be between 7 and 700 mg/m³, with a mean of 231 mg/m³ (eight-hour TWA).

2.3.9 Degreasing

Description

DCM is applied in a variety of degreasing processes in the electrometal industry. In this industry, metal is generally cleaned before painting, plating, plastic coating, etc.

Emission factors

A specific mass balance study carried out in the Netherlands (van der Most, 1993), showed for degreasing activities an emission factor of 0.3 % to water, 57.7 % to air, and 42 % to waste; these data were also used by Tukker et al. (1995) and Kleijn and v.d. Voet (1998). UBA (1991) mentions for 'Oberflächebehandlung', which includes degreasing, somewhat other data 90 % to air and 10 % to waste. Since Van der Most's data were based on a specific survey of companies with degreasing activities, we feel that his data are probably most reliable. The difference may have to do with the fact that more and more measures are taken to reduce organic solvent emissions to air. This implies less emissions to air, hence a lower input of DCM into the process, and a relatively greater fraction of DCM that becomes available as waste than say 10 or 15 years ago.

Direct industrial and professional occupational exposure

Here too, the occupational exposure to DCM will vary according to various factors like: the age of the equipment, the type of engineering controls, the maintenance, handling and drying methods, etc. The Swedish National Board of Occupational Safety reported to the IPCS that exposure levels can be kept below 124 mg/m³ if stringent controls are applied (IPCS, 1996). Data from the UK HSE's exposure database seem to confirm this statement: mean exposure values for cold degreasing were found to be some 280 mg/m³, but with ranges from 14 to over 1000 mg/m³ (HSE, 1998:27).

2.3.10 Coatings, textiles, detergents, food extraction

Food extraction

DCM is used for extraction purposes in the food industry, the best known example probably being the production of caffeine-free coffee by extracting caffeine using DCM. UBA (1991) indicated that virtually all the DCM used in this process is ultimately emitted to air (900 tpa for Germany); minor fractions are emitted to water (400 kg) and a small residue is left in the food itself. The concentrations are well below the applicable EU regulations on food. Exposure levels in the food industry, where DCM is used as an extraction agent, are generally considered to be low (IPCS, 1996). HSE (1998:13) reported values of some 110 mg/m³ for an eighthour TWA. Somewhat conflicting information is available about the residual concentrations in foodstuff after extraction, notably decaffeinated coffee beans. One source reported levels of 0.32 to 0.42 mg/kg coffee where a major coffee producer had reported the levels to be between 0.01 and 0.1 mg/kg (IPCS, 1996); research by Page and Charbonneau (1984) tended to be in the higher range.

HSE reported that other exposure of other open industrial applications, such as printing, gauze coating and fabric coating, are in the same range as those known for extraction processes.

2.3.11 Others

Description

No insight is available into other applications, which count for some 10 % of DCM use. As shown in Table 2.2, the ECSA data we use in this report are, compared to data available at national level, rather detailed. We did not find other studies that were more specific than the sources we used. Additional insight might only be gained by gathering primary data from producers and importers. Such intensive surveys fall far beyond the scope of this study.

Emission factors

Since no insight exists into the specific applications in this category, the overall emission factors have to be estimated. There has probably been no major mistake made in assuming that the average of the emission factors valid for the other categories was used (compare Kleijn and van der Voet, 1998).

Direct consumer and occupational exposure

Obviously, since the exact applications are not known, no specific analysis is possible of direct consumer and occupational exposure. However, it is likely that the exposure will be in the same range as the previously mentioned applications, according to their characteristics (e.g. closed production processes, open applications, etc.).

2.4 A review of emissions and exposure levels

2.4.1 Introduction

This section summarises and extends the information concerning emissions and exposure to DCM based on the former sections. Section 2.4.2 summarises the various uses of DCM and the emission factors on application, indicating the resulting total estimates for the emissions of DCM to water and air, and the amount of waste, of DCM in Europe. Section 2.4.3 reviews the direct exposure to DCM, and section 2.4.4 discusses, based on concentrations in the environmental media, the indirect exposure to DCM of the general population.

2.4.2 Total emissions of DCM in Europe

Table 2.3 gives a summary of the emission factors for each application and the total emissions of DCM to the different components of the environment. As described in the previous section, the majority of the emissions, 77%, of DCM are emitted to air, approximately 22.5 % of the DCM is emitted as waste and about 0.5% is emitted into water.

DCM is volatile so most of the released DCM will end up in the atmosphere. DCM in water will be rapidly removed due to its readily bio-transformation rate under aerobic and anaerobic conditions. In the air the substance reacts with hydroxyl radicals and has a lifetime of about five months (ECSA, 1995). There is no evidence that significantly bio-accumulation or bio-magnification of DCM in the environment or in the food-chain will occur (IPCS, 1996). DCM is believed not to have a significantly to photochemical smog formation (IPCS, 1996) and it does not significantly contribute to global warming (ECSA, 1995).

Product	EU use	e, 1995	Emission to						
			Air		Was	ste	Wat	Water	
	%	ton	%	Ton	%	ton	%	ton	
Production*			N/A	N/A	N/A	N/A	N/A	N/A	
Paint stripping	19,7%	29100	85%	24735	15%	4365	0	0	
Adhesives	10,2%	15089	100%	15089	0	0	0	0	
Aerosols	9,8%	14473	100%	14473	0	0	0	0	
Pharmaceutical	31,7%	46806	55%	25743	44%	20595	1%	468	
Other chemical	8,2%	12164	65%	7907	34.7%	4221	0,30%	36	
industries									
Degreasing	7,8%	11548	57,70%	6663	42%	4850	0,30%	34	
Coatings, textiles,	3,1%	4620	100%(food)	4620	0	0	0	0	
food, extraction									
Others**	9,3%	13703	77%	10551	22.5%	3083	0,5%	69	
Total:	100%	147500		109781		37114		607	

Table 2.3: The use and emissions of DCM by application in Europe, 1995.

* Emissions negligible compared to other applications

** Emission factors are assumed to be the weighted average of the other categories.

2.4.3 Review of direct exposure of DCM

In the previous sections, the direct exposure to DCM to workers (occupational health) and to consumers (consumer applications) has been reviewed. This information is summarised in Table 2.4.

2.4.4 Environmental concentrations and indirect exposure of DCM

One element that has not yet been addressed is the indirect exposure to man of DCM. Indirect exposure takes place via the pathways that are roughly indicated in Figure 2.3. DCM emitted to air or water that is distributed over the various environmental media (soil, water, air, etc.), is in part degraded by photochemical degradation and biodegradation processes. However, to some extent it may enter food chains, and in principle can be taken up by man via inhalation of air, intake of water and intake of food.

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Table 2.4: A summary	of the a	lirect exi	posure o	f consumers ar	ıd workers to	DCM	per application
	· · · · · ·						r · · · · · · · · · · · · · · · · ·

Product/ application	Populations exposed	Peak levels (mg/m ³)	Long term (mg/m ³)	Comments (Values in mg/m ³)
Production	Production personnel Plant & packaging personnel Tanker drivers:		8 hr TWA 35 (90% of the time) 8 hr TWA 3.5 (geometric mean) 8 hr TWA 63 (mean)	During maintenance activities exposure of 219- 374 is possible (HSE, 1987)
Paint stripping	Consumer application	Unventilated: Up to 14100 (worst case scenario) 1 hr TWA 840-2765 Ventilated: 1 hr TWA 129.5-948 (door open) 2 hr TWA 289 460 during application 710-1410 during scrap off (Majority below 1770 and never above 3530)	Unventilated: 8 hr TWA 460-2.980 8 hr TWA Ventilated: 8 hr TWA 187-226 8 hr TWA 60-400	
	Professional application	Up to 5400	8 hr TWA 18-1765 (average 212) 8 hr TWA 38.5- 7000 (700 mean value) 8 hr TWA 35-2100 (average:350-420) 8 hr TWA 98-321 (average 210) 8 hr TWA 25-3812	Maintenance activities During immersion stripping of wood period 1980- 1994 During immersion stripping of wood period 1990- 1994 Paint removal aircraft In furniture paint stripping without adequate control measurements (NECB, UK)
Adhesives	Workers	350 <1600	8 hr TWA 3.5 – 1500 (average: 200)	Spray applications

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Product/	Populations exposed	Peak levels (mg/m ³)	Long term (mg/m ³)	Comments (Values in mg/m ³)
application				
Aerosols	Consumer application	10 min TWA 353 (unventilated) Peak 265 5 min TWA <800 5 min TWA 90 5 min TWA 100 (with extreme ventilation) 5 min TWA 20 (with extreme ventilation) Peak 1765 (with average of 15 min TWA 36) Peak: 21-1060	8 hr TWA 7	8 hr TWA is calculated from STEL. Hairspray used around the head Hairspray used at the back of the head Hairspray used around the head Hairspray used at the back of the head The use of three different aerosols products in a small unventilated room resulted in this peak concentration (Dow chemical USA, 1975) Heavy salon use, 10 sec spray every 15 min
	Professional application	Peak 21-106 <180 during filling	8 hr TWA 77.7 8 hr TWA 3.5-17.7	
Pharmaceutical	Production personnel		8 hr TWA < 106 (enclosed process) 8 hr TWA 3.5-10 8 hr TWA 7-3750	According to a feasibility study (Zahm et al., 1987)
Other chemical industries	Production personnel	10 min TWA 350 Peak: ≤≤1770	8 hr TWA 23 8 hr. TWA 350 8 hr TWA 177-2436 8 hr TWA 18-1341 8 hr TWA 0-160 (average: 20) 8 hr TWA 13-570 8 hr TWA 7-700 (mean 231)	Filter changing, (dis)charging Cellulose triacetate production Sample one plant in processing area Sample one plant in preparation area. HSE, 1998. Foam industry. Other tasks in PUR production.
Degreasing	Production personnel		8 hr TWA < 124 8 hr. TWA 14-1000 (Average 280)	With adequate stringent measurements. Cold degreasing
Coatings, textiles, food, extraction	Production personnel		8 hr TWA 110	DCM used as a extraction agent
Others			N/A	

*The exposure levels of the category 'others' is believed to be in the same range with the same average exposure levels as the other categories

The indirect exposure can be assessed by estimating the total daily intake of a substance based on the exposure of the environmental compartments; air, fish, drinking water, crops, cattle meat and milk. According to the Technical Guidance Document, the following standard defaults for indirect exposure of humans can be taken when the total daily intake is calculated. Table 2.5 summarises the relevant default standard parameters for this calculation.

Table 2.5: A summary of the default parameters for the indirect daily up take by adults

Parameter	Value
Drinking water	2 l/d
Food total (incl. dairy products, root and leaf crops, meat and fish)	2.56 kg/d
Inhalation rate	20 m ³ /d

The level of DCM absorbed through inhalation is largely determined by the amount of indoor or outdoor air which is breathed in, dependent on the distance between the residence and the source. A considerable rise in the amount of DCM absorbed through inhalation can be caused by smoking, the use of paint stripper and/or spray cans. As this element is dealt with in section 2.4.2 we will concentrate here on indirect exposure only.

The average concentrations of DCM in suburban and urban areas, respectively, are reported to be $<2\mu g/m^3$ and $<15\mu g/m^3$ (IPCS, 1996). Near hazardous waste site concentrations of up to 43 μ g/m³ have been measured. At an inhalation rate of 20 m^{3} /day for adults, the daily amount of DCM absorbed through inhalation could therefore expected be in the range of 40-300 μ g and in some cases up to 860 μ g. The concentration of DCM in surface water ranges from non-detectable to $10 \mu g/l$. at most. Typical concentrations in river water and coastal water/estuaries tend to be below 0.1 µg (IPCS, 1996; Euro Chlor, 1999a). As for drinking water, concentrations are generally below 1µg /l. In a study in Spain, an average of 14.1 μ g /l and a range of 1.2 to 93.2 μ g /l was found (IPCS, 1996:60). This may have to do with halomethane formation due to chlorination of drinking water rather than the use of DCM. These data suggest an uptake via drinking water of around $2 \mu g$ /day in general, but higher values, up to 186 µg /day or some 2.5 µg /kg b.w./day for adults might be possible in very unfavourable situations. Although DCM is used in food processing (solvent extractions of coffee, spices, hops, oils and fats) there is little information on its residual levels in food. The residue levels of DCM in food can vary from 1-310 μ g/kg, where the highest concentrations are found in highly processed foods and 'ready to eat' cereal (IPCS, 1996). There is no data available to calculate the total daily intake of DCM through the intake of food. However, from different studies it appears that exposure routes via food and drinking water are relatively unimportant and that exposure via inhalation is by far the most important route (IPCS, 1996, Slooff and Ros, 1988, OECD, 1994).



Figure 2.3: Schematic review of exposure routes relevant for indirect human exposure

1 Inhalation

2 bioconcentration water-fish 3 bioconcentration soil-plant 4 bioconcentration air-plant 5 biotransfer to meat 6 biotransfer to milk 7 bioconcentration soil-worm 8 purification of drinking water 9 consumption

3. Dose -response assessment of DCM

3.1 Introduction

This section discusses the risks of the exposure to DCM for humans and animals through the assessment of a dose-response relationship of the exposure level and toxicological effects. The Terms of Reference (ToR) of this study indicated that in this dose-response assessment use should be made of the principles for the risk assessment of new and existing substances as laid down in the Technical Guidance Document.

The Technical Guidance Document distinguishes seven different toxicological effects necessitating assessment of a dose-response relationship. However, it should be made very clear that this six-month project can in no way result in a study of comparable depth as the regular EU risk assessments. Such assessments under the Existing Substances Programme usually take years and easily resulting in documents of several hundred pages. Considering the limited time available for this study it was necessary for us to perform a quick scan of the different health affects of DCM on humans and animals and the exposure levels at which they occur. We start this chapter with a description of the toxicokinetic aspects and the health effects of DCM on humans will be described as follows:

- Acute toxicity/irritation including the skin and respiratory effects;
- Repeated dose/chronic toxicity;
- Carcinogenic effects.

Through analysis of these groups of effects of DCM we think we can get a good impression of the health effects of DCM on humans and animals and the corresponding exposure levels. The description of the different health effects contains a brief definition of the health effect and the dose-response relationship of humans and animals. In Appendices 1, 2 and 3 an overview is given of a number of important toxicological reviews on DCM from animal test and known human case reports for the different health effects distinguished in this study.

For the dose-response assessment we rely on the data used in the reports of the IPCS, Environmental Health Criteria 164, 1996; RIVM, Integrated Criteria Document Dichloromethane, 1988 (Slooff and Ros, 198); and ECETOC, technical reports nos. 26, 32, 34 (ECETOC, 1987, 1988 and 1989). We assume that the data collected in these studies give a comprehensive and representative view of the data available on DCM.

Virtually all these review documents suggest that the effect on the environment is not one of the priorities of the potential environmental and health risks of DCM. For instance, risk assessments of Slooff and Ros (1988), Janus et al. (1994), IPCS (1996), Euro Chlor (1999) all suggest PNECs in the order of magnitude of 1 mg/l in water, which is well above the worst-case concentrations in river water and estuaries of some 10 μ g/l (IPCS, 1996). Therefore, we concluded that it would be best to concentrate on an analysis of human health effects. However, during the course of the study a memorandum from the German Environment Ministry (UNR, 1999) was obtained that mentioned a much lower PNEC. Based on an embryolarval test that included rainbow trout, in which among others teratogenic effects are being tested, a PNEC of 4 μ g/l. was proposed. Such low PNECs would give rise to a need for risk reduction, since concentrations in some surface water is still in the order of magnitude of this value. However, it falls beyond the scope of this study to serve as a referee between these very different analyses.

3.2 Toxicokinetics of DCM in humans⁷

3.2.1 Introduction

The term "toxicokinetics" includes toxicodynamics and is broadly used to describe the absorption, distribution, metabolism and elimination of a substance following exposure, and the kinetics of these processes, where appropriate.

3.2.2 Kinetics and metabolism

DCM is rapidly absorbed though the alveoli of the lungs into systemic circulation. It is also absorbed from the gastrointestinal tract and dermal exposure results in absorption but at a slower rate than of the other exposure routes. About 70-75% of the inhaled vapour is absorbed in human subjects exposed to different levels (varying between 180 and 710 mg/m³) of DCM. The absorption of DCM increases with exercise and with the amount of body fat. Therefore, there is a direct correlation between the steady-state blood DCM values and the exposure concentration. Steady-state blood levels appear to be reached after four hours and remain constant until the end of exposure. Distribution studies indicate that, via inhalation or dermal exposure, DCM distributes to all tissues. It can cross the blood brain barrier and it can be transferred across the blood placenta. Concentrations of DCM rise more slowly in adipose tissue and longer exposure is required before these tissue levels equal those of the blood. Data indicate that DCM and/or its metabolites do not accumulate in tissues.

Absorption of liquid DCM via the skin is slow. Animal studies *in vivo* show an absorption rate 6.58 mg/h cm². At current exposure levels, most of the DCM taken up is metabolised to carbon monoxide and carbon dioxide, mainly in the liver, kidneys and lungs. With high or repeated exposure the enzyme system may be saturated and ametabolic DCM may occur in fat.

⁷ This section relies heavily on the evaluation of human health risks and effects on the environment of the IPCS (IPCS, 1996).

DCM is metabolised to carbon monoxide, carbon dioxide and inorganic chloride and eliminated from the body primarily via the lungs in expired air. Urinary excretion plays a minor role in its elimination. As exposure levels increase, a large proportion of DCM is exhaled unchanged. Metabolism occurs by either or both of two pathways, their contribution to the total metabolism markedly being dependent on the exposure level and on the animal species concerned. One pathway involves oxidative metabolism mediated by cytochrome P-450 leading to carbon monoxide and carbon dioxide. This pathway appears to operate similarly in a qualitative and quantitative sense in all rodents studied and in humans. This is a predominantly metabolic route, saturation occurring at around 1800 mg/m³. Increasing the dose above the saturation level does not lead to extra metabolism by this route. The other pathway involves a glutathione transferase, and leads via formaldehyde and formate to carbon dioxide. This route seems only to become important at doses above the saturation level of the "preferred" oxidative pathway. There are marked differences in species and dose-dependence in the contribution that this pathway makes to the metabolism of DCM (IPCS, 1996).

3.3 Acute toxicity/irritation

3.3.1 Introduction

The term "acute toxicity" is used to describe the adverse effects on health which may result from a single exposure to a substance, via oral, dermal or inhalation. An aspect of the acute effects is the skin and respiratory sensitisation of a substance. A sensitiser is a substance which, if it is inhaled or if it penetrates the skin, is capable of eliciting such a hypersensitivity reaction that characteristic adverse effects are produced on further exposure to it. Criteria for classification of acute toxicity and skin and respiratory sensitisation are given in Directive 93/21/EEC.

Human data on the acute effects of substances might be available from (case) reports on the effects of accidents or abuse, from reports on effects following short-term exposures during use, from studies on volunteers, and/or from experience gained from the use of some substances as a medical agent. In most cases the exact dose of DCM to which the subject was exposed to is unknown. From animal tests, data should be acquired on any adverse effects occurring within a given time after administration of single doses of the substance to the test animals. For the standard acute oral and dermal test, the LD $_{50}$ should be determined. Similarly for an acute inhalation toxicity study, the LC $_{50}$ should also be determined. A summary of data of animal tests and human case reports on acute effects of DCM is given in Appendix 1.

3.3.2 Acute effects of DCM on humans and animals

Animal studies

Animal studies indicate that acute exposure to high levels of DCM can adversely affect the liver and the kidneys. Animal testing showed different LD_{50}/LC_{50} values for different species of animals and different types of exposure: for rats, a LD_{50} (oral) 1410-2524 mg/kg has been found. The LC(D)₅₀ (inhalation) range for rats is 197790 (15 min LC₅₀)- 28000mg/m³ (6-h LC₅₀). LD₅₀ (intraperitoneal) for rats is 350 mg/kg. The results for mice are slightly lower (ATSDR, 1993).

Human case reports

Acute contact with DCM can result in adverse effects to the central nervous system (CNS) and the heart and can cause corneal burns, erythema, and burning skin. DCM will irritate the skin and eyes especially when evaporation is prevented (ATSDR, 1993). Prolonged contact may cause chemical burns. Inhalation of high concentrations of DCM or ingestion of DCM can result in death. The lowest lethal ingested dose of DCM reported for humans is 357 mg/kg (RTECS, 1994).

Predominant acute effects in human beings are CNS depression and elevated blood carboxyhaemoglobin (CO-Hb) levels. These effects are reversible. Other targets can be the liver and, occasionally, the kidneys (IPCS, 1996). Mild CNS effects in humans have been reported following exposure to concentrations as low as 694 mg/m³ for 1.5 to 3 hours (Putz et al., 1976). More significant effects occur at concentrations in excess of 2000 mg/m³. Narcosis has been reported to occur following exposure to 69000 mg/m³. Fatal accidents have been reported under unknown but most probably extremely high concentrations, e.g. when using DCM paint remover in unventilated cellars (UNR, 1999). The metabolism of DCM to carbon monoxide leads to increase in blood CO-Hb levels following acute exposure. Exposure to either 100 or 530 mg/m³ for 7.5 hr. leads to CO-Hb levels of 3.4 % and 5.3 % respectively (Di Vincenzo and Kaplan, 1981 as cited by IPCS, 1996:87).

Review

Table 3.1 gives an impression of the relation between dose and response of DCM in humans and animals. A detailed review of tests is given in Appendix 1. The animal test data inventoried are of less relevance in the evaluation of possible acute effects on humans, since exposures tended to be orders of magnitude higher than the human case data cited above.
Table 3.1: An impression of the short-term effects of DCM

Species and pathway	Level	Response
Animals		
 Ingestion 	1410-2250 mg/kg bw	LD ₅₀ (oral) rats
Humans		
 Ingestion 	357 mg/kg bw	Death (lowest reported lethal dose for
 Inhalation 		humans)
	100-530 mg/m ³	CO-Hb levels in blood 3.5-5%
	694 mg/m ³	Mild CNS effect; generally used as a
	_	LOAEL for non-smoking healthy individuals
	>2000 mg/m ³	Significant CNS effect
	69000 mg/m ³	Narcosis

3.4 Repeated/chronic toxicity

3.4.1 Introduction

Repeated dose toxicity comprises the adverse general (i.e. excluding reproductive, genotoxic or carcinogenic effects) toxicological effects occurring as a result of repeated daily dosing with, or exposure to, a substance for a part of the expected life span (sub-acute or sub-chronic exposure) or for the whole life span (or the major part of the life span), in the case of chronic exposure

Human data may include epidemiological studies and other human experiences. There are a number of reports from case studies on long-term exposure of DCM to humans. Repeated dose toxicity tests on animals provide information on possible adverse effects likely to arise from repeated exposure of target organs, and on doseresponse relationship. Appendices 2 and 3 review a number of human case studies and animal studies that give information about long-term effects of DCM.

3.4.2 Chronic effects of DCM on humans and animals

Animal studies

The LOAEL for CNS oppression by inhalation in all animal species is set at 7100 mg/m³. Animal studies indicate that chronic exposure to high levels of DCM adversely affects the liver and the kidneys. From the chronic studies included in Appendices 2 and 3, the study of Nitschke et al. (1982, 1988) gives the lowest NOAEL for liver toxicity in rats by inhalation. It concerns a NOAEL for chronic intermittent inhalation exposure of 710 mg/m³. In an other study, slight cytoplasmic vacuolisation in the liver of both mice and rats of unspecified strain and sex was observed at 88-350 mg/m³ (Haun et al., 1972). Concerning oral intake, the two-year study executed on behalf of the US National Coffee Association (NCA, 1982; Serota et al., 1986) revealed that histological alterations of the liver of rats were evident at 50 mg/kg b.w. /day, and the low nominal dose, equal to an actual dose of 6 mg/kg b.w./day was considered to be the NOAEL.

Human case reports

Humans chronically exposed to DCM experience adverse effects of the central nervous system and the heart (ATSDR, 1993). Two workers who were exposed for 13 to 20 years reported arm and leg pain, dizziness and fatigue, loss of appetite and poor sleep. Others reported drowsiness, headache and tingling of hands and feet vision (US Airforce, 1989). Deaths occurring following chronic inhalation exposure have been attributed to cardiac injury and heart failure. No other target organs were identified (U.S. EPA, 1985).

Review

Table 3.2 gives an impression of long-term effects of DCM.

Species and pathway	Level	Response
Animals (rats) Ingestion Inhalation 	6 mg/kg b.w./day 35 mg/m ³ 88-350 mg/m ³ 710 mg/m ³ 7100 mg/m ³	NOAEL (rats) Slight redness of conjunctiva (rats) Slight cytoplasmic vacualisation (rats) NOAEL (rats) LOAEL (rats)

Table 3.2: An impression of the long- term effects of DCM

3.5 Carcinogenic effects of DCM

3.5.1 Introduction

Substances or preparations are defined as carcinogenic if they induce cancer or increase its incidence when they are inhaled or ingested or if they penetrate the skin. Classification criteria are given in Directive 93/21/EEC.

3.5.2 Carcinogenic effects of DCM on humans and animals

Animal studies

DCM has been shown to cause increase incidences of liver, mammary, and salivary gland tumours in rats and increase incidence of liver tumours in mice (ECSA, 1995). Various inhalation bioassays conducted in rodents, exposed to DCM concentrations up to 3500-4000 ppm six hours per day, five days a week for two years, showed statistically significant increases in the following types of tumours; benign mammary tumours and sarcomas in rats; alveolar/bronchiolar adenomas, alveolar/bronchiolar carcinomas and hepatocellular. The National Toxicology Programme (NTP, 1986) concluded that DCM shows some evidence of carcinogenicity in male rats and clear evidence of carcinogenicity in female rats and in male and female mice. The cited animal studies, particularly in mice, have raised concern over this chemical's potential to cause cancer in humans. However, the observation that carcinogenic effects were not found in the rat or the hamster, has led to additional research to seek the reason for this difference, and to determine the relevance for humans. A series of studies conducted by Green and colleagues suggests the following explanation as to why tumours are restricted to the mouse. According to Green (1995), DCM is metabolised via two pathways. At

low dose levels it is mainly metabolised by cytochrome P-450 which do not differ markedly between species. In mice, and then only at high dose levels, the glutathione-S-transferase pathway is dominant. Metabolites of this pathway are involved in the genotoxic mechanism that causes the tumours in mice. High enzyme activity within certain cells and within nuclei accounts for the markedly higher sensitivity of the mouse to genotoxic effects of DCM. Liver growth, pulmonary damage and increases in cell division are additional risk factors seen only in the mouse. Hence, Green (1995) concludes that the entire database indicates that the carcinogenic effects in the mouse are atypical of other species, including humans.

Human case reports

Human case reports and mortality studies (appendix 3) indicate the following. Two main studies of chemical factory workers exposed to DCM did not show an increased incidence of cancer. According to EPA (IRIS Substance File), the study of Ott et al. (1983) was designed to examine cardiovascular effects, and consequently the study period was too short to allow for latency of site-specific cancers. In the Friedlander *et al.*, 1978 study, exposures were too low, but the data provide some suggestion of an increased incidence of cancerous pancreatic tumours. This study was recently updated to include a larger cohort, followed through 1984, and an investigation of possible confounding factors (Hearne et al., 1987, 1990). Non-significant excess in pancreatic cancer deaths was observed, which was interpreted by EPA (1987) as neither clear evidence of carcinogenicity in humans, nor evidence of noncarcinogenicity. An update of the Ott et al. (1983) study based on longer follow-ups indicated possible elevation of liver and biliary tract cancers.

3.5.3 Conclusions with regard to carcinogenicity to humans

Some countries believe, based on animal tests that DCM has to be regarded as a possible cancer-causing substance. Appendix 4 gives a summary of the classification and legislation of the use of DCM in different countries. For instance, in the US the OSHA has reduced its DCM-exposure limit as a result of the *potential* carcinogenic effects of DCM to humans from 500 ppm to 25 ppm (82 mg/m³) eight-hour TWA, and 125 ppm (421 mg/m³) as a 15 minute permissible short-term exposure (U.S. OSHA, 1997).

However, many authors state that DCM cannot be considered to be a human carcinogen, mainly in view of the work of Green and colleagues cited above (Green *et al.*, 1986 and 1995; IPCS, 1996:185; Slooff and Ros, 1988). They believe that the analysis of different metabolic pathways in different animal species in combination with the inconclusive human epidemiological studies, show that the lung and liver cancer seen in mice is unique to that species and does not apply to humans.

The EU has labelled DCM as carcinogenic category 3, the lowest in the EU: 'Substances that need attention due to their possible carcinogenic properties for humans'. The chemical has to be labelled as Harmful (Xn), with the risk phrase R40 (possible risk of irreversible effects).

3.6 (Possible) standards with regard to exposure to DCM

3.6.1 Introduction

Deriving health risk standards from an available body of toxicological information in practice appears to be a cumbersome process, in which many choices have to be made that in quite some cases cannot be made entirely on objective grounds. Extensive sociological research has shown that it is possible, and even likely, that researchers working in different contexts, or at different times, will come to different conclusions when deriving risk standards (cf. Jasanoff, 1990; van Eijndhoven and Groenewegen, 1991). Furthermore, the national risk assessment and risk characterisation approaches that have led countries to take action have a strong national character. After inventory and analysis of the hazards and change to certain exposures and after taking into account the local social, economic and political changes countries develop their own risk reduction measurements. These decisions are usually arrived at after considerable debate on the numerous factors involved. Thus the legislation which applies in the different countries cover a broad range and are not consistent (OECD, 1994)⁸. A particular issue of relevance to this report is the use of safety factors when deriving maximum tolerable risk standards.

Traditionally, regulators have used default safety factors to translate test data like NOAELs, when available, to risk standards. Default factors of 10 were usually applied in the following cases (e.g. van Leeuwen and Hermens, 1995):

- 1. where the NOAEL was based on animal test data rather than effects on humans (interspecies variation);
- 2. to correct for the intraspecies variation among the human population;
- 3. where no comprehensive basis of test data was available. Examples include the situation where a LOAEL rather than a NOAEL was known for a specific effect or that for a specific chronic effect the NOAEL had to be based on a sub-chronic test since chronic test results were lacking.

In most cases this tradition led to the use of a safety factor of 100 on the NOAEL to correct for interspecies and intraspecies variation. The Technical Guidance Document does not follow this approach. It indicates that a NOAEL, without safety factors, can be used to calculate a margin of safety (MOS) in a specific exposure situation. Then, taking into account the relevance of interspecies variation, intraspecies variation, and other factors, the risk assessor is required to judge whether the MOS can be regarded as sufficient. The Technical Guidance Document seems to follow those authors who judge that a rigid use of default safety factors may be too conservative in many cases (e.g. Lewis et al., 1990).

⁸ Appendix 4 reviews exposure limits and the classification of DCM applicable in different countries.

In this section, we will indicate which main lines of argument lead to certain maximum exposure levels pointing to DCM. We will discern three types of exposure situations:

- long-term and short-term exposure of workers, which basically concerns direct exposure related to the industrial and professional use of DCM;
- short-term exposure of the general public, which basically concerns direct exposure as a result of consumer applications of DCM;
- long-term exposure of the general public, which basically concerns indirect exposure as a result of all uses of DCM in society.

In some cases, maximum short-term exposure levels are derived from standards with regard to chronic toxicity. Hence, we will discuss chronic toxicity first.

3.6.2 Chronic/long term exposure (general population)

Maximum levels for inhalation and oral ingestion need to be derived. Various lines of arguments can be found in literature, roughly sketched below.

In the first line of argument, one concludes that there are no sufficient grounds to consider DCM to be a potential carcinogen for humans (e.g. Slooff and Ros, 1988; IPCS, 1996). For inhalation, the study of Nitschke et al. (1982 and 1988) generally serves as a basis, since of the studies shown in Appendices 2 and 3 this study gives the lowest NOAEL. The critical effect is liver toxicity. There is some discussion about the exact level of the NOAEL. The IPCS (1996) and the authors of the study themselves (Nitschke et al., 1982 and 1988) concluded that the NOAEL in that study was 710 mg/m³. However, at that level the number of livers with enhanced multinucleated hepatocytes still was larger than in the control group, though not statistically significant. The Dutch RIVM therefore chose the lower level of 177 mg/m^3 as the NOAEL, but agrees that arguments are available for both choices (Könemann, 1996). Those who wish to apply default safety factors of 10 for interspecies and intraspecies extrapolation end up with standards of 7 or 1.7 mg/m^3 for chronic human exposure. However, since the original animal study concerned only an intermittent exposure of six hours a day, five days a week, some argue that a correction has also to be made to continuous exposure of 24 hr/day, seven days a week. This implies a correction with a factor 5.6 leading to chronic 'NOAELs' of 125 or 30 mg/m³ for human exposure, or including safety factors levels of 1.25 or 0.3 mg/m^3 , respectively. As for *oral* intake, the study of NCA (1982) once again is the best basis. Here, however, the lowest (actual) dose of 6 mg/kg b.w./day is considered as a NOAEL. Those who wish to apply default safety factors for intraspecies and interspecies extrapolation derive a TDI for humans of 0.06 mg/kg b.w./day. In sum, this line of argument leads to the following human toxicity limits for long-term exposure to DCM given below:

- Inhalation: NOAELs of 30, 125, 170 or 700 mg/m³; maximum exposure levels using a default safety factor of 100 would be 0.3, 1.25, 1.7 or 7 mg/m³;
- Ingestion: a NOAEL of 6 mg/kg b.w./day; the maximum exposure using a default safety factor of 100 would be 60 μg/kg b.w./day.

In the second line of argument, DCM is thought to be a carcinogen in view of its carcinogenic effects in animal studies. The argument that the mechanism behind this effect may be less relevant for humans is not taken into account. This is an effect for which no threshold exists. Hence, no NOAEL can be derived and the discussion on safety factors is irrelevant. Then, regulators have to make a subjective choice - by definition – which risk on effects are acceptable. Usually, a 1 in 10,000 chance of death in a lifetime (or roughly 1 in a million per year) is chosen as acceptable. Making use of the results of the study of NTP (1986) via a linear multi-stage procedure an inhalation unit risk of 4.7 E-7 per μ g/m³ can be derived. This implies a 1 in 10,000 chance of death in a lifetime at a concentration of 0.2 mg/m^3 . Similarly, making use of the data from studies of NCA (1983) and NTP (1986), a 1 in 10,000 chance of death in a lifetime at a concentration of 0.5 mg/l in drinking water can be calculated (US EPA, IRIS Substance File). Assuming a daily water intake of two litres for an adult of 70 kg this equals a TDI of 15 µg/kg b.w./day. Both the assumption of carcinogenic behaviour and the adequacy of linear multi-stage extrapolation models have been severely challenged (ECETOC, 1988 and 1989). Yet, assuming that a one in a million chance of death per year to be a reasonable standard, those following this line of argument end up with the following chronic health risk standards for DCM:

- Inhalation: 0.2 mg/m^3 in air;
- Ingestion: 15 µg/kg b.w./day.

Finally, the WHO Working Group on Volatile Organic Compounds (WHO-AQG) recently derived a standard for inhalation exposure to DCM for the general public choosing another critical effect. This working group chose the formation of CO-Hb as end-point rather than liver toxicity. The criterion they chose was a CO-Hb-level not exceeding 0.1 % from indirect exposure to DCM alone, equal to a concentration of 3 mg/m³ (WHO, 1996)

In sum, depending on the line of argument, for humans one can defend limit values of 0.2 to 700 mg/m³ for long-term inhalation exposure, and of 15 to 6000 μ g/kg b.w./day for ingestion. The lower values are based on the assumption that DCM is a carcinogen, and that a 1 in 10,000 chance of death in a lifetime is acceptable. The higher values assume that effect thresholds exist and reflect the NOAELs without using any margin of safety. If one follows the arguments of IPCS (1996), suggesting that DCM should not be considered as a human carcinogen, and that the NOAEL for liver toxicity in rats is 710 mg/m³, these ranges are:

• Inhalation: 3 mg/m³ (the WHO air quality guideline based on a maximum of 0.1 % increase in Co-Hb levels) to 125-700 mg/m³ (the NOAEL for liver toxicity. The 125 mg/m³ is corrected for the fact that the 700 mg/m³ NOAEL is derived from a six-hour, five day a week exposure test). If a default safety factor of 100 is used to translate the NOAEL for liver toxicity to a limit value, this range can be narrowed to 1.25 to 7 mg/m³;

 Ingestion: 60 µg/kg b.w./day when a default safety factor of 100 is used. However, this value can be up to 0.6 mg/kg b.w./day when safety factors are seen as irrelevant.

3.6.3 Short-term exposure (general population)

Relatively few attempts have been made to derive a standard for short-term exposure of DCM for protection of the general population. As will be discussed in the next section, most of such standards have been developed within the framework of occupational health protection. But, as has been pointed out on various occasions, such standards are not likely to be adequate for the general public. Consumers belong, in terms of susceptibility to health effects, to a much more diverse population than workers (healthy workers effect).

One approach to derive a short-term exposure limit for inhalation is to use the longterm exposure limit for the general population as a starting point. For instance, in its 1989 risk assessment RIVM proposed a maximum short time exposure limit (inhalation) on 490 mg/m³. The short-term exposure limit is calculated based on the same results from the same animal study as that of the long-term exposure limit (where RIVM chose a NOAEL a value of 173 mg/m³). The following formula is applied: *Peak value* (*t min*)= *limit value* (24*h*)* 60 *min/t**24*h*/1*h*. With a 24h limit value of 1.7 mg/m³, a five minute peak value can be calculated of 490mg/m³, and a one hour value would be 40 mg/m³. However, the criticism of this approach is that deriving a short-term exposure limit related to a chronic health effect (liver toxicity) is difficult to justify (Slooff and Ros, 1988; Könemann, 1996).

The alternative is to use data from short-term toxicity tests. From Appendix 1 the conclusion can be drawn that effects on the CNS occur at an exposure of about 700 mg/m³ for several hours (laboratory study on human volunteers). RIVM proposed to take this as a LOAEL. RIVM further argued that a margin of safety of 100 with this LOAEL is necessary to correct for extrapolation to a NOAEL and for intraspecies and interspecies variation. Via this line of argument, a short-term exposure limit of 7 mg/m³ was suggested that would be a safe value for exposure of the general population for one to several hours (Könemann, 1996). In the US, the ATDSR (1993) also suggested a short-term exposure limit, based on a study showing effects on the CNS at levels of 1060 mg/m³, arriving at a minimal risk level of 1.4 mg/m³ for a 24-hour exposure.

This line of argument leads to a possible standard for acute exposure of the general population of some 7 mg/m³ for one to a few hours. If exposures to a higher level during shorter periods, e.g. 15 minutes, can be averaged over this period, the 15-minute exposure limit could be a factor 4 to 10 higher.

Compared to the (possible) chronic exposure limits, these possible limit values for acute exposure are rather low. A clear point of discussion that cannot be decided upon with scientific arguments is the relevance of protecting the general population to (reversible) short-term CNS-effects. Furthermore, whether or not the use of a safety factor of 100 compared to the LOAEL as suggested in Könemann (1996) is too stringent, is debatable.

3.6.4 Short-term and long-term occupational exposure limits

As for occupational health standards, according to IPCS (1996) most, if not all, are based on increases in blood of CO-Hb levels. This implies that occupational health limits are based on a different end-point as the long-term exposure limits for the general population reviewed in section 3.6.2. In most cases, an increase in CO-Hb level of 5 % is judged as acceptable. Exposure to 100 mg/m³ and 530 mg/m³ would lead to levels of 3.4 % and 5.3 % respectively (IPCS, 1996). Hence, as is shown in Appendix 4 most of the eight-hour TWAs appear to be in this range, with short-term exposure limits (STELs) often derived on a time-weighted basis from this standard:

- The range of eight-hour TWA limits in EU member states is between 120 and 350 mg/m³. US OSHA proposed a limit of 82 mg/m³, and several other countries still use looser standards, up to 500 mg/m³;
- The range of the 15 minute short time exposure limits between the different EU member states is 250-2500 mg/m³.

To a certain extent, occupational exposure may be seen as a long-term exposure situation. One can observe that in quite a few EU member states the occupational exposure limits (OELs) leave only a margin of safety of two with the loosest longterm NOAEL of 700 mg/m³ derived in section $3.6.2^9$. Even the most stringent standard of 120 mg/m³ within EU member states leaves a margin of safety of only a factor six. Though it is generally accepted that lower safety factors can be applied for occupational exposure than for exposure of the general public, such MOS seem at first sight low in view of the possible interspecies and intraspecies variation. However, it must be noted that various aspects of the evaluation, such as the exposure situation, are not fully comparable. For example, the NOAEL is meant for lifetime exposure, where occupational exposure takes place during (a part of) a professional career. An assessment of whether the OELs and the NOAEL are compatible or not falls beyond the scope of this study. In this respect, a rather fundamental question is at stake. The EU Technical Guidance Document demands the evaluation of exposure to workers, but virtually all EU member states have their own evaluation and expert structure for deriving OELs. Hence, one could argue that this evaluation should be left entirely to the existing (national) structures in which OELs are set.

⁹ Note that the NOAEL of 700 mg/m3 already is based on a 6 hour a day, 5 days a week exposure .

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4. Risk characterisation of DCM

4.1 Introduction

The risk characterisation follows the principles for the risk characterisation of new and existing substances as laid down in the Technical Guidance Document. It entails the comparison of the quantitative and/or qualitative information on exposure of a human population to the NOAEL and the LOAEL or, where appropriate, a qualitative evaluation of the likelihood that an effect will occur at the given exposure. This is done separately for each potential population exposure and for each effect as was described in Chapter 3.

4.2 Risk characterisation

Table 4.1 summarises the criteria derived in section 3.6 for the evaluation of the short-term and long-term exposure of workers and the general public. As discussed in section 3.6, exposure standards can be derived via different approaches, consequently in some cases ranges rather than single values are shown. For the risk characterisation, three exposure situations are relevant:

- 1. long-term and short-term exposure of workers, which basically concerns direct exposure related to the industrial and professional use of DCM;
- 2. short-term exposure of the general public, which basically concerns direct exposure as a result of consumer applications of DCM;
- 3. long-term exposure of the general public, which basically concerns indirect exposure as a result of all uses of DCM in society.

The Technical Guidance Document indicates that if in an exposure situation the NOAEL is exceeded, the situation should be regarded as 'of concern'. In other situations, the magnitude by which the NOAEL exceeds the estimated exposure needs to be considered. Taking into account several factors such as the nature and severity of the effect, the human population to which the exposure applies, and the uncertainty arising from the variability in the experimental data and intraspecies and interspecies variation, the risk assessor will decide which of the following results is applicable:

- (i) there is a need for further information and/or testing;
- (ii) there is at present no need for further information and/or testing and no need for risk reduction measures beyond those already being applied;
- (iii) there is a need for limiting the risks taking into account the risk reduction measures which are already being applied.

Table 4.	1: The	basis for a	a toxicologica	l evaluation of	f exposure to	DCM
		j		· · · · · · · · · · · · · · · · · ·		

Population	Short-term	Long-term
General public Inhalation 	700 mg/m ³ (LOAEL, humans; 1-few hours) ^a	125-700 mg/m ^{3 b} (NOAEL, liver toxicity, rat)
 Ingestion 	N/A	6 mg/kg b.w./day (NOAEL, liver toxicity, rat)
Workers (occupational exposure)	250-2500 mg/m ³ (15-min STEL) ^c	120-350 mg/m ³ (8 hr. TWA in EU countries) ^c

- a. Based on protection against light, reversible CNS effects. The traditional safety factor approach would require a margin of safety of 100 to correct for the fact that a LOAEL rather than a NOAEL is used, and to include intraspecies variation. This would result in a standard of 7 mg/m³. For shorter time frames (e.g. 15 minutes), a value which is a factor 4 to 10 higher may be defensible.
- b. The traditional safety factor approach would require a margin of safety of 100 in relation to interspecies and intraspecies extrapolation. This leads to standards of 60 μg/kg b.w./day for oral intake and 1.25-7.0 mg/m³ for inhalation. The latter value is well in line with the Air Quality Guideline of 3 mg/m³ derived by the WHO based on a maximum increase in CO-Hb levels of 0.1 % in the general population by indirect exposure to DCM.
- c. Range of occupational health standards in different countries. In most cases based on a maximal increase of 5 % in CO-Hb levels

Hence, the evaluation basically hinges on the margin of safety chosen to arrive at conclusion (i), (ii), and (iii). Inevitably, this choice has many subjective elements and can always be challenged. Given the limited budget of this project, we opted for a rather pragmatic approach in each of the exposure situations mentioned above.

1. Short-term exposure of workers (professional and industrial occupational exposure)

For short-term exposure, judgement (ii) is applied when the lowest short-term 15 minute STEL of 250 mg/m³ is not exceeded. This is just a factor 2-3 lower than the LOAEL for short-term exposure, but the STEL applies for a shorter period than the derived LOAEL. Between this value and the LOAEL of 700 mg/m³ judgement (i) is applied, providing that the exposure is considerably shorter than the one hour or more for which the LOAEL is derived. In case the short-term exposure is above the LOAEL, judgement (iii) is applied. In sum, the judgements will be:

- (i) between 250 mg/m³ (lowest STEL in EU member states) and 700 mg/m³
 (LOAEL for short-term exposure);
- (ii) below 250 mg/m^3 (lowest STEL in EU member states);
- (iii) above 700 mg/m³ (LOAEL for short-term exposure).

2. Long-term exposure of workers (professional and industrial occupational exposure)

As discussed in section 3.6.4, the margin of safety between the higher occupational health standards in the EU and the NOAEL for long-term exposure is low. Pragmatically, we take the most stringent occupational health limit in the EU (120 mg/m³), which corresponds with a MOS of about six with the NOAEL, as the boundary below which judgement (ii) will apply. Between 120 and 350 mg/m³, the latter being the highest European occupational health standard, we will apply judgement (i). Above 350 mg/m³ judgement (iii) will apply, since in that situation a MOS of less than two is at stake exceeding even the loosest occupational health standard. In sum, the judgement will be:

- between 120 mg/m³ (lowest OEL in EU member states; MOS of a factor six with the NOAEL) and 350 mg/m³ (highest OEL in EU member states, MOS of a factor of two with the NOAEL);
- (ii) below 120 mg/m^3 (lowest OEL in EU member states);
- (iii) above 350 mg/m³ (highest OEL in EU member states; MOS of a factor of two with the NOAEL).

3 Short-term exposure of the general public

As for short-term exposure of the general public, we feel that a more prudent approach has to be taken than for short-term exposure of workers. The general public is a much more diverse population. Hence, to a certain extent we tend to follow the RIVM's proposal of applying a MOS of 100 on the available LOAEL, and use the resulting limit of 7 mg/m³ for a one or more hours exposure as the boundary below which judgement (ii) will apply. However, this approach to deal with short-term exposure of consumers is rather stringent and for some debatable (since it is based on short-term, reversible CNS effects). On the other hand, it seems obvious that judgement (iii) (risk reduction) should apply when even the lowest available occupational health standard has been exceeded (the 15 minute STEL of 250 mg/m³). This target group can be expected to be more vulnerable than professional workers. In the range between these extremes judgement (i) will apply. In sum, the judgement will be:

- between 7 mg/m³ (MOS of 100 with the LOAEL) and 250 mg/m³ (lowest STEL in the EU for workers; MOS of 2-3 with the LOAEL);
- (ii) below 7 mg/m³ (MOS > 100 with the LOAEL);
- (iii) above 250 mg/m³ (lowest STEL in the EU for workers, MOS of 2-3 with the LOAEL).

4 Long-term exposure of the general public

The classical safety factor approach for long-term exposure of the general public would call for a MOS of 100 compared with the NOAEL, or a reference level of 1.25 to 7 mg/m³. This is well in line with the air quality guideline of 3 mg/m³ derived by the WHO. Pragmatically, we take this as a reference point below which judgement (ii) will apply. Above this level, judgement (i) or (iii) will apply depending on the level and frequency of exposure. In sum, the judgement will be: (ii) below 1.25-7 mg/m³ (MOS of 100 with the NOAEL); (i) or (iii): above 7 mg/m³, depending on MOS (irrelevant in practice).

In Tables 4.2 to 4.10 this evaluative framework is confronted with the exposures summarised in Table 2.4. Each table ends with a conclusion if in the exposure situation at stake there has: (i) a need for further information and testing; (ii) no need for further information or risk reduction, or (iii) a need for risk reduction.

Table 4.2 Production of DCM

Industry	Production of DCM
Activity	Production activities
	Process plant
Population exposed	Plant personnel
Exposure level 8 hr TWA mg/m ³	3.5-63 (219-374 maintenance activities)
Peak exposure mg/m ³	-
Evaluation	Exposure levels are within limits of the whole
	range of occupational health standards
	identified. Maintenance activities can probably
	considered as incidental exposure
Overall Risk characterisation	(ii) No need for further information or risk
	reduction

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Table 4.3 Paint stripping

Use	Paint stripping		
Activity	Paint stripping by consumers and workers		
Population exposed	Consumers/Professionals		
Exposure level 8 hr	Consumers 460-2,980(unventilated, 8 hr TWA)		
TWA mg/m ³		60-400(v	entilated, 8hr TWA)
	Workers:	350-420	(8 hr TWA average)
		25-7,000	(8 hr TWA range)
Peak exposure mg/m ³	Consumers:	up to14.1	00(unventilated, worst case)
		840-2,76	5 (1 hr TWA, unventilated
		129.5-94	8 (1 hr TWA, door open)
		289 (2 hr	average, well ventilated)
	Workers:	up to 5,40	00
Evaluation	Consumer applicatio	n (unvent	ilated):
	Unventilated consume	r application	ons lead to exceeding even the
	regular 8 hr TWA occupational health standards. Short term		
	exposure orders of magnitude higher than the derived short-		
	term exposure standard for the general public.		
	Consumer application (ventilated):		
	Even if ventilation is good, the short-term exposure seems a at		
	least a factor 10-20 higher than the (stringent) short-term		
	exposure standard for	the generation	al public of 7 mg/m ³ . Even in
	well-ventilated situations, the lowest available short-term STEL		
	for workers of 250 mg/	/m² may be	e exceeded.
	Professional/industri	ial applica	ntion:
	Long-term concentration	ons will in	some cases exceed the 8 hr
	TWA limits. The avera	ge long-te	rm exposure is within 8 hr TWA
	limit for workers.		
	Peak concentrations w	/ill in some	e cases exceed the range of
	STELs for workers.		
Overall Risk	Consumer app. (unver	ntilated):	(iii) risk reduction needed
characterisation	Consumer app. (ventil	ated):	(iii) risk reduction needed/ (i)
			more information needed
	Professional/industrial	app.:	(iii) risk reduction needed/ (i)
			more information needed

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Table	4.4:	Adhesives
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Industry/use	Decorative industrial, Aerosols		
Activity	Application adhesives		
Population exposed	Workers/Consumers		
Exposure level 8 hr TWA mg/m ³	3.5-1500 (average 200)		
Peak exposure mg/m ³	350		
(note: only data for workers)			
Evaluation	For short-term and long-term exposure of workers occupational health standards may be exceeded i countries with low standards. It has to be noted that the maximum exposure occurs during sprayin application, only relevant for occupational exposure. No exposure data for consumers are available. If the above exposure data also apply, peak exposures are clearly above the range considered acceptable for consumers in this repor Since actual use of DCM-containing adhesives by consumers may be minimal (see Chapter 5), more		
Overall Risk characterisation	Occupational exposure: Specific ap	plications: (iii)	
	risk reducti	on needed	
	Consumer exposure: (i) More inf	ormation	
	needed		

Table 4.5: Pharmaceutical applications

Industry	Pharmaceutical	
Activity	Production work	
Population exposed	Production personnel	
Exposure level 8 hr TWA mg/m ³	<106	
Peak exposure mg/m ³	-	
Evaluation	Long term exposure is in general below the lowest 8 hr TWA applicable in the EU. It is likely that if the higher exposure levels occur in countries with relatively high exposure standards.	
Overall Risk characterisation	(ii) No need for further information or risk reduction	

Use	Aerosols		
Activity	Hairdressing (salon)		
	Hairdressing (h	nome)	
Population exposed	Personnel/Con	sumer	
Exposure level 8 hr TWA	Consumers:	7 (calcul	ated from STE, unventilated)
mg/m ³	Workers:	77.7 (he	avy salon use)
Peak exposure mg/m ³	Consumers:	<800 (5	min TWA, unventilated)
		100 (5 m	in TWA, extreme ventilation)
		20 (5 mii	n TWA, spray at back of head,
		extreme	ventilation
	Workers:	21-106;	<180 during filling
Evaluation	In adverse conditions (no ventilation, small room)		
	short-term consumer exposure may be above 250		
	mg/m ³ . Short-term consumer exposure in most		
	cases will be above 7 mg/m ³ .		
	Long-term and peak exposures for professional use		
	seem in most cases lower than the range of 8 hr		
	TWAs resp. STELs for workers. However, we feel		
	that much depends on the ventilation and hence		
	regard this as an important uncertainty in our		
	evaluation for which more information is de		nore information is desirable.
Overall risk characterisation	Consumer exp	osure:	(i) more information needed/
			(iii) risk reduction needed
	Occupational e	exposure:	(i) more information needed

Table 4.6: Aerosols

Table 4.7: Other c	hemical industry
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Industry	Foam		
Activity	Foam industry: blowing, m	ould release, glue spraying, etc	
Population exposed	Workers and personnel		
Exposure level 8 hr TWA	0-160 (average 20)		
mg/m ³	13-700 (Foam industry)		
Peak exposure mg/m ³	up to 350 (10 min. TWA)		
	≤≤1770 (Foam industry)		
Evaluation	Long-term average exposure levels are within the 8 hr TWA		
	limits, with the exception of some cases in the foam industry.		
	Peak exposure levels are within the range of the STELs.		
Overall risk	Other chemical industry:	(ii) no need for information or risk	
characterisation		reduction	
	Foam industry:	(iii) risk reduction needed/ (i)	
		more information needed	

<i>Table 4.8:</i>	Degreasing
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Industry	General Manufacturing, cleaning and degreasing
Activity	Cleaning and degreasing
Population exposed	Workers, plant personnel
Exposure level 8 hr TWA mg/m ³	14-1000 (average 280)
Peak exposure mg/m ³	-
Evaluation	Long-term exposure limits exceeds in quite
	some cases even the least stringent 8 hr
	TWA limits for workers in the EU.
Overall risk characterisation	(iii) risk reduction needed/ (i) more
	information needed

Table 4.9: Coatings, textiles, detergents, food extraction

Industry	Food industry
Activity	Extraction
Population exposed	Plant personnel
Exposure level 8 hr TWA mg/m ³	110
Peak exposure mg/m ³	-
Evaluation	Long term exposure is in general below the
	most stringent 8 hr TWAs in the EU
Risk characterisation	(ii) no need for information or risk reduction

Table 4.10: Others

Use/industry	Different/diffuse
Activity	Different/diffuse
Population exposed	General
Exposure level 8 hr TWA mg/m ³	N/A
Peak exposure mg/m ³	
Evaluation	N/A
Risk characterisation	N/A

Use/industry	All/indirect exposure
Activity	All/indirect exposure
Population exposed	Consumers/generic population
Exposure via air mg/m ³	0.002-0.03 mg/m ³ in urban air
	0.9 mg/m ³ near hazardous waste sites
Exposure via water	1.2 μg/kg b.w./day (worst case)
Exposure via food	Negligible compared to exposure via air
Evaluation	There is a margin of safety of 1000 or more
	compared to any NOAEL considered, except
	maybe close to production plants where
	DCM is used.
Risk characterisation	(ii) no need for information or risk reduction

4.3 Review

Table 4.12. provides a summary of the risk characterisation of the different exposure situations.

It is clear that indirect exposure of the general population is not a problem. The average concentrations in the environmental media are so low that it is unlikely that risk levels are exceeded. A possible exception is exposure of the general population close to industrial plants where DCM is used. However, solving such problems seems primarily a matter of better emission controls rather than measures in terms of a restriction of marketing and use of DCM, which form the primary point of attention in this study.

Four of the nine different applications to do with direct exposure of workers and consumers specified in this study (excluding the category 'others') to not seem to be a priority. For the following situations, there is at present no need for further information and/or testing and no need for risk reduction measures beyond those already being applied (ii):

- the production of DCM;
- pharmaceutical applications;
- other chemical industry (with the exception of the foam industry);
- coating, textiles, detergents and food extraction.

In these applications, only direct exposure to workers is at stake. Occupational health standards are in general not exceeded, excepting for situations where exposure levels found in literature are confronted with the stringent eight-hour TWA proposed by the US OSHA. Yet, one can expect that the higher exposure values found in literature are applicable to situations where the stringent OSHA standard does not apply. It is not unlikely that better exposure control measures can ensure that also this stringent standard is met if necessary.

Exposure category	(ii) no need for information or risk reduction	(i) need for further information and/or testing	(iii) there is a need for limiting risks
Production of DCM	Х		
Paint stripping			
Consumer			
(unventilated)			Х
 Consumer (ventilated) 		Х	Х
 Occupational 		X	X
Adhesives			
 Consumer 		X	
 Occupational 	Х	Χ	
Aerosols			
Consumer		Х	Х
 Occupational 	Х	Х	
Pharmaceutical	Х		
application			
Other chemical industry			
 Other industries 	Х		
 Foam industry 		Х	Х
Degreasing		Х	Х
Coatings, textiles,	Х		
extraction			
Others	N/A	N/A	N/A
Indirect exposure	Х		

Table 4.12: A review of risk characterisation of the different exposure situations to DCM.

For most other applications, the situation is not so clear, calling indeed for further information and or testing (ii), or a possible need for risk reduction (iii), sometimes in specific exposure situations only:

- the use of paint stripper (occupational and consumer exposure);
- the use of adhesives (occupational and consumer exposure);
- the use of aerosols (occupational and consumer exposure);
- foam industry;
- degreasing.

As for consumer exposure, particularly the (unventilated) use of paint strippers by consumers may be most critical, since in such situations even the STELs for workers will be exceeded. Data on the use of adhesives exposure is lacking and short-term exposure to aerosols may be above the limits derived in section 4.2 in unfavourable situations (heavy use, low ventilation, small rooms)

In all these applications occupational exposure seems to be within the eight-hour TWAs range for occupational health standards applicable in various countries. They may be exceeded if good housekeeping (sufficient ventilation, best practice) is not applied. The use of aerosols by workers may be the least critical, mainly since the exposure to classical aerosols from spray cans is not a continuous process and the actual average emission thus is limited. The spraying of adhesives applied in the foam industry are effectively covered under the heading 'adhesives'. Of these applications, the professional use of paint stripper seems to be the most critical. Industrial workshops and professional use alike have little options for applying closed system technologies. Even in ventilated situations, exposure below occupational health standards may not always be ensured. Ensuring that good housekeeping is applied may prevent problems, but policy makers might consider enforcing restrictions on marketing and use of DCM in favour of a less critical alternative.

In view of a selection of activities useful for the evaluation of restrictions on marketing and use of DCM, we feel that foam blowing and degreasing are not a priority. Here, technical measures (closed systems) are probably an appropriate first means to solve any problems rather than a restriction of marketing and use of DCM. Such technical measures are less feasible for the safe use of paint remover, adhesives and aerosols, particularly in consumer applications, so market restrictions could be one of the options if risk reduction is seen as necessary and/or desirable. We therefore selected these applications for further research.

4.4 Conclusion

In sum, section 4.3 leads to the following suggestions for investigating the consequences of the restriction of marketing and use:

- the use of paint stripper;
- the use of adhesives;
- the use of aerosols.

Our selection excludes the following applications from this report:

- the production of DCM;
- pharmaceutical applications;
- other chemical industry (with the exception of the foam industry)
- coating, textiles, detergents and food extraction;
- foam industry;
- degreasing.

The need for measures like the restriction of marketing and use with regard to paint remover, aerosols and adhesives invoke the observations that follow. As for professional applications and industrial applications, other types of measures may be adequate to deal with situations where risk reduction is desirable, or to ensure compliance with safe standards. Analysis of the type of measure most desirable and adequate is beyond the scope of this study. Consumer applications (particularly in the case of paint removers and adhesives) concerns rather infrequent exposure. Therefore, the risk evaluation was based on an assessment of short-term risks. Here, a clear point of discussion is that the derived health standard is based on (reversible) CNS effects, and that it may be regarded as being too stringent. Yet, particularly in unventilated situations, exposure may well be above the regular short-term exposure limits valid for workers. Consumers are a very inhomogeneous population, and one cannot expect they will apply on a broad scale the same 'best occupational practice' as professional users. At the same time, one has to acknowledge that consumers will not use products like paint strippers and adhesives on a regular basis. To conclude, suggestions to apply the rather stringent measure of restrictions of marketing and use will inevitably lead to counterarguments, and no simple, clear-cut and decisive logic is available that can underpin a choice in favour or against any of the two positions.

The following chapters contain an assessment of the economic and socialeconomic effects of possible market restrictions of DCM on producers, formulators and users community-wide, including the possible effects on trade. Furthermore, the risks, economic and technical aspects and implications related to possible alternatives will be discussed.

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5. Economic and social implications of market restrictions

5.1 Introduction

Specific DCM products indicated as priorities in Chapter 4 in the analysis of socioeconomic effects of market restrictions and concern the following:

- the use paint stripper;
- the use of adhesives;
- the use of aerosols.

The production-consumption chains of these products all have the same structure:

- 1. The first step is the production of DCM;
- 2. Then, DCM is formulated into a product by formulators;
- 3. Finally, the products are applied by end-users.

Three main market end-use sectors of the three different applications can be distinguished: the consumer market, the professional market and the industrial sector. Although we indicated in Chapter 4 that consumer applications and to a lesser extent professional applications were the main priorities, we will also include some results of industrial applications. The reason for this is that for some applications the distinction between professional and industrial use is not always well defined. In addition, experiences with socio-economic effects concerning transitions in the industrial sector may give additional insight into the effects of transition in the consumer or professional sectors.

In the next sections, we will discuss the socio-economic effects of possible marketing restrictions for each product group. The sections are structured as follows:

- 1. First, an overview of the production-consumption chain will be given.
- 2. Second, alternatives for the different applications will be discussed together with the advantages and drawbacks of these alternatives in terms of environmental risks.
- 3. Third, we will present for each step in the production-consumption chain any advantages and drawbacks of possible market restrictions of the use of the DCM-containing product.

The impact on the producers of DCM is not directly related to an end-use product, and will therefore be discussed in a final section. Where available, estimates will be given of the ratios of turnover and employment per ton DCM used. Any available information pertaining to differences in technical performance, costs and effects on employment of the use of alternatives will be discussed. This analysis was mainly based on a search of the literature and a rather broad inquiry of the industry sector and users related to the product at stake. Other problems concerning a change to alternatives of DCM will be mentioned as well.

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5.2 Production and use of paint stripper

5.2.1 Overview of the production-consumption chain

DCM is claimed to be the most powerful paint stripper solvent available in common use. Paint strippers based on DCM were introduced around 1950 as an effective and non-flammable replacement for the older paint-stripping agents invented in the thirties, which were mainly based on solvents such as aromatics, esters, and ketones (VVVF, 1997). Since DCM is too volatile to be used in its pure form, it is blended with special ingredients like thickening agents, and some organic solvents (Environment Canada, 1998). A typical DCM-based paint stripper contains 50 to 80 % DCM (VVVF, 1997; HSE, 1998; CEPE, 1999, Henkel, 1998, Boius, 1993). There are also DCM-lean formulations on the market with a DCM content of some 10 to 15 % containing other solvents like methanol as a replacement mainly for cost-effective reasons.

The DCM-containing paint strippers are used by consumers for do-it-yourself (DIY) activities, professional painters, and in the industrial branch. Paint stripper is mainly used to remove an old, bad coat of paint (blistered, cracked etc, and to which fresh paint may not be applied). The field of application of stripping agents by the DIY and professional painters is mainly restricted to the removal of bad and blistered paintwork on wood, both indoors and outdoors. It is also applied for restoring old furniture and removing glue residue from staircases and floors. In the industrial sector paint strippers are used for surfaces that need to be stripped completely, for example, during the maintenance of aeroplanes, refinishing activities for automotive parts, furniture, etc. Industrial stripping takes place either by immersion in a DCM-bath, or by spraying the surface with paint stripper (HSE, 1998).

Chapter 2 mentioned that the total use of DCM in paint stripper in 1995 in the EU was about 30,000 tons. With 50 to 80 % DCM in paint stripper, this corresponds with some 45,000 tons of paint stripper. From various producers of paint stripper and their industrial representative organisations we got the impression that the volume sales of DCM-containing stripping agents has been rather stable during the last few years.

As for a breakdown between DIY, professional use and industrial use, data are a bit contradictory. The European society of paint producers (CEPE, 1999) estimated that in the UK and in France most products containing DCM are used in the professional and industrial sector. However, information obtained from a major UK paint stripper producer indicated that also in the UK the DIY market is large. About half the volume is sold in pack sizes of 1 litre or less, which are generally considered to be used by consumers (Henkel, 1999). HSE (1998) estimated that in the UK some 7,000 to 8,000 tons of DCM is used in paint removal, of which 50 % in the DIY and professional sector, and 50 % for industry-related applications

(aircraft stripping, furniture restoration, etc.)¹⁰. In Italy about 40-50% of the paint strippers based on DCM are applied by professionals and about 50-60% by individual consumers (CEPE, 1999). In the Netherlands the paint stripper market was estimated at 2,400 tons in 1995 (or some 1,600 tons DCM), 30% of which in the DIY, 40% the professional market and about 30% in the industrial sector (VVVF, 1997). The total Danish market was estimated at about 100 tons DCM per annum, but no further breakdown was given (Danish EPA, 1999). The German market in 1994 was estimated at some 5,540 tpa (UNR, 1999); more recent estimates of ECSA give a value of 3,780 tpa (ECSA, 1999). Outside the EU, Environment Canada has published a detailed study into DCM. In Canada, in 1995 about 44 % of the paint remover was used in consumer products (1,500 tpa DCM), 44 % in industrial applications (mainly aircraft paint stripping (some 200 tpa DCM), furniture stripping (some 1260 tpa), and auto body shops (100 tpa)), and 13% in other applications (Environment Canada, 1998).

The analysis of these figures in Table 5.1 indicates that the amount of DCM used in paint stripping is not always proportional to the size of a country. Furthermore, it is impossible to give a clear breakdown between the DIY, professional and industrial applications. Based on the data available, we feel that probably the best guess is that these three markets are roughly of equal importance.

Country	Use (in tonnes)			Market split DIY-
	DCM	Paint stripper	Year	professional- industrial
Denmark	100	150	Not specified	Unknown
Germany	3780	5670	1998	Unknown
Netherlands	1600	2400	1995	30-40-30 %
UK	7-8000	11250	Not specified	25-25-50 %
EU Total	30000	45000	1995	Unknown

 Table 5.1:
 Literature data on the use of DCM in paint stripper in EU member states by market

¹⁰ This fits with an estimate of Henkel of a DCM use of 3,000 tpa, assuming that Henkel concentrated on the DIY and consumer market in the UK.

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5.2.2 Alternatives and their environmental performance

The available alternatives for the use of DCM-containing paint removers vary somewhat per market segment.

DIY and professional applications

The following alternatives are available for the DIY and the professional market. First, there are the *mechanical* alternatives. Well-known mechanical alternatives include hot air strippers, blowtorches, and scrapping or polishing. Data on how much of the paint stripping market is covered by such alternatives are lacking, but rough estimates of producers attribute some 15-20 % to DIY activities (Henkel, 1999). Second, *alternative chemical* paint stripping systems can be used. Currently, these only have a very limited market penetration, reports from various sources indicating that the market penetration is 10 % or less (e.g. OECD, 1996; Kapteijns, 1997; Henkel, 1999, Environment Canada, 1998)¹¹. Our literature review and interviews with paint stripper producers indicate that the following systems are currently available. It concerns paint removers based on (see e.g. Environment Canada, 1998; Kaye Whitfield et al., 1999; Boius, 1993; Kapteijns, 1997; Danish EPA, 1999):

- 1. Mixtures of acetone, toluene and methanol (ATM);
- 2. Dibasic esters (DBE; e.g. dibasic adipate, dibasic glutamate, or dibasic succinate);
- 3. 1-methyl-2-pyrrolidon (NMP);
- 4. DMSO.

Some producers offer mixtures of the formulations above, particularly by adding solvents like acetone and toluene to form an NMP formulation. The main reason is that such formulations have a higher stripping speed than formulations based on NMP alone. Stripping agents based on caustic material are also available, but these are mainly used as alternatives to DCM in industrial applications.

Industrial applications

For industrial applications, in many cases the same alternatives are available as for the DIY and professional market. Reviews of Environment Canada (1998), US EPA (1994) and Kaye Whitfield et al. (1999), as well as interviews with users, indicate the following possibilities:

- Metal stripping (e.g. auto body shops). Here sanding is already applied as the main option to remove paint. Paint stripper is used for special coating removal problems; here NMP- or DBE based alternatives would be an option as well (Environment Canada, 1998). Kaye Whitfield et al. (1999) describe an immersion stripping process in which DCM was replaced with NMP;
- 2. Wood stripping (e.g. furniture restoration). Also here NMP- of DBE based alternatives would be an option (Environment Canada, 1998);

¹¹ Values for the UK and the Netherlands.

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3. Aeroplane stripping. Here DCM is reported to be replaced by either dry media blasting or the use of softeners (e.g. based on benzyl alcohol), possibly in combination with high-pressure water blasting (US EPA, 1994; Environment Canada, 1998).

Environmental and health considerations

There are several arguments for the environmental advantages and drawbacks of these alternatives. One argument often heard is that mechanical methods, when applied particularly on older lead containing paint systems, may lead to a risk of exposure to lead pigment in dust. Bednarz et al. (1988) described a case of acute lead poisoning due to paint-removing activities with a blowtorch. Two DIY-ers were exposed some 5 to 10 to minutes to lead containing paint dust, which lead to acute effects like coughing and head aches. Elevated levels of lead in blood were found, and lung oedema occurred. Blowtorches have an additional a fire risk; a reason why hot air strippers are generally preferred.

ATM-based strippers have a rather high volatility, they contribute to photochemical ozone creation, and are flammable. Paint strippers based on dibasic esters or NMP have the advantage that they evaporate slowly, hence exposure to these is likely to be lower than to paint strippers based on rather volatile compounds like DCM or ATM. However, the strippers based on DBE or NMP have a rather slow stripping speed of up to 24 hours, whereas DCM paint removers do the job in one hour or less. Exposure time thus may be longer. Bouius (1993) calculated the Relative Inhalation Risk (RIR) for DCM and alternative paint strippers. The RIR is defined as the vapour pressure divided by the occupational health risk standard for the substance at stake. It gives a rough indication of the potential risk of exposure, but does not consider differences in exposure times. Table 5.2 gives an indication of the RIRs calculated by Boius and the underlying data. In general, relatively high volatility of DCM and/or somewhat more stringent occupational risk standards lead to a less favourable RIR of DCM-containing paint stripper. In this context, it must be noted that the toxicological database for DCM is relatively strong. For NMP in particular, some indications in the literature are that teratogenic effects could occur (Solomon et al., 1996). NMP can be absorbed via skin, against which the use of gloves (non-latex) is a sufficient protection. Environment Canada (1998) warns about the use of lower cost recycled NMP, since these have found to contain potentially harmful impurities such as npropylamine, pyrrolidone and vinyl pyrrolidone.

Substance	Vapour pressure (20º C (ppm)	8-hr TWA (ppm)	RIR
DCM	463890	100	4639
Methanol	125349	200	627
NMP	382	100	4
DBE	< 200	~ 100	2

Table 5.2: Relative inhalation risk of some paint stripper components (Boius, 1993) (a)

a) Based on Dutch occupational health standards. Due to a lower stripping efficiency, exposure to NMP and DBE may take place over longer periods than exposure to DCM

If alternatives are truly better then the original DCM formulation is subject to debate. The German 'Technical Guidelines for Hazardous Substances' on paint remover (BAS, 1998), states unambiguously that the use of DCM in professional use should cease, and that in industrial applications it should only be used if no alternative is available. Concerning the alternative chemicals it is stated that they 'all lead to lower exposures, and therefore lower health risks as with DCM can be expected'. Similarly, a study of Danish EPA (1999) states that 'there are chemical substitutes for methylene chloride with less impact on health and environment'. Several industrial organisations tend to stress that particularly for the infrequent consumer exposures the risks of DCM are minimal, and that the alternative solvents are not as well researched (e.g. VVVF, 1997). The Dutch Environment Minister in answer to questions from Dutch Members of Parliament stated that 'no alternative to DCM is as universally applicable...other systems will bring risks to human health and environment as well. Choosing between different methods is hardly possible'. Environment Canada (1998) concluded that 'scientific assessments of the environmental and human health toxicity of nondichloromethane paint stripping solvents should be undertaken. Information from these assessments is necessary before actions to eliminate dichloromethane in paint stripper can be considered'.

5.2.3 Impact of market restrictions on formulators.

Paint strippers are mainly produced by paint manufacturers or formulators. The production process of making paint strippers is chiefly a mechanical process. Different liquid substances are mixed and stirred in a closed tank, then the formulation is packed in a container adequate for the market at stake. In order to obtain some quantitative data for a socio-economic assessment we contacted various producers. We got the impression that paint remover is just one of the many products a paint manufacturer produces. The general picture from companies interviewed was that considerably less than 10 % of the employees of a plant were involved in the production of paint remover. Some companies indicated how many persons were involved in paint remover formulation and their annual turnover in tons. The data suggests that some 250-300 ton paint remover of 45,000 tpa (see Table 5.1) this indicates that some 150 to 180 persons are involved in paint

remover formulation. Various sources suggest a retail price of 7-10 Euro per litre or more for smaller package sizes, down to some 3 Euro per litre for large containers (Henkel, 1999; Environment Canada, 1998; Consumentenbond (Consumentengids, 1998). This would imply an EU market for paint remover at retail prices of 125 to 325 Million Euro. One has to acknowledge, though, that the price obtained by the formulators is considerably lower, and might be only 50 % of the retail price.

Based on interviews with various producers we got the impression that a switch to alternative chemical-based paint removers will result in limited socio-economic problems, provided that the paint remover market as such stays stable. The most critical factor in making a proper paint remover is not the production process, but rather having knowledge of the right formulations. The equipment used to produce paint removers (mixers, tanks, filling lines, etc.) are rather versatile. It may even be possible - with minor modifications - to use the same production lines that are now in use for DCM-containing paint removers for the alternatives. There could be minor changes like the speed of production for instance, but they do not seem to constitute an important bottleneck¹². Also, there is no clear reason to assume that there will be major effects on employment, since the same amount of operators would still be required. However, particularly smaller producers might have difficulty in making a smooth switch, especially during the transition period when DCM sales gradually decline and the sales of the alternative gradually go up. The two products will need to be produced simultaneously, which could be a problem for smaller firms.

The crux of the matter is that raw materials for alternative paint removers, particularly NMP-based formulations, are much more expensive than DCM. Prices for NMP have been reported to be a factor 4 higher than for DCM, which currently can be purchased for some 500 Euro per tonne (Kaye Whitfield, 1999; Henkel, 1999; ECSA, 1999)¹³. Since the active ingredient comprises some 50 to 80 % of the paint stripper, it is obvious that this is a main factor of influence on its cost price. In general, prices of DCM-free paint removers are about 50 % to 100 % more expensive than the DCM-containing product (compare OECD, 1996; Consumentenbond, 1998; Environment Canada, 1988; Henkel, 1999).

Therefore, some of the companies interviewed fear that there will be considerable effects when market restrictions are introduced for DCM paint remover. First, they sell most of their paint removers to the DIY market via major retail chains. These retail chains have a very powerful position, and it is uncertain if the producers can manage to persuade the retailers to accept a higher cost price once DCM is restricted. Furthermore, they fear that users will move away from chemical-based

¹² One comment on a draft of this report, not from producers of paint remover, suggested that materials of constructions of pumps, seals and gaskets may not be appropriate for every alternative. None of the paint remover producers we contacted mentioned such possible problems.

¹³ For DBE, Environment Canada (1998) assumed no extra costs are at stake.

paint removers. Especially the professional market is expected to move away from chemical-based paint removers, since alternatives are more expensive, need longer time to extract the paint and the results are not as satisfactory for certain paint systems. As for consumer applications, the producers we interviewed did not envisage such a great threat to the market. They believe that alternative paint removers will still be easier to apply than mechanical methods, and the longer stripping time will probably be of less importance to consumers than to professionals – in the absence of quicker alternatives.

In sum, the socio-economic impacts on formulators of marketing restrictions of DCM will be limited, provided that they can charge the additional material costs of alternatives to the downstream users, and the market of chemical-based paint removers remains stable.

5.2.4 Impact of market restrictions on consumers

It is rather difficult to assess the influence of market restrictions on consumer uses. Within the context of this project, a direct inquiry into this target group was not feasible. As indicated above, we asked formulators of paint strippers about the possible consequences of possible market restrictions of the use of DCM in paint stripper. Most parties in the production chain expect that market restrictions will not affect the individual consumer as they most probably will continue to use chemical-based paint stripping methods. The main effect will be that a different planning of paint stripping work has to be applied, in order to account for the longer stripping time needed. In general, DCM-based paint strippers will do their work within the hour, and often much faster. Alternative paint removers based on e.g. DBE and NMP may need up to 12 hours or more. Many alternative formulations may be ineffective on particularly old, multi-layer high solid paints (Environment Canada, 1998; Consumentenbond, 1998; Henkel, 1999).

The main effect of using alternatives will be that higher costs will be charged for paint stripper. As indicated before, we assumed that 33 % of the total paint stripper market of 45,000 tpa to be the DIY market. This is some 15,000 tpa corresponding with a retail price of some 125 Million Euro. Even if retail prices of alternatives would be twice as much this would mean an extra cost of some 125 Million Euro, which is less than 1 Euro per EU citizen a year. A study of Environment Canada (1998) suggests that on average lower extra costs will be at stake since less expensive alternatives than NMP will also be used. They counted some 50 to 60 % additional costs for replacement of DCM in the consumer market.

5.2.5 Impact of market restrictions on professional users

The professional market and the DIY market use paint stripper for the same purpose. Here too DCM-based paint remover plays a major role, though in some EU countries the application is somewhat under pressure in relation to occupational exposure (compare BAS, 1998). We approached several professional users asking them about the consequences that would be at stake if the use of DCM-based paint remover would be restricted. The problem here is that professional users are comprised of a large number of small and heterogeneous groups of companies. Furthermore, there could be different work practices in the EU at stake. We were unable to unravel this heterogeneity in full within the confines of this project.

The companies we selected to approach already had hot air strippers in use as a fairly common alternative. Those companies using methylene chloride products envisaged no major problems when market restrictions come into play. Different combinations of mechanical and chemical methods in principle can be substituted for DCM use. The companies using alternative paint strippers tend to be satisfied with the results. Though they are less effective than DCM, the alternative product is an improvement where working conditions are concerned. Since clients increasingly expect companies to use safe and environmental-friendly working methods, the use of such alternative methods is goes down rather well.

The companies interviewed expect that the prohibition of DCM will have only a marginal affect on the price per m². The effects of the slower stripping speed of alternative chemicals means that one has to wait before one can finish a paint-removing job, but in general a good work planning can ensure that this waiting time can be used productively for other tasks. The companies already using the alternative products said the effects were barely discernible. Two companies who still use DCM expect a rise in price of about 10%. It has to be noted that this 10 % is not only related to the cost price of paint stripper, but to the price of a paint-stripping job including man-hours, VAT, etc.

These findings are in line with those from a recent study published in Denmark (Danish EPA, 1999). Here too, feasibility of substitution was confirmed by the paint stripping branch. The Danish study concluded that a tax of approximately 30 to 35 DKK (some 5 Euro) per kg DCM would ensure a substitution of almost 100% in professional use. Assuming that this tax is equal to the additional costs for alternatives for professionals, it implies some 75 Million Euro additional annual costs in the EU at an annual professional use of some 15,000 tpa.

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5.2.6 Impact of market restrictions on industrial use

As indicated above, industrial uses of DCM-containing paint stripper mainly concern metal stripping, wood stripping (mainly furniture) and aeroplane stripping. Noteworthy is that though occupational exposure may be critical in these applications too, reduction of exposure to DCM can be achieved just as well by technical means and not only by switching to an alternative. For instance, HSE (1998) suggests that fairly simple measures like using large rooms, the covering of stripping baths, and the use of lifting gear to move objects can reduce exposure to DCM considerably. Hence, a policy of exposure reduction instead of restrictions of marketing and use seems a viable option if one wants to diminish possible occupational health problems with DCM.

However, during our literature review and interviews we came across some analyses of the socio-economic effects of implementation of alternatives.

For *metal stripping*, for example, in auto-body shops and shipyards, sanding or treatment with blasting grit is the main option to remove paint. However, in some cases immersion stripping in a solvent bath is a more effective option. Kaye Whitfield et al. (1999) describe an immersion stripping process in which DCM was replaced with NMP. The plant had to be retrofitted with a distillation unit in order to be able to recycle the NMP. It used some 40 tpa DCM. Compared to the DCM-based unit (some US\$ 20,000) an additional investment of US\$ 146,000 was needed, and the annual costs including labour, overhead, etc., rose from about US\$ 95,000 to US\$ 124,000. This is in the order of magnitude of 700 Euro per tonne DCM.

As for *furniture stripping*, Environment Canada (1998) gives an example of the costs of a switch to NMP and DBE. Here no additional capital costs are foreseen, since in mainly concerns hand stripping. They assume an average of 60 % for additional costs of the paint remover, and a 20 % productivity loss due to extra stripping time. At a use of 900 tonnes of paint stripper, extra costs were calculated to be CND\$ 3.3 Million for the alternative paint stripper, and CND\$ 8.4 Million for additional employee costs. In total, some CND\$ 11.7 Million or about 7.6 Million Euro were expected to be needed to replace DCM. This is about 20 to 25 % of the original cost price for this activity, and equals about 800 Euro per tonne DCM replaced.

In the case of *aeroplane stripping*, DCM used to be one of the most important stripping agents. Here in particularly one would expect that higher prices and lower stripping efficiencies (leading to larger downtimes for expensive aeroplanes) would lead to socio-economic consequences and loss of competitiveness: the aeroplanes would simply look for the service in another country. However, our inquiry revealed that three of the EU's biggest aeroplane maintenance companies have stopped using DCM or will soon do so. One uses a paint stripper-based benzylalcohol, another uses a water-based paint softener. The aeroplane maintenance companies are satisfied with the results. Under normal conditions it takes a little longer for the softener to work but the time to remove it from the aeroplane is a lot quicker. Our interviewees claim that also the price is comparable¹⁴. A clear advantage was the reduction of hazardous waste treatment costs. DCM-containing residues had to be treated as chemical waste. Now the paint can be sprayed off with high-pressure water canons and flushed through to the water treatment plant; only the paint residues are sieved out in advance and need treatment by incineration. According to one maintenance company, the alternative is an improvement because the working conditions have improved, it is better for the environment, and even helped to increase their market. Several airline companies have chosen their services because it fits their environmental care programme. These findings correspond fairly well with those of a study of Environment Canada (1998). In that study, however, it appeared that maintenance companies for small aircraft may have more problems in making a switch.

5.2.7 Conclusions

The overall conclusions of the analysis of the socio-economic effects of a possible restriction of the marketing and use of DCM containing paint removers are as listed below.

Formulators

- The total production of DCM-based paint remover is some 45,000 tpa (some 30,000 tpa DCM), roughly equally divided over consumer, professional and industrial applications.
- It is estimated that some 150 to 180 people in Europe are directly involved in the formulation of DCM-based paint remover.
- A rough estimate of the total turnover (retail prices) is 125 to 325 Million Euro; the turnover of the formulators is probably about half of this.
- The production lines and technologies used for producing DCM-based paint stripper are rather versatile. It is likely that alternative paint removers can be produced with only minor adaptations or investments.
- There is no reason to assume that less (or more) employees are needed to produce DCM-based paint remover or alternative paint remover.

¹⁴ Environment Canada (1998) calculated some additional costs, mainly since they assumed a longer turnaround time in case of benzyl alcohol stripping, and proposed a rather capital intensive starch media blasting option as an alternative for stripping larger aircraft.

- The main point is that the basic chemicals for the alternative paint remover, particularly NMP, are up to a factor 4 more expensive than DCM. Alternative paint removers therefore are on average 60 to 100 % more expensive per litre than DCM.
- If these additional costs can be charged to the retailers and consumers, and the market for chemical paint removers stays stable, little socio-economic effects are expected for formulators. Market effects will be reviewed below. Since retailers have a rather powerful position in the production-consumption chain, there may be a need for help from third parties to convince them that charging additional costs is reasonable.

Consumer applications

- Consumers are only expected to move away from chemical paint removers in those cases where alternative paint removers will technically not do the job. Particularly for older and multi-layer high-solid systems, alternative systems may not give a satisfactory result.
- Stripping time will be much longer for alternatives than for DCM.
- The additional costs for consumers for alternative paint removers may be up to 100 Million Euro per annum.

Professional applications

- It is expected that a mix of alternative chemical paint strippers and mechanical methods will deal properly with all paint removal problems.
- If work is properly planned, the longer stripping times of alternative removers cause no or little inefficiencies.
- A part of the current DCM paint stripper will be replaced by mechanical methods, but the amount is difficult to specify.
- Additional costs for the final client can be expected, but they seem to be relatively limited: some 10 % per paint stripping job, or some 75 Million Euro per annum in total.

Industrial applications

- Regular occupational exposure reduction measures may be able to tackle the bulk of the problems with DCM.
- Two examples of alternatives for metal and wood stripping indicate some 20 to 30 % additional costs when alternatives are used, or some 700 to 900 Euro per tonne of DCM originally used. However, upfront investments may be high in some cases.
- For aeroplane stripping, it appears that three of the major European airline service companies have replaced or will replace DCM at short notice (e.g. by benzyl alcohol or softeners combined with high pressure water stripping). Results are satisfactory and the additional costs seem to be limited to zero. The situation in small aeroplane maintenance companies might be different.

To sum up, restrictions on marketing and use of DCM may have some implications for formulators since professional users may move in part to mechanical methods. Consumers and professionals will have to count on much longer stripping times. In particular, since the alternative chemicals are more expensive, additional costs of some 100 to 300 Million Euro per annum in the EU are at stake. However, almost all markets affected are within the EU. Regulation at EU level will have little influence on competition. Only aeroplane stripping is an activity where competition from outside the EU could play a role, but here the companies (at least the larger ones) who already switched to alternatives feel rather comfortable about their competitive position. Hence, two main points in deciding on restrictions on marketing and use of DCM-based paint remover remain. First, given the discussion on the severity of effects described in Chapter 4, the question is to what extent should current exposure be diminished by switching to alternatives that have the disadvantage of longer stripping times. Second, for at least some of the alternatives, most notably NMP, whether or not the toxicological database is strong enough to ensure absence of danger is debatable.

5.3 Production and use of adhesives

5.3.1 Overview of the production-consumption chain

DCM can be used as a solvent in adhesives. Unlike the case of paint remover, where DCM forms a single essential component in the product, adhesives are made in many types of formulations. Adhesive types include adhesives based on natural polymers, polymer dispersions and emulsions, hotmelt adhesives, reactive polymerising systems, adhesives based on water-soluble polymers, and solvent-based adhesive systems. The total adhesive market in the EU was some 1.6 Million tonnes, and solvent-based adhesives made up less some 15 % of this total (FEICA, 1999). Table 5.3 gives a breakdown of the EU adhesive market by type.

Product Groups	Tonnes 1998	Mio DM
Adhesives based on natural polymers	99,908	261
Polymer dispersions and emulsions	652,625	1,968
Hotmelt adhesives incl. moisture-cure types	237,187	1,067
Solvent based adhesives systems	228,643	1,255
Reactive (polymerising) systems	153,996	1,341
Adhesives based on water-soluble	61,203	302
polymers		
Other adhesives	177,991	352
Total	1,611,544	6,546

Table 5.3: Adhesive product groups, EU market in tonnes and turnover (FEICA, 1999)

Worth mentioning is that DCM is just one of the solvents applied in solvent-based adhesives. In fact, the vast majority of the solvents used in the adhesive sector are regular, non-chlorinated organic solvents like toluene. Most of these organic solvents have a high flammability, and DCM is mainly used in those adhesives where non-flammability is a priority. Other qualities of DCM include its high volatility and high solvency power. Formerly, 1,1,1-trichloroethane was also used in adhesives, but with the advent of the Montreal protocol this solvent has been phased out and often replaced with DCM.

The sector consists of at least 600 companies in the EU, employing some 30,000 staff. Most of them have a very broad register of products. This makes it rather difficult to get a clear view how much DCM is used, by whom, and in which applications. Representative organisations at EU level do not generally collect information at such a detailed level. However, information in the literature and specific surveys made in individual countries suggest that some 10 to possibly 15% of the solvent-based adhesives are made with DCM (cf. Environment Canada, 1998; VNL, 1999; FEICA, 1999). Also clear is that the amount of solvent-based (and DCM-based) adhesives used in different member states varies considerably. Table 5.4 reviews the DCM in adhesives per country summarised earlier in Table 2.1. It appears that there is a considerable difference in the percentage of DCM used in adhesives (compared to a country's total DCM use) between EU member states. In Denmark, Sweden and the Netherlands this use is very low, where in countries like Germany and the UK the amounts are relatively higher¹⁵. For comparison: the Dutch Association of Adhesive Manufacturers (VNL) found in their most recent inquiry that the total amount of solvents (non-chlorinated and chlorinated) was some 1,000 ton per annum, where a country about four times the population, the UK, uses 3,000 tpa DCM alone. This may well have to do with a Dutch long-term VOC emission reduction programme, a factor that might also play a role in the Nordic countries. In sum, there are probably considerable differences in DCM use between EU member states, but detailed statistics on the specific level of use are lacking.

Country	Use		
	ton	As % of total DCM-	Year
		use	
Denmark	12.5	2.6	Not specified
Germany	1793	12	1997
Netherlands	100	1.2	1999
Sweden	15	0.6	1988
UK	3000	10	Not specified
EU Total	15089	10.2	1995

Table 5.4: DCM uses in adhesives in some EU member states

¹⁵ The German use of 1793 ton DCM fits rather well with an inquiry of the German sister organisation of the FEICA, the Association of European Adhesives Manufacturers. They gave a value of 1300 ton for their members, but indicated that there may be important amounts used by non-members (FEICA, 1999).

For this reason, it is also rather difficult to obtain specific data about the split of the DCM-containing adhesives market between consumer use, professional use and industrial use. Data from the Association of European Adhesives Manufactures (FEICA) clearly show, however, that the consumer market is just a small part of the total adhesive market: some 8 % in volume. Table 5.5 gives the market segments of adhesives in general in the EU. To what extent DCM-based adhesives are over or underrepresented in this market is unclear. However, the information obtained from various adhesive producers we interviewed, a report of Environment Canada (1998), and others (e.g. VNL, 1999), strongly suggests that DCM-based adhesives are not or hardly used in the consumer sector. The same applies probably to the professional sector. DCM seems to be mainly used in speciality applications, where its non-flammability is a particularly important advantage. This is less so in the case of consumer and professional use of adhesives, than in specific processes in industry and workshops. The production of foam products and the furniture industry were mentioned as the most important niche markets for DCM-based adhesives. For instance, in the Canadian situation one of the major applications (about 50% of total) is the gluing of foam parts cut from polyurethane foam slabstock or other materials (e.g. in the mattress and furniture industry). Lamination of several layers of foam to achieve the desired firmness of foam products is a common adhesive fabrication process. Also, polyester fabric materials can be bonded to foam underlay using DCM-based adhesives. Such adhesives are usually applied using a specialised spray gun. Since working with foam pieces creates a lot of static electricity it necessitates working with a non-flammable DCM-based adhesive. The UK Exposure Assessment Document of HSE on DCM also made such industrial uses a priority. Hence, we will mainly concentrate on these industrial applications (HSE, 1998).

Market Segments	Tonnes 1998	Mio DM
Paper, board and related	550,734	1,773
products		
Building, construction, civil	434,449	1,323
engineering, craftsmen		
Woodworking and joinery	246,909	653
Transportation	68,129	491
Footwear and leather	78,135	330
Consumer / DIY (retail)	124,869	1,167
Assembly operations	114,581	804
Total	1,617,806	6,541

Table 5.5: Market segments of adhesives in tonnes and turnover in the EU (FEICA, 1999)

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5.3.2 Alternatives and their environmental performance

Alternatives for adhesives with DCM can, in principle, be found in the other adhesive categories mentioned in Table 5.2. It concerns in particular:

- solvent-based adhesives (with e.g. acetone, hexane, etc.);
- hotmelts;
- water-based adhesives.

There has been a trend in several countries to move away from solvent-based adhesives in general, including DCM. The alternatives described seem in principle not technically unrealistic. For instance, Environment Canada (1998) reported that various polyurethane slabstock manufacturers have switched to water-based adhesives. Technical problems will be discussed further in section 5.3.3.

As for the environment, health and safety aspects, much of the analysis on paint remover is valid here as well, particularly with regard to solvent-based adhesives. It seems unlikely that the overall environmental and health performance of nonhalogenated solvents will be worse than that of DCM: their occupational health risk limits are in the same range, and their volatility is probably somewhat less than that of DCM. The exception is that hydrocarbons have a higher contribution to photochemical ozone creation. Apart from the last-mentioned point, a similar analysis applies to hotmelts and water based adhesives.

The main disadvantage of hydrocarbon-based solvents is that they are flammable and therefore present flammability hazards during their manufacture as well as during their end-use. Especially in those companies were foam is glued and manufactured, this can be a focal point.

5.3.3 Impact of market restrictions on formulators

Adhesives are made by specialised companies generally offering a broad product range. As indicated before, in Europe there are over 600 adhesive producers, employing about 30,000 people, with a turnover of some 6,000 Million DM (about 3,000 Million Euro). This implies a turnover of some 100,000 Euro per employee. As indicated in Table 5.4, the solvent-based adhesives form about 16 % of this market in terms of turnover and some 12 % in terms of volume. If indeed the DCM-related adhesive market is some 10 % of the solvent based adhesive market (cf. Environment Canada, 1998; VNL, 1999), the total of DCM-based adhesives forms 1 to 2 % of the adhesives market. This is in line with the information we obtained from interviews with some individual adhesive producers. It would imply that some 300 to 600 full-time jobs would be related to the formulation of DCM-based adhesives.
Somewhat in line with paint removers, is the production of adhesives in large mechanical processes. Here too, the components of the formulation are mixed, stored, and finally packed in a container adequate for the targeted market. It may be that the production lines are a bit less versatile as in the case of paint remover. Formulations differ greatly among the different adhesive types and some production lines should take steps to ensure safety of working with flammable (or even explosive) mixtures.

Nevertheless, also here we got the strong impression of the limited socio-economic consequences of a switch from DCM-based products to other products, provided that the market as a whole stays stable. To put it simply: the same producers now supplying the DCM-based paint will supply the alternatives as well. Hence, employment loss is not expected. There may be a need for some upfront investments in changing production lines, but the information we obtained from adhesive producers does not indicate that this would be a major problem. Furthermore, we do not see a good reason why the economics of the alternative adhesive systems would be fundamentally different than the DCM-based systems. In any case, here one needs to be reminded that DCM-based adhesives seem to form only a minimal part of the turnover in this sector. It is thus unlikely that changes in the sub-sector of DCM-based adhesives would have major consequences for the adhesive producer sector as a whole.

On the topic of possible market losses, the producers we interviewed expect that the effects of market restriction on the use of DCM are diverse. Most companies think that especially the mattress industry is well able to switch to alternatives, like hotmelts or adhesives on water basis. The furniture industry may be a more sticky. These little shops are not able to invest in different equipment or processes¹⁶. Here, some activities may just be replaced or taken over in countries with less stringent regulations; it was believed this to be the case in Eastern Europe already. However, the formulators generally felt that market losses would be marginal and temporary. They felt it would be possible to develop technically suitable alternatives that give the same result, at more or less the same costs. Provided that regulations are introduced in the EU as a whole, no major effects are anticipated.

¹⁶ However, our interviewees also wondered if such small companies would be able to comply with appropriate health and safety standards for DCM.

5.3.4 Impact of market restrictions on consumers and professional users

Our analysis reveals that currently hardly any DCM-containing adhesives are used by consumers and professional users. Hence, restrictions on marketing and use of DCM in adhesives will have no effect on these groups. At the same time, the low market penetration of DCM-containing adhesives means that the (potential) exposure on which our evaluation in Chapter 4 was based, is probably rather infrequent for the vast majority of consumers and professional users. Hence, the need for marketing restrictions, particularly for consumers, is mainly related to the discussion if this target group should indeed be protected against short-term exposure that may cause mild CNS effects. We refer further to the discussion in Chapter 4.3.

5.3.5 Impact of market restrictions on industrial users

Under industrial uses we include all the use of DCM-containing adhesives at fixed locations. As indicated, the polyurethane slabstock foam manufacturers and the furniture industry may be the bulk users.

As for the technical feasibility, both the report from Environment Canada (1998) as well as our own inquiry suggest that alternatives are feasible. Environment Canada (1998) reported that some of the larger polyurethane slabstock foam manufacturers have switched to water-based adhesives. For producing mattresses, hotmelts were mentioned as an alternative. With this technology, small lines of molten adhesives are applied. The basic adhesive material is somewhat more expensive, but since less is used the overall costs do not change. The main problem is that both hotmelts as water-based adhesives call for investment in new equipment. Our interviewees called these problems manageable.

Various problems were foreseen with the switch to adhesives with non-halogenated solvents. Because these adhesives are flammable necessitating very stringent insurance demands and working procedures. Water-based adhesives require investment in new spray equipment and air filtration equipment to capture overspray. Annualised sector capital and operating cost could be up to 7,000 Euro per tonne of DCM used (Environment Canada, 1998). Especially smaller companies may be unable to make the necessary investments. Environment Canada (1998) remarked on similar problems in their analysis, and noted in the case of smaller users that even conversion to water-based systems had been slow because of conversion costs and technical reasons. Furthermore, they indicated that some adhesives are formulated with DCM for its compatibility with certain plastics or resin compounds, a property that is not easily achieved with other solvents.

Overall, it seems that there is room to move to alternative adhesives and away from those based on DCM. This is suggested by the very low use of DCM-based adhesives in the Nordic countries and the Netherlands, and the reports that various users have made a switch and feel comfortable about it. However, some impediments apply as well. Within the context of this study, it is not possible to trace in detail the type and use of each DCM formulation that might have - at this moment - a clear-cut technical alternative that still needs optimisation. Furthermore, new working practices and the need for new equipment may be an impediment for smaller users to make a smooth switch. For such reasons, Environment Canada decided not to opt for a ban on specific DCM-based adhesives. They proposed a 'bubble concept' agreement with adhesive producers and users under which the overall use of DCM would be reduced by some 70 % in the course of the next 5 to 10 years. Industry could then find out how best to achieve this reduction.

5.3.6 Conclusions

The overall conclusions of the analysis of the socio-economic effects of a possible restriction of the marketing and use of DCM containing adhesives are as follows.

Formulators

- The total production of adhesives in Europe is some 1.6 Million tonnes per annum, with a value of some 3,000 Million Euro. Probably only 1-2 % of this is related to DCM-based adhesives.
- It is estimated that some 300 to 600 people in Europe are directly involved in the formulation of DCM-based adhesives.
- Virtually all firms have a broad range of products. Hence, it is likely that a firm will also produce the alternative for DCM-based adhesives. A switch to alternatives is thus unlikely to have major employment effects.
- Like for paint remover, the production lines and technologies used for producing DCM based adhesives are rather versatile. However, some alternatives may need different production equipment, e.g. in relation to the use of more flammable materials.
- If the market for adhesives stays stable, little socio-economic effects are expected for formulators. Market effects will be reviewed below.

Consumer and professional applications

- There is a strong suggestion that DCM plays no role in adhesives for the consumer market and for professional use.
- On one hand, this would imply that marketing restrictions have hardly any socio-economic effects. On the other hand, exposure to DCM is very infrequent, and particularly for consumer applications the need for marketing restrictions depends on whether or not one wishes to protect consumers against short-term exposure that may cause mild, reversible CNS effects.

Industrial applications

- It is difficult to obtain a full, detailed view on the specific uses of DCM-based adhesives and the reasons for use. The foam processing sector and the furniture sector seem to be the major users
- It would appear that hotmelts, water based adhesives are promising potential alternatives. They are in use already by several producers.
- However, there may be some dedicated applications where DCM is used for its compatibility with certain plastics or resin compounds, a property that is not easily achieved with other solvents.
- Furthermore, a switch to alternatives may invoke the need for investments in new spray technologies, for instance. This may be a problem particularly for the smaller users.

In sum, there is probably much scope for reducing the use of DCM-based adhesives without major socio-economic consequences. However, particularly in view of what is indicated under industrial applications, we got the impression that a short-term, outright ban may have consequences that could not be foreseen and analysed in full within the confines of this report. If the EU were to strive for restriction of marketing and use of DCM in these industrial applications, we would rather suggest finding a way for a gradual reduction of use, for example, via the 'bubble concept' method proposed by Environment Canada.

5.4 Production and use of aerosols

5.4.1 Overview of the production-consumption chain

Aerosols were first used in Norway in 1929. The first aerosol insect repellents were sold in shops in England in 1949 (BAMA, 1997). Because aerosol products are easy and efficient in use a vast number of products are packaged in aerosol containers. The product dissolves or is suspended in a liquid solvent concentrate. A liquefied gas usually acts as the propellant; the propellant in its liquid state is very often part of the solvent system.

According to the European representative organisation of aerosol producers, the FEA, about ten billion aerosol products are produced yearly worldwide. About 40% of them are consumed in Europe (FEA, 1999). The production of aerosols has doubled in Europe since 1975 and the production has been growing ever since (BAMA 1997; NAV, 1998). A total of over 2000 brands of aerosol products are on the market which are used in over 200 different applications. Table 5.6 gives an overview of the different applications of aerosol products and their relative market share in England (BAMA, 1998); Table 5.7 gives a similar breakdown for the Netherlands (NAV, 1998).

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User groups		s	Category	1991	1992	1993	1994	1995	1996	1997	1998
(TNO estimate)		ate)									
	Р	С	Insecticides	3%	3%	3%	3%	3%	2%	1%	1%
I	Р	С	Paints & Lacquers (inc.	3%	2%	2%	2%	2%	1%	2%	1%
			automotive)								
		С	Air Fresheners	8%	7%	7%	7%	9%	7%	7%	8%
I	Ρ	С	Waxes & Polishes (excl. automotive)	5%	5%	4%	4%	3%	3%	3%	3%
		С	Oven Cleaners	1%	1%	1%	0%	0%	0%	0%	0%
I	Р	С	Starches & Fabric Finishes	2%	2%	2%	2%	2%	1%	1%	1%
	Р	С	Window/Glass Cleaners	1%	1%	1%	1%	2%	2%	2%	0%
	Р		Shoe/Leather Cleaners								0%
	Р	С	Bathroom/Kitchen Mousses	1%	1%	1%	1%	2%	2%	2%	0%
	Р	С	Other Household		-						2%
	Р	С	Haircare Products	16%	15%	12%	15%	12%	13%	17%	15%
	Р	С	Hair Mousse	6%	6%	6%	6%	5%	5%	4%	4%
	C		Colognes & Perfumes	4%	4%	4%	3%	2%	2%	2%	0%
с		С	Deodorant/Body Sprays	26%	26%	19%	19%	22%	23%	19%	18%
		С	Antiperspirants			10%	10%	10%	9%	10%	12%
	Р	С	Shaving Lather	7%	9%	10%	10%	10%	11%	10%	11%
		С	Other Personal Products	1%	1%	0%	0%	0%	0%	0%	1%
I		С	Medicines & Pharmaceuticals	8%	9%	9%	10%	12%	14%	16%	17%
I			Automotive Products	5%	3%	3%	2%	2%	2%	2%	1%
I			Industrial Products	2%	3%	2%	3%	2%	1%	2%	2%
	P C		Veterinary/Pet Care Products	20/	40/	E0/	20/	20/		20/	0%
I			Novelty, Food, Misc.	3%	4 70	5%	3%	3%	2%	3%	3%
14%	16%	68%	Total	100%	100%	100%	100%	100%	100%	100%	100%
			Total number of units * 1.10 ⁶	837	880	935	1.034	1.243	1.442	1.521	1.476

Table 5.6:Market share of aerosol products and most likely user group by application
in the UK, 1991-1998 (BAMA, 1999)

Both tables indicate that although the total aerosol market is growing the market share of the some specific applications remains practically the same. Although the declining and increase in sales differ per country, interestingly, the market breakdowns per application in the two countries are practically the same. We were unable to obtain a detailed breakdown of the market into consumer, professional and industrial use from either the national representative organisations or the European Federation of Aerosol Producers (FEA). However, an educated guess can be made which market will be the main user based on the type of aerosol application. Our estimates are also included in Tables 5.6 and 5.7. From these two tables, at rough guess about half of the aerosol products concerns consumer use, some quarter professional use, and some quarter industrial use.

User group		oup	Category	1994	1995	1996	1997	1998
(TNC) est	imate)						
	Р	С	Hair foam	7%	6%	4%	5%	6%
	Р	С	Hairspray	18%	15%	14%	13%	13%
	Р	С	Other hair products	1%	1%	1%	1%	0%
		С	Deodorants	22%	21%	19%	20%	25%
		С	Shaving foam	2%	2%	2%	2%	2%
		С	Other cosmetics	0%	0%	0%	0%	0%
I	Р	С	Insecticides	3%	3%	3%	3%	5%
		С	Air fresheners	5%	7%	7%	6%	6%
		С	Other household products	5%	5%	6%	5%	3%
I	Р	С	Automotive car maintenance parts	5%	4%	7%	8%	6%
			(excl. lacquers and paints)					
I	Р	С	Technical industrial products (excl.	10%	8%	8%	6%	6%
			lacquers and paints)					
I	Р	С	Lacquers and paints	5%	6%	6%	9%	9%
I	Р	С	Pharmaceutical and veterinary	0%	0%	0%	0%	0%
			products					
I			Other/food	17%	21%	25%	23%	22%
30%	18%	52%	Total	100%	100%	100%	100%	100%
			Total number of units *1000	76630	79171	82251	79386	91413

Table 5.7:Market share of aerosol products and their most likely users by application
in the Netherlands, 1994-1998 (NAV, 1998)

DCM is used in aerosol products mainly because of its high solvent capacities, non-flammability and its high density, making it an ideal solvent. For instance, DCM used to be a very important aerosol for personal care products, like hairsprays. In the early eighties, the EU produced a directive that limited the use of DCM in such products to 35 % on mass basis, and during the last decade many aerosol producers switched to non-chlorinated solvents. Although data on how much DCM is used in aerosols are somewhat confusing, the ECSA market information in Table 2.4 strongly suggests that some 10 % of the DCM use in the EU - almost 15,000 tons - is via aerosols. We already concluded that the information we were able to get from national DCM market surveys i.e., Germany, the Netherlands, Sweden, Denmark and the UK, the share of the aerosol market for DCM use was shown to be 2 % or less. All our contacts in the aerosol sector, which included a survey of national representative organisations via FEA suggested that the use of DCM is very limited and indeed virtually non-existent in personal care products. The information obtained from FEA did suggest, however, that some of their members still produced DCM-containing aerosols for export. In sum, we have no option but to pose some questions regarding the 15,000 tons used for aerosol applications suggested by ECSA. We would not be surprised if the real figures, at least concerning the EU market, would turn out to be a few factors lower, and that the remainder constitute aerosols produced for export. One has to

bear in mind, however, that because both paint removers and glues are also available in spray cans, these may not have been included under the heading aerosols in the national studies we used.

With these remarks, a cautious estimate of the number of aerosol units containing DCM can be made. The amount of DCM per unit differs per application. Paint removers contain up to 70-85 %, mould release agents some 50 %, personal care products are legally restricted up to 35 %, and other products may contain only up to 10 % DCM (UNR, 1999). The total amount of DCM used in aerosols must be estimated between 10 % (ECSA data) or some 1 % of the total DCM use (national studies). At a total European DCM consumption of 147,500 tpa in 1998 this is between 1,500 and 15,000 tpa. Assuming that some 50 % of the aerosol consists of DCM, this would imply some 3,000 to 30,000 DCM-based aerosol products. A typical aerosol container has a content of some 420 g (Environment Canada, 1998). This implies an EU market of some 7 to 71 Million aerosol units containing DCM, or 0.17 viz. 1.7 % of the total EU market of 4 Bio units.

However, there are also applications where the use of aerosols with DCM is unambiguously confirmed. These include (e.g. Environment Canada, 1998; several industrial sources):

- Insect repellents;
- Metallic paints;
- Mould release agents.

Insect repellents and metallic paints seem to be dominant in terms of numbers of cans, whereas in industrial use mould release agents are the dominant (Environment Canada, 1998; various industrial sources).

5.4.2 Alternatives and their environmental performance

Actually, the most important substances used as a propellant and a solvent, include isobutane, CO_2 , and dimethylether, or a mixture of them. Having spoken to several international companies we got the impression that the volume of sales of DCM containing aerosol products has been declining over recent years. The use of DCM in personal care products such as hair sprays appears to be minimal as the industry has moved away from the use of chlorinated hydrocarbons in its products (Environment Canada, 1998, UNR, 1999). Industry has managed to find formulations based on these main propellants/solvents, which are acceptable in most of these products. Even in Austria, which has a rather stringent legislation on the storage of flammable substances preventing the use of alternative organic and flammable propellants, solutions have now been found for phasing out DCM (Windesperger et al. 1998). However, there are areas where some specific technical problems may be at risk. This will be discussed further in section 5.4.3. Furthermore, it has to be acknowledged that a non-aerosol packaging is also a possible option to reduce DCM-use. The advantage of aerosol cans is that they make it possible to apply a large amount of product in a quick and effective way.

Also the can conserves the products longer. However, there are several alternative ways to pack the same product. For example, regular cans or bottles can be used for aerosol paint removers or solvent cleaners. Insecticides can be formulated as body sticks, in hand pumps, etc.

With regard to the environment, health and safety aspects, much of the analysis made for adhesives is valid here as well. It seems unlikely that the overall environmental and health performance of non-halogenated solvents will be worse than that of DCM: their occupational health risk limits are in the same range, and their volatility probably is somewhat less than of DCM. Few environmental problems can be expected with aerosols based on CO_2 and other inert gasses. The same applies for alternative packaging systems.

Again, a main disadvantage of particularly hydrocarbon-based aerosols is that they contribute to photochemical ozone creation and that they are flammable, thus posing flammability hazards during their manufacturing as well as during their end-use.

5.4.3 Impact of market restrictions on formulators

As indicated in section 5.4.1, the use of DCM in aerosols is likely to be 15,000 tpa at most, but could be as low as 1,500 tpa. The related number of units is about 71 Mio, or 7.1 Million in the lower estimate, amounting to some 1.7 to 0.17 % of the European aerosol market.

On approaching several aerosol producers with questions about the turnover per employee and the number of units produced per employee, we only obtained very limited information about such aspects. A very cautious guess based on the information obtained indicates a turnover per employee of some 300,000 Euro, and some 30 tons of DCM per full-time employee. Taking the use of DCM in aerosols to be between 1,500 and 15,000 tpa, this corresponds to between 50 to 500 employees and a turnover of 15 Million to 150 Million Euro related to DCM aerosols.

The same firms generally produce the DCM-containing aerosols and the alternative aerosols. Because of this, and since DCM aerosols form such a small part of the total turnover, it can hardly be expected that a switch to alternatives will have major effects on employment or turnover.

However, there are a number of effects that should be taken into account. Most of the alternatives are flammable, with the exception of water vapour and CO_2 . This implies that the production site must take measures against the danger of explosions and fire. Also the user of the aerosol products must take actions and invest in safety measurements. Insurance companies will demand approval of these measures against fire and explosion hazards before the alternatives can be used. A drawback of these alternatives is that they are almost all hydroscopic. Water can

dissolve in the solvents, which can effect the effectiveness of the active ingredients, which means that the producing companies must also invest in special drying equipment to avoid water dissolving in the products. From our own inquiry it appeared that most companies managed to cope with such technical problems rather well, but they were not prepared to invest in making the switch. Environment Canada (1998) estimated in their analysis that the cost for reformulation would be some CND\$ 5,500 (or some 3,500 Euro) per tonne of DCM in aerosols. For 1,500 tonnes of DCM this would be some 5 Million Euro, for a use of 15,000 tonnes this would be 50 Million Euro.

Remarkably, the use of DCM already seems to be restricted to those applications that require specific evaporation rates, DCM's unique solvency, or nonflammability. For instance, replacing DCM in aerosol metallic paints for consumer applications used to be an important bottleneck. At the same time, Environment Canada (1998) found that DCM could be replaced by increasing the aluminium flake content by up to three times the existing level. Furthermore, some specific problems were mentioned particularly with insect repellents in the interviews we made with some specific producers. The feasibility and technical problems related to a switch to alternatives depends very much on which kind of active ingredient is used. Where the active ingredient is dissolvable in water the resulting water vapour can be used. In other cases a different solvent has to be used. Insect repellents with DCM are often used in closed rooms. Because DCM has a high volatility and surface tension, the active ingredient spreads around in the room very quickly and the DCM fills the entire room. The 'knock down' effect of the insect repellent is therefore very high. In comparison to water as a carrier for the active ingredient, this will result in spraying little droplets instead of a fine cloud. The droplets will fall down more quickly instead of filling the room. The 'knock down' effect will therefore be less then when DCM is used as carrier. One producer of insect repellents said that when DCM will be banned, specific active ingredients no longer can be sold in aerosol packaging. Although other companies have abandoned DCM in their aerosol products, including insect repellents, it must be said that in some cases not all the insect repellent ingredient can be sold in aerosol cans, because there is no appropriate solvent. Here, alternative packaging is the only solution. The companies who still use DCM in some of their insecticide aerosols fear significant effects when market restrictions are introduced. Developing a new formula for an insect repellent takes time and to get a new recipe approved is a two-year procedure. Some of our interviewees felt that DCM is part of an approved formula and therefore no need for a ban on DCM¹⁷.

¹⁷ Some formulator also feared that in case of market restrictions products will be bought in the US where DCM is still approved. However, if the EU ensures a level playing field such imports, obviously, are not possible any more.

Despite our expectations of the role of such problems, we believe on the strength of our interviews that they are probably surmountable. This is suggested by the fact that some of the major aerosol producers in the EU interviewed by us claimed to have reduced the use of DCM to zero, also for special applications like insecticides. At the same time, our study was not detailed enough to establish that a switch to a non-DCM formulation would be feasible for every type of formulation. What is clear, however, is that DCM is fully replaceable in many of the aerosol applications that used to be of importance in the eighties, against acceptable costs: hairsprays, personal care products, etc. Indeed, one could say that the EU directive regulating the maximum DCM content in aerosol products almost outlived itself.

5.4.4 Impact of market restrictions on consumers

The major part of the aerosol products is applied on the consumer markets. However, as stated before the relevance of DCM seems to be limited to very special applications (some insect repellents, some types of paint spray cans). It is hardly foreseeable that any important socio-economic consequences could be at risk if alternative packaging forms or alternative aerosol formulations would be used. It is rather certain that DCM is virtually absent in consumer products particularly in the countries in the North of the EU. However, we cannot exclude in full that somewhere in the EU consumers can still get access to the classical, DCMbased aerosols (e.g. in hairspray), in which case the exposures on which we based our evaluation still would apply.

5.4.5 Impact of market restriction on professional use

In the professional market aerosol products are used for almost the same application as the consumer market. The conclusion therefore is that a ban on the use of DCM will not have a large impact on the professional market either. Large quantities of aerosol products are used for personal care applications, for example, by hairdressers, but because DCM is no longer used in their products market restriction will not have an effect on the professional market (Environment Canada, 1998; Windesperger, 1998; UNR, 1999).

The difficulty is that the aerosol products have a vast number of applications and that the number of professional users is large and that the companies are small and form a heterogeneous group. As mentioned above the use of aerosol products formulated with DCM in the professional market is also rather small. We were not able to find any users of aerosol products. In all cases the aerosol products which were used did not contain DCM but one of the common alternatives.

To sum up, a tentative statement is that a ban on the use of DCM in the aerosol products for professional use will not have a large impact.

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5.4.6 Impact of market restriction on industrial users

Probably about a quarter of the aerosol products is used in industrial applications. It was quite difficult to find specific users of DCM-containing aerosols. Again, we got the impression that no major problems will arise when alternative aerosol formulations will be used. The only problem may be that the alternatives for DCM are often flammable and hygroscopic. There may be incidental cases where the non-flammability of DCM is a clear advantage.

5.4.7 Conclusions

The overall conclusions of the analysis of the socio-economic effects of a possible restriction of the marketing and use of DCM in aerosol products are as follows:

Formulators

- The total production of aerosol products in Europe is about 4 billion products annually, of which roughly half is used by consumers, and the remainder roughly equally split up between professional and consumer use.
- The indications of how much DCM is used for the EU market vary very much: between 15,000 tpa (ECSA data), and less than 1,500 tpa (several national inquiries and information from formulators). An explanation could be that DCM-based formulations are largely exported.
- This corresponds with 71 or 7.1 Million aerosol units, or some 1.7 or 0.17 % of the total EU market, some 500 or 50 employees, and some 150 Million or 15 Million Euro of turnover.
- Effects on employment and turnover will be minimal since the same firms produce DCM-containing aerosols and DCM-free aerosols. Some initial investment costs may be needed to cover research into new formulations and investment in equipment that can deal with some drawbacks like the flammability and hygroscopy of some alternative propellants. Such costs can be estimated at roughly 30 % of the current turnover.
- For the bulk of the DCM aerosol applications relevant in the eighties, e.g personal care products like hairsprays, all companies interviewed have already made the switch. Hence, it seems obvious that for all those applications restrictions on marketing and use of DCM will have no socio-economic effects.
- Also for some special applications, like insecticide sprays and paints, there seems quite some room for a switch. However, our analysis could not afford the level of detail in the time allowed to ensure the absence of technical problems for every conceivable formulation. Hence, we feel that some prudence is required with regard to pursuing outright bans without leaving sufficient slack for a transition.

Consumer applications

- For the past several years it would appear that DCM has hardly been used in products for personal care. However, we cannot totally exclude a situation where somewhere in the EU there could still be consumers with access to classical DCM-based aerosols (e.g. in hairsprays). In that case, the exposures on which we based our evaluation would still be valid.
- If any products for consumer use containing DCM remain, the consumer will be able to choose an alternative product after the use of DCM has been banned.
- It is expected that the consumers will not be affected by possible market restrictions on the use of DCM in aerosol products.

Professional and industrial applications

• For professional and industrial users, the analysis is very much the same as for consumer use. There may be some applications where the non-flammability of DCM is an advantage, but we found no prohibitive problems in our analysis.

5.5 Production of DCM

5.5.1 Overview of the production chain

Around nine major multinationals active in the chlor-alkali industry produce DCM. They produce some 250 ktpa DCM, of which some 100 ktpa is exported (ECSA, 1999). In general, DCM production takes place in conjunction with a lot of other chlorinated solvents. The same plant often produces other solvents like methylchoride, chloroform, perchloroethylene, and carbon tetrachloride. It is not possible to produce DCM alone. Figure 5.1 shows the relations between these processes. The production of chlorinated solvents generally starts by chlorinating methanol with HCl. In a second step, methylchloride is chlorinated with chlorine producing a mixture of DCM, chloroform and tetra. HCl is set free as a by-product, which in turn is used in the chlorination of methylchloride. Meanwhile, a production unit for the chlorination of propane may be available at the same location, in order to produce tetra and perchloroethylene. Then the solvent mixtures are separated by distillation to obtain pure products. Adjusting the relative quantities of produced solvents within each production unit is possible only within certain limits and may need major investments. Typical production mixes for DCM/chloroform may vary per producer, between 75/25% to 50/50 %.





As for the use of the other solvents, the tetra produced has rather little use since the advent of the Montreal protocol and the later bans on ozone-depleting substances. Tetra used to be applied as a solvent and a basic chemical in the production of CFCs. Since both tetra itself and CFCs have been banned as ozone-depleting substances, the production of tetra has been kept to a minimum. Any tetra produced is either applied for essential applications still allowed, or transformed into other components (e.g. by incineration with HCl-recovery). Chloroform is used as a solvent and base chemical in other products, most notably the production of HCFCs. HCFCs are in use as replacements of CFCs, but also being used as a feedstock in the Teflon production. Though HCFCs are likely to be banned as cooling agent, their demand in the production of Teflon is rising, leading to a stable market for its basic feedstock chloroform. Perchloroethylene used to be applied in the production of CFCs, but now is only used as a solvent.

Furthermore, many of the plants for the production of chlorinated solvents are placed on a site where also chlorine and caustic soda is produced¹⁸. We asked the ECSA members about this relationship. From those firms that replied to our questionnaire it appears that up to over 50 % of the chlorine produced on a specific location may be used directly on-site in the production of chlorinated solvents.

¹⁸ Chlorine, caustic soda and hydrogen are produced inevitably together in chlor-alkali electrolysis.

5.5.2 Alternatives and their environmental performance

As indicated in the sections on paint remover, adhesives and aerosols, in many cases the alternatives for DCM are non-chlorinated solvents (bulk products line propane, butane, methanol, acetone, etc.), rather special chemicals (like NMP or DBE), or products or practices in which much less chemicals are used (e.g. hot air strippers and water-based adhesives). In some cases, the firms involved in the production of chlorinated solvents are also active in the production of these alternatives, particularly the non-halogenated solvents, but this is not always the case.

It is rather difficult to give a detailed analysis of the environmental pros and cons of the production of such alternative basic materials. However, as discussed in Chapters 2 and 4, it is clear that on large industrial production sites, emissions and occupational health problems related to DCM are generally under control. We see no particular argument why this should not be the case for plants producing nonhalogenated solvents, substances like propane and butane, or special chemicals like NMP and DBE. In sum, we see no reason to assume that the production of alternative basic materials would lead to relatively important environmental problems.

5.5.3 Impacts of market restrictions on producers of DCM

In order to analyse the impacts of marketing restrictions of DCM, first an estimate has to be made of how much of the DCM market may be affected. In this calculation, two scenarios can be thought of:

- 1. The EU embarks on a rather stringent marketing restriction policy for DCM. This would include an active restriction policy of the use of DCM in paint removers for professional and consumer use, a ban on its use in aerosols except for some specific applications, and a major reduction of the use in adhesives using a 'bubble concept' reduction target of 70 % in this sector.
- 2. The EU pursues no active policy, leading to a continuation of the autonomous market decline that took place in the last 15 years of some 30 % in total.

The first scenario would imply that the use of DCM will cease in some 20,000 tpa paint removers, some 10,000 tpa adhesive applications, and in some 15,000 tpa aerosols. Remarkably, we found a considerable difference between the rather high use of aerosols estimated by ECSA and the very low use reported in various country-specific studies and reported by aerosol producers. However, assuming that the ECSA data are right the high-reduction scenario would imply a 45,000 tpa reduction in the use of DCM in Europe, or about 33 % of the current market.

In order to analyse the implications of such market losses, we asked ECSA members to give us some key figures about production volumes and employee numbers. We obtained data from a limited number companies, which varied by a factor of 3 in terms of number of employees per tonne DCM and turnover per employee. Hence, we are only able to use order of magnitude estimates.¹⁹ Probably a good estimate is to assume that the turnover per employee is some 500,000 Euro. This is in between the extreme figures we obtained and a figure that is often used as a rule of the thumb for the chemical industry. The total value of the solvent production in the EU can be estimated as follows. The total production of DCM for the EU market is 147,500 tonnes at an average market price of some 450 Euro per tonne. The market price of chloroform is similar. Assuming that the chloroform production is at most two-thirds of the DCM production (or some 100,000 tpa)²⁰ a combined turnover of DCM and chloroform can amount to about 110 Million Euro. This would imply that some 220 people would be directly involved in the production of DCM and the co-produced chloroform. Another approach would be to extrapolate the number of employees we obtained from one producer involved in the production from one plant, to the whole production for the EU market. At most, this would lead to some 400 staff directly involved in the DCM/chloroform production for the EU market²¹.

According to Euro Chlor (1999b), the total production of chlorine in the EU was about 9.2 million tonnes in 1998. Roughly, the value of 1 tonne of chlorine-alkali production (1 tonne chlorine and 1.12 tonne NaOH) is some US \$400 or 380 Euro per tonne. This would imply a turnover in the chlorine-alkali industry of some 3.5 Bio Euro. According to Euro Chlor, the European chlorine-alkali producers employ some 39,000 people at 85 plants in 19 countries. However, from various producers we obtained data that the direct staffing is much lower. The turnover per employee was indicated (with large margins) as some 500,000 Euro, suggesting that the direct employment would be in the order of magnitude of 7,000 persons. A production of 147,500 tpa DCM (chlorine content some 71 %) and some 100,000 tpa chloroform (chorine content some 2% of the total European chlorine production.

¹⁹ Data from individual companies cannot be disclosed due to confidentiality reasons.

²⁰ Based on information from a few DCM and chloroform producing companies.

²¹ It has to be noted we concentrated on the production for EU use only. If the production of 100,000 tpa DCM for export and the about 66,000 tpa related chloroform is taken into account as well, one can calculate that some other 250 staff is involved.

Now, the consequences of market restrictions for DCM can be estimated as follows. In the high reduction scenario, the production DCM will diminish by some 45,000 tpa. If there were no indirect effects of such a production reduction, the effects would be limited to a loss of a turnover of some 20 Million Euro for chlorinated solvent producers. This is approximately 20 % of the current turnover made on the EU market, and if a proportional relation can be assumed this would probably lead to an employment loss of some 80 staff. In the chlorine-alkali business, some 32,000 tpa less chlorine would have to be produced. This is some 0.3 % of the total chlorine production in Europe. If a proportional number of employees is affected, this would involve some 20 to 30 direct staff and about 120 total staff in the chlorine-alkali business. However, it has to be noted that there will be a clear multiplier effect. Since particularly the chlorinated solvent production is so interrelated, market losses of DCM will probably also lead to production problems for related solvents. Hence, the number of employees and the turnover at stake could be up to a factor 2 or 3 larger in the chlorine and chlorinated solvents industry as a whole. This would imply, at most, an effect on 240 direct employees in the solvent production, and some 60 to 360 employees in the chlorine production. However, at a more local level much more dramatic effects could occur. The production of chlorinated solvents is concentrated at just some nine locations in the EU, near chlorine plants for which solvent production is the major market. If the DCM production would cease by another 30 %, with possible knock-on effects on the related solvent production, it can well be that producers will decide to close one or more production plants. In turn, this could have similar implications for the related chlorine production plant. So where at an EU level the socio-economic effects seem to be within limits, a drastic reduction of the DCM market could be a driver for a rearrangement of the chlorinated solvent and chlorine production structure, which may lead to closure of one or more major production locations²². Taking into account the fact that the EU already exports 100 ktpa on a total production of 250 ktpa, we cannot exclude the fact that further reductions of the domestic market would lead to a relocation of DCM production on an above-EU scale.

Solvent producers would at least have to try to adapt the production ratio of DCM and the co-produced solvents. It was claimed that this would need major investments, though for reasons of confidentiality no specific data could be given by industry.

²² For instance, one of our industrial respondents indicated that severe market losses of DCM could undermine the economic basis of one specific chlor-chemicals production plant, involving several 1,000 employees.

Hence, it is obvious that a loss in the DCM market will affect the chlorinated solvent producers with losses of employment and turnover. At the same time, in most cases alternative products for the DCM products also need production of (non-chlorinated) solvents or other substances (e.g. alternatives in aerosols). Reduction of the DCM use will probably lead to a larger production of these alternatives, and more employment and turnover in these sectors. It is very difficult to quantify these effects. However, it is often stated that the turnover per employee in the chemical industry is, for different processes, in the same range (some 500,000 Euro per employee). Therefore, one might assume that at least to a certain extent these developments will form a counterweight for the employment and turnover losses in the chlor-chemicals sector. But once again, it is likely that the problems of reducing DCM use will affect firms other than those who have the benefits of making the alternatives, since not all the chemical industries involved produce both DCM as well as the alternatives.

5.5.4 Conclusions

The overall conclusions of the analysis of the socio-economic effects of a possible restriction of the marketing and use of DCM in final products for the production of the relevant base chemicals are as follows:

- Assuming as a worst-case a very stringent market reduction policy of the EU (banning DCM in paint remover for professional and consumer use and in aerosols, and reducing DCM use in adhesives by 70 %), the DCM market would decline by 45,000 tpa (some 33 % of the current EU market). Indirectly about 32,000 tpa less chlorine would have to be produced (some 0.3 % of the current EU market).
- The number of staff related to this production is some 80 direct staff for DCM and 30 direct staff (120 total staff) in the chlorine-alkali production. The turnovers involved are 20 Million Euro for DCM, and 10 Million Euro for the chlor-alkali business.
- The production of DCM, however, is closely intertwined with the production of other solvents like particularly chloroform. There could be a knock-on effect of a factor 2 to 3 since the production of other solvents could also be affected.
- At local level the chlorinated solvent production is often linked to captive use of chlorine produced on-site. Drastic reductions of the DCM market could be a driver for a rearrangement of the chlorinated solvent and chlorine production structure which may lead to closure of a major chlor-chemical production location.
- There is already a large imbalance in the EU production (some 250 ktpa) and the EU market (some 150 ktpa). With a further decline of the domestic market in the EU rearrangements of the DCM production structure on an above-EU level cannot be excluded.

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• Furthermore, the producers of the basic chemicals of the alternative products are likely to benefit from a larger demand for those alternative products if the use of DCM products diminish. If this corrects employment and turnover losses in the chlor-chemical industry in full is not clear, but this possibility cannot be excluded. However, it is also clear that it will concern at least to some extent other firms, and in any case other business units than those currently involved in the production of chlorine and chlorinated solvents.

In sum, a drastic reduction scenario of DCM use will lead to the typical effects that occur to a transition in industry. It will probably have negative effects on employment, turnover and the competitiveness of specific current production locations, and have benefits for producers of the alternatives. As a rule, very disruptive effects related to such a transition can be reduced if a reasonable time horizon for arranging the transition is allowed. This would imply that, if the EU were to embark on a stringent reduction programme for the use of DCM, a reasonable period for its implementation should be allowed.

6. Overall conclusions

In this study, an analysis has been made of the risks of exposure to DCM. Furthermore, a selection of priority applications of DCM has been made for which restrictions on marketing and use could be considered as one of the means of reducing the risks involved. Finally, the socio-economic consequences of such restrictions of marketing and use have been analysed.

It is imperative to know that this six-month risk assessment project can in no way be compared with the in-depth, multi-year assessments that are currently being performed under the Existing Substances Programme of the EU. We mainly re-evaluated a number of extensive existing risk assessments on DCM (e.g. IPCS, Environmental Health Criteria 164, 1996; RIVM, Integrated criteria document Dichloromethane by Slooff and Ros, 1988; and ECETOC, technical reports n° 26, 32, 34). Using where possible the principles of the Technical Guidance Document as a basis, the NOAELs derived were confronted with exposure data for different exposure situations found in other studies.

Noteworthy, is that in such an analysis many subjective elements are at stake. For instance, a crucial point with regard to consumer exposure of paint remover and adhesives is that individuals are only very infrequently exposed. Hence, we evaluated the risks of short-term exposure only. As stated in Table 4.1, for this purpose we used a LOAEL for a mild, reversible CNS effect during short-term exposure. Just how important protection of the general population against such low-frequent, reversible CNS effects is, however, debatable. Furthermore, occupational health situations are in general regulated by specific legislative structures. Table 4.1 indicates that there is a MOS of two between many of the occupational health standards in EU member states and the least stringent NOAEL based on liver toxicity in rats for long-term exposure. Though this MOS is small in view of the possible interspecies and intraspecies variation, it must be noted that the exposure situation is not fully comparable (e.g. life time exposure versus exposure during (a part of) a professional career). In this respect, a rather fundamental question is at stake. The EU Technical Guidance Document demands to evaluate exposure to workers, but one could also argue that this evaluation should be left in its entirely to the existing (national) structures in which OELs are set.

Exposure levels appeared to be acceptable in most regular industrial plants using DCM, where closed technology can be applied. For applications like degreasing and application in the foam industry, the most logical approach seems to be exposure reduction of workers, where needed, rather than imposing market restrictions. For a number of inherently 'open' DCM applications the evaluation framework used suggests a need for further information and testing, or limiting the risks. Hence, we concentrated on analysis of the advantages and drawbacks of

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marketing restrictions on those applications only, for which such restrictions form one of the possible policy approaches. Of the total of 147,500 tpa DCM used in the EU in 1995 it concerns:

- the use of paint remover (some 30,000 tpa DCM in Europe);
- the use of adhesives (some 15,000 tpa DCM in Europe);
- the use of aerosols (estimates between 1,500 and 15,000 tpa DCM in Europe).

In all these cases, an analysis was included of the socio-economic consequences of the reduction of marketing and use for consumer, professional and industrial applications. However, it should be stressed that particularly for professional and industrial applications regular occupational exposure reduction measures rather than market restrictions could well be sufficient. Assessing which measure would be preferable was not part of this study. The socio-economic consequences of market restrictions can, in principle, affect the following actors:

- the formulators of paint remover, adhesives, and aerosols;
- the users of these products (consumers, professionals and industrial users);
- the producers of DCM and the related chlor-chemicals industry.

As for **paint removers**, restrictions on marketing and use of DCM may have some implications for formulators since professional users may move in part to mechanical methods. The rest will not be affected much since the same formulators produce both the DCM-related product and the alternative and as the technology is similar no major investment will be needed. What is really important is that the basic chemicals for the alternative paint remover, particularly NMP, are up to a factor 4 more expensive than DCM. Since retailers have a rather powerful position in the production-consumption chain, there may be a need for the help from third parties to convince them that charging additional costs is reasonable.

Consumers and professionals will have to count on much longer stripping times, and because the alternative chemicals are more expensive, it will involve additional costs of some 125 to 325 Million Euro per annum in the EU. However, almost all markets at stake are within the EU. Regulation at EU level will have little influence on competition. Only aeroplane stripping is an activity where competition from outside the EU could play a role, but here the companies (at least the larger ones) who already switched to alternatives feel rather comfortable about their competitive position. Hence, two main points in deciding on restrictions on marketing and use of DCM-based paint remover remain. First, given the discussion on severity of effects described in Chapter 4, the question is to what extent should current exposure be diminished by switching to alternatives that have the disadvantage of longer stripping times. Furthermore, for at least some of the alternatives, most notably NMP, whether or not the toxicological database is sufficiently strong to ensure absence of danger is a topic for debate.

The total production of **adhesives** in the EU is approximately 1.6 Million tonnes per annum, with a value of some 3,000 Million Euro. Probably only 1-2 % of this turnover, and some 300 to 600 employees, is related to DCM-based adhesives. Formulators are generally involved in the production of DCM-based adhesives and alternatives. However, some alternatives may need different production equipment, for example, in relation to the use of more flammable materials.

DCM-based adhesives seem to be far and few in consumer and professional use, so market restrictions thus will have little implications. However, also exposure thus seems infrequent. The need for market restrictions mainly depends on whether humans need to be protected against reversible CNS effects during short-term exposure. Industrial users include foam product manufacturing and the furniture industry, where especially spray applications may lead to the most problematic exposure situations. It would seem that hotmelts and water-based adhesives are promising potential alternatives and several producers already use them. Nonetheless, there may be some dedicated applications where DCM is used for its compatibility with certain plastics or resin compounds: a property not easily achieved with other solvents. Furthermore, a switch to alternatives may invoke the need for investments like new spray technologies. This may be a problem for the smaller users in particular. In sum, there is probably much scope for reducing the use of DCM-based adhesives without major socio-economic consequences. However, we got the impression that a short-term, outright ban may have consequences that could not be foreseen and analysed in full within the confines of this report. If the EU were to strive for restriction of marketing and use of DCM in these industrial applications, we would rather suggest seeking a way for a gradual reduction of use, for instance, via the method of the 'bubble concept' proposed by Environment Canada.

Indications of how much DCM is used in **aerosols** for the EU market vary greatly: between 15,000 tpa (ECSA data), and less than 1,500 tpa (several national inquiries mainly from countries in the North of the EU, and information from formulators). An explanation could be that much of the DCM-based formulations are exported. This corresponds with 71 or 7.1 Million DCM-containing aerosol units, or some 1.7 or 0.17 % of the total EU market, about 500 or 50 employees, and some 150 Million viz. 15 Million Euro of turnover. It is claimed that use in the consumer applications is virtually absent. If socio-economic effects occur, they will mainly be of relevance for the formulators. Consumers, professionals and industrial users are unlikely to be confronted with major effects.

For the formulators effects on employment and turnover will be minimal since the same firms produce DCM-containing aerosols and DCM-free aerosols. Some initial investment costs may be needed to cover research into new formulations and equipment that can deal with some of the drawbacks like the flammability and hygroscopy of some alternatives. Such costs can be estimated at roughly 30 % of the current turnover. For the bulk of the DCM aerosol applications relevant in the eighties, e.g. personal care products like hairsprays, all companies interviewed already have made the switch. Hence, it seems obvious that for all these applications restrictions on marketing and use of DCM will not have any socio-economic effects. Also for some special applications, like insecticide sprays and paints, there appears to be quite some room for a switch. However, our analysis could not have the level of detail to ensure the absence of any possible formulation technical problems. Hence, we feel that some prudence is required with regard to pursuing outright bans without leaving sufficient slack for a transition.

The effects on the producers of DCM and the related firms in the chlorchemicals industry are evident. Assuming a worst-case very stringent marketreduction policy of the EU (banning DCM in paint remover for professional and consumer use and in aerosols, and reducing DCM use in adhesives with 70 %), the DCM market would decline by 45,000 tpa (some 33 % of the current EU market). Indirectly, some 32,000 tpa less chlorine would have to be produced (some 0.3 % of the current EU market). Approximately 110 direct staff and 30 Million Euro of turnover in the DCM and chlorine production could be affected. Since the production of DCM is in chemical terms inevitably related to other solvents (e.g. chloroform), a knock-on effect of a factor 2 or 3 could occur because the economic basis of production of other solvents could be affected. As the solvent production is often linked to captive use of chlorine produced on-site, the same applies here. Drastic reductions of the DCM market could be a driver for a rearrangement of the chlorinated solvent and chlorine production structure which may lead to closure of a two chlor-chemical production location, and thus socio-economic consequences on local level. Since the EU production of DCM is much larger than the EU market (250 versus 150 ktpa), further reduction of the domestic market may lead to an adaptation of the production structure on an above-EU level. Obviously, a positive effect outside the chlor-chemical industry will be an increased demand for alternative solvents or chemicals.

Summing up, the most important problems with a drastic reduction of marketing and use of DCM may occur in the chlor-chemical industry. A drastic reduction scenario of DCM use will lead to the effects typical to a transition in industry. It will probably have negative effects on employment, turnover and the competitiveness of specific current production locations, and have benefits for producers of the alternatives. As a rule, very disruptive effects related to such a transition can be reduced if a reasonable time horizon for arranging the transition is allowed. This would imply that, if the EU were to embark on a stringent reduction programme for the use of DCM, a reasonable period for its implementation should be allowed. However, the need for such a policy depends on the following discussion points:

- 1 For consumer applications of DCM (particularly those leading to a rather infrequent exposure, like paint remover and adhesives): the desirability and need to protect consumers against short term, reversible CNS-effects;
- 2 For professional/industrial applications of DCM: the extent to which the EU should leave standard setting and policy making to the existing (national) evaluation structures for occupational health, and to what extent other measures than market restrictions could be appropriate and/or preferable.

Literature

ATSDR (1993). Toxicological profile for Methylene chloride. TP-92/13.

Ayres, RU and LW Ayres. (1996), The life cycle of chlorine, part I, II,III an IV, Working paper of the Centre for the Management of environmental Resources, INSEAD, Fontainebleau, France.

Barrowcliff DF & Knell AJ. (1979) Cerebral damage due to endogenous chronic carbon monoxide poisoning caused by exposure to Methylene chloride. J. Soc. Occup. Med., 29:12-14.

BAS, (1998), Technische Regeln für Gefahrstoffe, Eratzstoffe, Ersatzverfahren und Verwendungsbeschrankungen fur dichlormethananhaltige Abbeizmittel, TRGS 612, fur den Bundesministerium fur Arbeit und Sozialordnung. Berlin, Brd

Becker CE & Lash A. (1990) Study of neurological effects of chronic Methylene chloride exposure in airline maintenance mechanics [abstract 7]. Vet. Hum. Toxicol., 32:342.

Bednarz, A. (1988). Toxische lugenodem und inhalative Schwermetallintoxikation udrh Ablosen alter Farbreste mittels Heissluft. Medizinische Klinik (83), No. 20

Bouieus, H., (1993), Verfverwijdering, onderzoek naar de gezondsheidsrisico's en milieuaspecten van verfverwijderen door doe-het-zelvers, Chemiewinkel, UvA. (Universiteit van Amsterdam), NL

Britisch Aerosol Manufacturers' Association, BAMA. (1999), UK Aerosol Fillings, website <u>www.BAMA.co.uk/ukfillings.htm</u>.

Buie SE, Pratt DS, & May JJ. (1986) Diffuse pulmonary injury following paint remover exposure. Am. J. Med., 81: 702-704.

Burek JD, Nitschke KD, Bell TJ, Wackerle DL, Childs RC, Beyer JE, Dittenber DA, Rampy LW, & McKenna MJ. (1984) Methylene chloride: A two-year inhalation toxicity and oncogenicity study in rats and hamsters. Fundum. Appl. Toxicol., 4:30-47.

Cherry N, Venables H, Waldron HA, & Wells GG. (1981) Some observations on workers exposed to Methylene chlorides. BR. J. Ind. Med., 38:351-355.

Coleman M. (1993) Environmental barriers to trade and European Community law, European Environmental Law Review.

Conseil Européen des Industries des Peintures, Encres d'imprimerie et Couleurs d'Art, CEPE., (1999). Letter from Mr Warnon, J. to Mr. L.Ph. Simons, TNO-STB, dd 25-06-1999, CEPE, Belgium.

Consumentenbond (1998), Dossier Afbijtmiddelen, Ongezonde krachtpatsers voor moeilijke klusjes, Consumentengids, september 1998, Den Haag, NL.

Danish EPA (1999), National Substance Flow Analysis on DCM, Kopenhagen, Dk.

Di Vincenzo GD & Kaplan CJ. (1981a) Uptake, metabolism and elimination of Methylene chloride vapour by humans. Toxicol. Appl. Pharmacol., 59:130-140.

Dow Chemical USA. (1975) Aerosol Age 20:5. May.

Duprat P, Delsaut L, & Gradiski D. (1976) Pouvoir irritant des pricipaux solvents chlorés aliphatiques sur la peau et les muqueuses oculaires du lapin. J. Eur. J. Toxicol., 9(3):171-177.

ECETOC. (1987) The Assessment of Carcinogenic Hazard for Human beings exposed to Methylene chloride. Brussels, European Centre for Ecotoxicolgy and Toxicology of Chemicals (Technical Report No. 26).

ECETOC. (1988) Methylene chloride (dichloromethane): human risk assessment using experimental animal data. Brussels, European Centre for Ecotoxicology and Toxicology of Chemicals (Technical Report No. 32).

ECETOC. (1989) Methylene chloride (dichloromethane): an overview of experimental work investigating species, differences in carcinogenicity and their relevance to man. Brussels, European Centre for Exotoxicology and Toxicology of Chemicals (Technical Report No. 34).

ECSA (European Chlorinated Solvents Association. (1995) Methylene chloride: An update on human and environmental effects.

ECSA (1999), Written and oral information on the DCM market in the EU. ECSA, Brussels, BE.

Eijndhoven J, van & Groenwegen P. (1991) The construction of expert advice on health risks, Social studies of Science. Vol. 21 No. 2, pp.257-278.

Environment Canada (1998), A Technical & Socio-Economic Comparison of Options, Chapter 14, Part 3-Other Chlorinated Substances, and , Strategic Options for the Management of Toxic Substances, Dichloromethane, Report of Stakeholders Consultations, Internetsite; <u>http://www.pwc.bc.doe.ca/ep/dcm</u>. Euro Chlor (1999a). Euro Chlor Risk Assessment for the Marine Environment – OSPARCOM Region – North Sea. Dichloromethane. February 1999. Euro Chlor, Brussels, Belgium

Euro Chlor (1999b). Chlorine Industry Review 1998-1999. Euro Chlor, Brusssels, Belgium

European Commission. (1996) Technical Guidance Document in support of Commission Directive 93/67/EEC on Risk Assessment for new notified Substances and Commission Regulation (EC) No 1488/94 on Risk Assessment for Existing Substances, Part I.

European Commission. (1996) Technical Guidance Document in support of Commission Directive 93/67/EEC on Risk Assessment for new notified Substances and Commission Regulation (EC) No 1488/94 on Risk Assessment for Existing Substances, Part II.

FEA (1999), European Aerosol Federation, Written and oral communication, Summer 1999, Including use of information from www.fea.be

FEICA (Association of European Adhesives Manufacturers, 1999), Letter from M. Hagwell to Mr L.Ph. Simons (TNO-STB), dd 25-06-1999. Information on Methylene Chloride in the Adhesive industry, Dusseldorf, Germany.

Friedlander BR, Hearne T, & Hall S. (1978) Epidemiologic investigation of employees chronically exposed to methylene chloride. J. Occup. Med., 20:657-666.

Friedlander BR, Hearne T, & Hall S. (1978) Epidemiologic investigation of employees chronically exposed to Methylene chloride. J. Occup. Med., 20:657-666.

Gibbs GW. (1992) The mortality of workers employed at a cellulose acetate and triacetate fibers plant in Cumberland Maryland, a "1970 " cohort followed 1970-1989. Final report by Safety Health Environmental International Consultants, Winterburn, Alberta (TO). Somerville, New Jersey, Hoechst Celanese.

Gradiski D, Bonnet P, Raoult G, Magadur JL, & Francin JM. (1978) Toxicité aiguë comparée par inhalation de principaux solvants alphatiques chlorés. Arch. Mal. Méd. Trav. Sécur. Soc., 39:249-257.

Green T, Nash JA, & Mainwaring G. (1986) Methylene chloride (dichloromethane): In vivo inhalation pharmacokinetics inB6C3F1 mice (using stable isotopes) and F344 rats. Alderley Park, Macclesfield (Cheshire), ICI (Technical Report CTL/R/879). Green, T. (1995), Overview of research into mechanism of action of Methylene Chloride and its relevance to humans. In: ECSA, Methylene Chloride. New Science: Future USE. Workshop Report. ECSA, Brussels, Belgium

Hall AH & Rumack BH. (1990) Methylene chloride exposure in furniture-stripping shops: Ventilation and respirator use practices. J. Occup. Med., 32:33-37.

Haun CC, Vernot EH, Darmer KI, & Diamond SS..(1972) Continuos animal exposure to low levels of dichloromethane. In: Proceedings of the 3rd annual Conference on Environmental Toxicology, Dayton, Ohio, Wright-Patterson Air Force Base, Aerospace Medical Research laboratory, pp 199-208 (paper No, 12; AMRL-TR-130).

Hearne, FT, Grose, F, Pifer, JW et al., (1987) Methylene chloride mortality study: Dose response characterisation and animal model comparison. J. Occup. Med 29:217-228 (as cited in ATSDR 1991).

Hearne, FT, Pifer, JW and Grose, F. (1990). Absence of adverse mortality effects in workers exposed to Methylene chloride: an update. J. Occup. Med. 32:234-240

Heineman EF, Cocco P, Gomez MR, Dosemeci M, Stewart PA, Hayes RB, Zahim SH, Thomas TL, & Blair A. (1994) Occupational exposure to chlorinated aliphatic hydrocarbons and risk of astrocytic brain cancer. Am J Ind Med, 26(2):155-169.

Henkel (1999), Personal communication with Henkel, Winsford, Cheshire CW7 3QY, UK

Heppel LA, Neal PA, Perrin TL, Orr ML, & Porterfield VT. (1944) Toxicology of dichloromethane (Methylene chloride). 1. Studies on effects of daily inhalation. J. Ind. Hyg. Toxicol., 26:8-16.

HSE UK (Health and Safety Executive) (1998) Dichloromethane Exposure assessment document EH74/1.

IJC (International Joint Commission). (1993), A strategy for virtual elimination of persistent toxic substances, Volume 1, Report of the Virtual Elimination Task Force to the International Joint Commission, ISBN 1-895085-65-9, Windsor, Ontario, Canada, August 1993.

IPCS (International Program on Chemical Safety). (1996) Environmental Health criteria 164, Methylene chloride (sec. edition), World Health Organization.

Jasanoff SS. (1990) The fifth Branch: Science Advisers as Policymakers. Harvard University Press, Cambridge, MA, US.

Janus, J. A., J.M. Hesse, and M. Rikken (1994). Aandachtsstoffen in het Nederlands Milieubeleid. Overzicht 1994. RIVM Report no. 601014006. Bilthoven, the Netherlands

Kapteijns, A.J.F. (1997), Evaluatie van het gebruik van Dichloormethaan als afbijtmiddel en mogelijke alternatieven, MEBO Milieu-advies Bureau, Den Haag, NL.

Kari FW, Maronpot RR, & Anderson MW. (1992) Testimony for the OSHA hearing on the proposed occupational standard for Methylene chloride. Research triangle Park, North Carolina, National Institute of Environmental Health Sciences.

Kaye Whitfield, J., et al., (1999), Demonstration of *n*-methyl pyrrolidone (NMP) as a pollution prevention alternative to paint stripping with methylene chloride, Journal of Cleaner Production, No 7 331-339, Elsevier.

Kelly M. (1988) Case reports of individuals compound sampling survey of public water supplies. Washington, DC, Environmental Protection Agency (NTIS PB85-214427).

KemI (1991), Risk reduction of chemicals, A government commission report, KemI, Solna, Sweden (written in cooperation with Swedish EPA)

Kleijn, R and E van der Voet (1998), Chlorine in Europe. MACTEMPO Case Study, CML, Leiden, the Netherlands.

Könemann. WH. (1996), Letter from the RIVM (Rijksinstituut voor Volksgezondheid en Milieuhygiene) to The department of VROM, subject: MTL of Dichlorometahne.

Kozana L, Frabntik E, & Vodickova A. (1990) Methylene chloride does not impair vigilance performance at blood levels simulating limit exposure. Acta. Nerv. Super, 32:35-37.

KPMG Milieu. (1992), Organisatiestructuur voor de verwijdering van verf-Kcaafval binnen de verfbedrijfskolom [Organisational structure for the disposal of chemical paint within the paint industry column], Den Haag.

Laham S. (1978) Toxicological studies on dichloromethane, a solvent simulating carbon monoxide poisoning. Toxicol. Eur. Res., 1:63-73.

Lanes SF, Cohen A, Roterman KJ, Dreyer NA, & Soden KJ. (1990) Mortality of cellulose fiber production workers. Scand. J. Work .Environ. Health., 16:247-251.

Lash AA, Becker CE, SO Y, & Shore M (1991) Neurotoxic effects of Methylene chloride: are they long lasting in Humans?. Arch. Exp. Pathol. Pharmakol, 141: 19-24.

Leeuwen, C.J. van and J.L.M. Hermens (1995). Risk Assessment of Chemicals. And Introduction. Kluwer Academic Publishers, Dordrecht/Boston/London

Leuschner F, Neumann BW, & Hubscher F. (1984) Report on subacute toxicological studies with dichloromethane in rats and dogs by inhalation. Arzneimittel forschung, 34: 1772-1774.

Lewis, S.C., J.R. Lynch and A.I. Nikiforov (1990). A New Approach to Deriving Community Exposure Guidelines from "No-Observed-Adverse-Effect Levels". Regulatory Toxicology and Pharmacology 11, p314-330

Maltoni C, Cotti G, & Perino. (1988) Long-term carcinogenicity bioassys administered by ingestion to Sprague-Dawley rats and Swiss Mice and by inhalation to Sprague-Dawley rats. Ann. Ny. Acad. Sci., 534:352-366.

Manno M, Rugge M, & Cockeo V. (1992) Double fatal inhalation of dichlormethane. Hum. Exp. Toxicol., 11(6):540-545.

Mattson JL, Albee RR, & Streeter CM. (1988) Neurotoxicologic evaluation of rats after 13 weeks of inhalation exposure to dichloromethane or carbon monoxide. Pharmacol. Biochem. Behav., 36: 671-681.

McCarty LP, Flannagan DC, Randall SA, & Johnson KA. (1992) Acute toxicity in rats of chlorinated hydrocarbons given via the intracheal route. Hum. Exp. Toxicol., 11: 173-177.

Mennear JH, McConnell EE, Huff JE, Renne RA, & Giddens E. (1988) Inhalation toxicology and carcinogenesis studies of Methylene chloride (dichloromethane) in F344/N rats and B6C3F1 mice. Ann. NY. Acad. Sci., 534: 343-351.

Miller L, Pateras V, Friederici H, & Engel G. (1985) Acute tubular necrosis after inhalation exposure to Methylene chloride. Report of a case. Arch. Intern. Med., 145:145-146.

Most, PFJ. van der (1993), Emissies van halogeenkoolwaterstoffen ten gevolge van reinigen en ontvetten in kleine bedrijven [emissions of halogenated hydrocarbons as a result of cleaning and degreasing in small companies], Publikatie reeks Emissieregistratie no. 15, Switzerland.

NCA (National coffee association) (1982) Twenty-four-month chronic toxicity and oncogenicity study of methylene chloride in rats. Final report. Prepared by Hazleton Laboratories, America, Inc., Vienna, VA.

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NCA (National Coffee Association) (1983) Twenty-four-month oncogenicity study of methylene chloride in mice. Final report. Prepared by Hazleton laboratories, America, Inc., Vienna, VA.

Nederlandse Aerosol Vereniging, NAV, (1998), Jaarverslag 1998, Tilburg, NL.

Nitschke, KD et al (1982). Methylene Chloride: A two-year inhalation toxicity and oncogenicity study. Toxicological Research Laboratory, Health and Environmental Sciences, Dow Chemical, Midland, Michigan, USA

Nitschke KD, Burek, JD, Bell TJ, Kociba RJ, Rampy LW, Rampy LW, & McKenna MJ (1988a) Methylene chloride: A 2-year inhalation toxicity and oncogenicity study in rats. Fundam Appl. Toxicol., 11: 48-59.

Nitschke KD, Eisenbrandt DL, Lomax LG, & Rao KS (1988b) Methylene chloride Two-generation inhalation reproductivity study in rats. Fundam Appl. Toxicol. 11:60-67.

Nitschke, K.D., Burek, J.D., Bell, T.J., Rampy, L.W. and McKenna, M.J. (1984) Methylene Chloride: A two year inhalation and oncogenicity study in rats and hamsters. Journal Fund. Appl. Toxocol. 4:30-47.

NTP (National Toxicology Program) (1986) Toxicology and carcinogenesis studies of dichloromethane (Methylene chloride) (CAS No. 75-09-2) in F344/N rats and B6C3F1 mice (inhalation studies). NIH Publication NO. 86-2562. Research Triangle Park, NC, and Bethseda, MD

OECD (1994) environment Monograph Series No. 96, Risk Reduction Monograph No.2 Methylene chloride.

OECD (1996) Methylene Chloride information exchange programme Survey Results. OECD Series on Risk Management. No. 6, France.

Otson, R., D.T. Williams and P.D. Bothwell (1981). Dichloromethane levels in air after application of paint removers. Am. Ind. Hyg. Assoc. 7. 42 56-60

Ott, GM, Skory, LK, Holder, BB Bronson, JM and Williams, PR (1983) Health education of employees occupationally exposed to methylene chloride. Scand. J. Work. Environ. Health. (Sup 1), 1-7.

Page, BD and Charbonneau. (1984) Headspace gaschromatographic determination of residual methylene chloride in decaffeinated tea and coffee with electronic conductivity detection. J. Assoc. Off. Anal. Chem. 67:757-761 (as quoted by IPCS 1994).

Putz VR, Johnson BL, & Mansfield JI (1976) A comparative study of the effects of carbon monoxide and Methylene chloride on human performance. J Environ Pathol Toxicol, 2: 97-112.

Putz VR, Johnson BL, & Setzer JV. (1976) A comparative study of the effects of carbon monoxide and

RTECS, 1994 Online database. U.S. department of Health and Human Services. Registry of Toxic Effects of Chemical Substances. National Toxicology Information Program, National Library of Medicine, Bethesda, MD.

Serota DG, Thakur AK, Ulland BM, Kirschman JC, Brown NM, Cotts RG, & Morgareidge K. (1986a) A two-year drinking-water study of dichloromethane in rodents. I. Rats. Food. Chem Toxicol., 24:951-958.

Slooff, W and Ros, JPM RIVM (Rijksintsituut voor Volksgezondheid en Milieuhygiene (1988) Integrated Criteria Document Dichloromethane. National Institute for Public Health and Environment Protection, the Netherlands. Report No. 758473009

Slooff, W en. Ros JPM (1987), Integrated criteria document chlorobenzenes, rep. No 710401015, RIVM, Bilthoven

Solomon, J. et al. (1996). Stillbirth after occupational exposure to N-methyl-2pyrrolidone. Journal of Occupational Medicine, Vol. 38, No. 7

Steen JJD van der. (1991), Inventarisatie halogeenkoolwaterstofhoudende afvalstromen uit het Wca-meldingenbestand van 1988 en de toetsing aan verwerkingstechnieken [Survey of waste flows containing halogenated hydrocarbons from the chemical Waste Act notification in 1988 and the testing of processing techniques], TNO, Apeldoorn (not published).

Steward RD & Dodd HC. (1964) Absorption of Carbon tetrachloride, trichloroethylene, tetrachloroethylene, Methylene chloride, and, 1,1,1,trichloroethane through the human skin. Am Ind Hyg Assoc J, 25:439-446.

Tariot PM (1983) Delirium resulting from Methylene chloride exposure: Case report. J. Clin. Psychiatry., 44:340-342.

Tukker, A, R. Kleijn, E van den Voet, M. Alkemade, J. Brouwer, H. de Groot, J. de Koning, T. Pulles, E Smeets and JJD van der Steen (1995), A chlorine balance for the Netherlands, report 95/40, TNO-STB and CML, Apeldoorn, Holland.

U.S. EPA (1985) Health assessment document for dichloromethane (Methylene chloride). Washington, DC, US Environmental Protection Agency (EPA/600/8-82/004F).

U.S. EPA (1990). Paint stripping; options selection paper. U.S. EPA, Washington, DC

U.S. EPA, IRIS substance file-Dichloromethane; CASNR 75-09-2

U.S. EPA (1994), Guide to Cleaner Technologies Organic Coating Removal. EPA/625/R-93 Office of Research and Development. Washington DC, USA,

U.S. OSHA (The Occupational Health and Safety Administration, 1997). Methylene chloride. OSHA publication 3144, U.S. Department of Labor

UBA (1991), Handbuch Chlorochemie I, forschungsbericht 10404348 Umweltbundesambt, Bonn, Germany. UmweltBundesambt (UBA, 1999), letter dd.

UNR (1999), Letter of Prof. Dr. Basler of the Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit to Dr. A. Tukker of TNO-STB, 1 September 1999, with as annex 1 a paper titled 'Dichlormethan'.

Van Beek L. (1990) Investigation of a possibility to reduce the use of rabbits in skin irritation test; experiments with dichlorometahne, trichloroethylene, tetrachloroethylene and, 1,1,1,-trichloroethane. Doc. 56645/34/90, rep. V 89.265. Zeist, The Netherlands, TNO-CIVO Institutes.

Vereniging van Verf- en Drukinktfabrikanten, VVVF (1997)., Investigation into the position of paint stripping agents, VVVF Leiden, NL.

Vereniging Nederlandse LijmIndustrie, VNL (1999). Telefax with information from Mr F.J. Baarslag to Mr. L.Ph. Simons (TNO-STB). Dd 6-8-1999, Gebruik dichloormethaan (DCM) in de lijmindustrie, Ref: FB/FB/VNL/0623, Leidschendam, NL.

Verhage H. (1991), Informatiedocument halogeenkoolwaterstoffen [Information document on halogenated hydrocarbons], RIVM, Bilthoven.

Weinstein RS & Diamond SS. (1972) Hepatotoxicity of dichlomethane (methylene chloride) with continued exposure at a low dose –level. In: Proceedings of the 3rd Annual Conference on Environmental Toxicology.

Weiss G. (1967) Toxic encephalosis in occupational contact with Methylene chloride. Zent.bl. Arbeitsmes. Arbeitsschutz, 17(9): 282-285.

Wells GG & Waldron HA (1984) Methylene chloride burns. Br J Ind Med., 41:420.

WHO-AQG. (1996), Updating and Revision of the Air Quality Guidelines for Europe. Report on a WHO Group on Volatile Organic Compounds. Brussels, Belgium, 2-6 October 1995. WHO Regional Office for Europe, Copenhagen, Denmark.

Windsperger, A.S., et al. (1998). Verminderung der Umweltbelastungen von CKW in Osterreich-Reduktion von Dichlormethaneemissionen., Institute fur Industriele Okologie, im aufrag des, Bundesministerium fut Umwelt, Jugend und Familie, St.Pölten, Austria.

Zahm, SH, Stewart, ZP and Blair, A, (1987) A study of mortality among workers exposed to methylene chloride report. National Cancer Institute (USA).

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Appendices

- 1 A review of animal test data and human case studies on acute effects (1a) and skin and eye effects (1b)
- 2 A review of animal test data and human case studies on repeated dose/chronic effects
- 3 A review of animal test data and human case studies on chronic/carcinogenic effects
- 4 Classification and standards for DCM in different countries
- 5 List of persons and institutes contacted within the framework of this study

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Appendix 1A: Acute effects of DCM on humans and animals

Species	Duration/h(hours)/ d(days)	Route	Concentration	LC50/LD50/LOAEL/ NOAEL/Effects	Comments	Reference
Human	Acute	Oral	Unknown	Acute and severe poisoning, cardiac irregularities, corneal burn.		Hall & Rumack, 1990
Human	Acute	Inhalation	Unknown	Headache, chest pain, confused, disorientated, loss of alertness, increased fatigue, lethargy, little recall, slurred speech	Using paint stripper in poorly ventilated house	ATSDR,1993
Human	Acute	Oral/ingestion	2.5 mg/l	No vigilance performance	Human volunteers; time of exposure and number of subjects not known	Kozana et al., 1990 As cited in IPCS, 1996: 173
Human	Acute	Inhalation	538 mg/l (air samples)	Death	Two men fell in a well with DCM	Manno et al.,1998)
Human	Acute	Ingestion	357 mg/kg/bw	Death		RTECS, 1993
Human	Acute	Inhalation	Unknown	Pulmonary oedema with bilateral exudative pleural effusions, respiratory distress		Buie et al.,1986
Human	Acute	Inhalation	Unknown	Liver enzyme, lower abdominal pain	Use of paint remover	Miller et al., 1985
Human	7.5 hr for five days	Inhalation	180 mg/m3 350 mg/m3 530 mg/m3 710 mg/m3	Related CO-Hb levels 1.9 % 3.4 % 5.3 % 6.8 %	Volunteer study	De Vicenzo and Kaplan (1981a), as cited by IPCS (1996:87)
Human	1,5-3 h	Inhalation	694 mg/m ³	Neurobehavioral changes were observed at low exposure level. Vigilance disturbance and combined tracking monitoring performance were found. light-headedness, LOAEL	Volunteers, non- smoking healthy individuals	Putz et al., 1976

Species	Duration/h(hours)/	Route	Concentration	LC50/LD50/LOAEL/	Comments	Reference
	d(days)			NOAEL/Effects		
Humans	Exposure time	Inhalation	1650 mg/m ³	Increase in red cell counts,	Volunteers. 266	Ott et al., 1983)
				hematocrit among white	and 251 reference	
				women Increased CO-Hb	volunteers	
				levels A dose-related	Voluntooro	
				increase was observed in		
				serum bilirubin for exposed		
				subjects of both sexes		
Rat (Sprague-Dawley)	Acute	Oral	530 mg/kg/bw	Hypotension, hypothermia,		Laham, 1978
				haematuria, increased CO-		
				Hb levels		
Rat and dog	Acute	Oral	3000 mg/kg/bw	LD50		Gradiski, 1978
Mouse and rat	Acute	Inhalation	49000-79000mg/m ³	LC50		Gradiski, 1978
Rabbits	Acute	Liquid DCM in	N/a	Reversible eye irritation,		Gradiski, 1978
		eye		severe skin irritation		
Rats (Sprague-Dawley)	Acute	Intratracheal	350 mg/kg/bw	Lethal		Mc Carty, 1992
Rat (Wistar), male	Acute	Oral	1710-2250	LD ₅₀		Cited in IPCS,
			mg/kg/bw			1996: 105
Rat CDF (F344)	Acute	Oral	1530-2524	LD ₅₀		
			mg/kg/bw			-
Rat (Sprague-Dawley)			0400 ""			
Young male	Acute	Oral	2120 mg/kg/bw	LD ₅₀		_
Rat (Sprague-Dawley)	Acute		0000			
		Oral	2280 mg/kg/bw	LD ₅₀		
Female Maura (OF 4) mala	Asuta	Oral	1410 mg/kg/bw	LD ₅₀		-
Mouse (CF-1), male	Acute	Oral	1987 mg/kg/bw	LD ₅₀		-
Dog Dot (Alderly Dod)	Acute	Orai	3000 mg/kg/bw	LD ₅₀		-
Rat (Alderly Park)	Acute	Innalation	197790 mg/m	15-min LC ₅₀		-
Rat (Sprague-Dawley), male	Acute	Innalation	52000 mg/m ⁻	6-n LC ₅₀		4
Rat (Sprague-Dawley)	Acute	Innalation	>28000 mg/m°	6-n LC ₅₀		4
Mouse (CF-1), male	Acute	Inhalation	92680 mg/m	20-min LC ₅₀		4
Mouse (LF-1), female	Acute	Inhalation	49100 mg/m [°]	6-h LC ₅₀		
Species	Duration/h(hours)/ d(days)	ration/h(hours)/ Route Concentration d(days)		LC50/LD50/LOAEL/ NOAEL/Effects	Comments	Reference
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Mouse (ICR), male	Acute	Inhalation	55870 mg/m ³	6-h LC ₅₀		
Guinea-pig	Acute	Inhalation	40200 mg/m ³	6-h LD ₅₀		
Rat (Sprague-Dawley), male	Acute	Intratracheal	350 mg/kg/bw	ALD		
Mouse (CF-1), male	Acute	Intraperitoneal	448 mg/kg/bw	LD ₅₀		
Mouse	Acute	Intraperitoneal	500 mg/kg/bw	LD ₅₀		
Mouse (Swiss-Webster), male	Acute	Intraperitoneal	1990 mg/kg/bw	LD ₅₀		
Dog	Acute	Intraperitoneal	1260 mg/kg/bw	LD ₅₀		
Mouse	Acute	Subcutaneous	6500 mg/kg/bw	LD ₅₀		

Appendix 1B: Skin and eye effects of DCM on humans and animals

Species	Duration/h(hours)/	Route	Concentration	LC50/LD50/LOAEL/	Comments	Reference
	u(uays)	-	-	NOAEL/Ellects		
Human	30 min	Direct skin	Liquid DCM and	Unconscious, second		Weels &
		contact and	DCM vapour	and third degree		Weldron, 1984
		inhalation		burning		
Human	2*d for 12 weeks	Direct skin	Deodorant with	Slight erythema,		Steward &
		contact	aerosol of DCM	burning sensation and		Dodd, 1964
				pain		
Rabbits	24h	Direct skin	0,5 ml DCM	Severe erythema and		Van Beek,
		contact		oedema with necrosis		1990
				and acanthosis.		
Rabbits	Acute	DCM vapour in	17700 mg/m ³	Slight increase in		Duprat et al.,
		the eyes	-	corneal thickness and		1976
		-		intraocular tension		

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Appendix 2: Repeated/chronic toxicity of DCM on humans and animals

Species	Duration/h(hours)/ d(days)	Route	Concentration	LC50/LD50/LOAEL/ NOAEL/Effects	Comments	Reference
Humans (1 individual)	5 years, occupational exposure	Inhalation	2290-125000 mg/m ³	Irreversible damage CNS, acoustic and optical illusions, hallucinations	8 hr. TWA is unknown	Weiss, 1967
Humans (1 individual)	3 years, occupational exposure	Inhalation	1735-3470 mg/m ³	Bilateral temporal lobe degeneration	8 hr. TWA is unknown	Barrowcliff & Kneel, 1979
Humans (1 individual)	4 years, occupational exposure	Inhalation	Unknown	Headache, nausea, blurred vision, shortness of breath, memory disturbance	All symptoms and signs cleared with removal from workplace	Tariot, 1983)
Humans (34 individuals)	Occupational exposure	Inhalation	11-544 mg/m ³ Mean: 240 mg/m ³	CNS dysfunction, testicular, epididymal or lower abdominal pain, clinical histories relating tom infertility, low sperm counts	Uncertain if effects were due to DCM, since also exposure to other chemicals occurred	Kelly, 1988
Humans (29 individuals)	Occupational exposure, several years	Inhalation	260-347 mg/m ³	No exposure-related, long- term damage was found		Cherry et al., 1981
Humans (1758 individuals)	Occupational; 22 years	Inhalation	Unknown	All outcomes were within the "normal" range. No statistically significant difference was found between exposed and control groups, Although subtle differences in attention and memory were detected	Telephone survey Aeroplane strippers	Becker & Lash, 1990; Lash et al., 1991)
Humans	Occupational exposure, duration unknown	Inhalation	114 mg/m ³ (time weighted average)	Increased CO-Hb levels of 0.8 -2.5%. No effects were found on clinical chemistry, haematology or electrocardiograms	Morbidity study	Di Vincenzo & Kaplan, 1981
Sprague-Dawley rats	6h/d for 90d	Inhalation	35 mg/m ³	Slight redness of conjunctiva (for 1-10h)		Leuschner et al., 1984

Species	Duration/h(hours)/ d(days)	Route	Concentration	LC50/LD50/LOAEL/ NOAEL/Effects	Comments	Reference
F-344 male and female rats	6h/d 5d/week for 13 weeks	Inhalation	177, 710, 7100 mg/m ³	No treatment related alterations in sensory- evoked potentials (flash, auditory brainstem, somatosensory or caudal nerve), or neuropathology were observed at <u>any</u> of the exposure levels	Assessment concentrated on neuropathology and sensory- evoked potentials	Mattson et al., 1990
Rats	7h/d, 5 d/week for 6 months	Inhalation	35000 mg/m ³	CNS depression		Heppel et al., 1944
10 male, 10 female F344 rats	6h/d, 5d/week for 13 weeks	Inhalation	1850 mg/m ³ 3700 mg/m ³ 7400 mg/m ³ 14800 mg/m ³ 29700 mg/m ³	Related dose-response: Effect unknown Effect unknown Foreign body pneumonia was observed in some rats exposed to 7410 Liver lipid was significantly reduced The mean body weight in males and females in this category was lower then in the control group	One male and one female died before end of study (none of the rats in the control group died)	NTP, 1986
Female mice ICR	Continuously exposure for 10 weeks	Inhalation	350 mg/m ³	Fatty infiltration, vacuolisation and enlargement hepatocyte nuclei persisted up to the end of the exposure period. A reversible increase in plasma triglycerides was also observed		Weinstein & Diamond, 1972

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Species	Duration/h(hours)/ d(days)	Duration/h(hours)/ d(days)RouteConcentrationLC50/LD50/LOAEL/ NOAEL/Effects				Reference
Mice	100 days (duration per day/week unknown)	Inhalation	88 or 350 mg/m ³	Slight cytoplasmic vacuolisation, decrease in microsomal cytochrome P- 450 in liver	Strain and sex unspecified	Haun et al., 1972
Beagle male/female	6h/d for 90 d	Inhalation	17700 mg/m ³	Slight sedation, slight erythema (till 10h after exposure)		Leuschner et al., 1984

Appendix 3: Chronic/carcinogenic effects of DCM on humans and animals

Species	Duration/h(hours)/ d(days)	Route	Concentration	LC50/LD50/LOAEL/ NOAEL/Effects	Comments	Reference
Humans	At least 1 year occupational exposure	Inhalation	Unknown	The study showed no excess of respiratory cancer or circulatory disease. The results for liver and biliary cancer were not reported. But three cases of pancreatic cancer (0.9 expected) were reported. All three had worked in the production facility and were exposed to DCM, chloroform and carbon tetra-chloride, this limits the interpretations of the results to DCM	Mortality study 226 men, 42 deaths	Ott et al., 1983 Lanes et al., 1990
Humans	At least 1 year occupational exposure	Inhalation	8 hr TWA 35.3-402 mg/m ³ mean exposure was 91.8 mg/m ³	An excess of pancreatic cancer mortality was observed. It was suggested that the excess of pancreatic cancer mortality increased with time since first exposure (latency) was greater among workers in the highest exposure and latency. No new pancreatic cases were found during follow-up and with the additional data the excess was not statistically significant Increased risk of ischaemic heart disease, lung cancer, liver cancer or other cancers were not statistically detected	Mortality studies of Kodak personnel. N=1013 Kodak personnel were not allowed to smoke at their workstations . This may have induced a negative bias in these studies particularly with respect to lung cancer	Friedlander et al., 1978 Hearne et al., 1990

Species	Duration/h(hours)/ d(days)	Route	Concentration	LC50/LD50/LOAEL/ NOAEL/Effects	Comments	Reference
Humans	Occupational exposure for at least 3 months	Inhalation	494-1677 mg/m ³	Mortality from cardiovascular disease or any other cause was not significantly found. But there was a significant increase in the risk of ischaemic heart disease among white men. There was no report of cancer mortality but the study was not designed to evaluate increase in cancer mortality. Seven malignant neoplasms were included	Mortality study 1271 males and females. Workers were also reported to be exposed to methanol and acetone	Ott et all., 1983
Humans	Occupational exposure	Inhalation	Three exposure groups: High >1235 mg/m ³ Low 176-350 mg/m ³ No exposure	(high exposure group) Prostate cancer was significantly elevated among men, particularly among those with latency and with high exposure levels to DCM. (low exposure group) Significant excess of cervical cancer among woman compared to Maryland rates. But there was no evidence for a dose–response relationship. (high and low exposure groups) Two cases of biliary cancer were observed (1.4 expected) (all three exposure groups) there was an excess in ischaemic heart disease in comparison to Maryland rates, not in comparison to county rates No significantly elevated lung, pancreatic, liver/biliary cancers risks were observed.	Mortality study, 3211 workers Results of the study were compared to USA, Maryland and county mortality. The workers were not allowed to smoke on their workstations, this may have induced a negative bias in these studies particularly with respect to lung cancer or cardiovascular disease	Gibbs, 1992

Species	Duration/h(hours)/ d(days)	Route	Concentration	LC50/LD50/LOAEL/ NOAEL/Effects	Comments	Reference
Humans	Occupational exposure	Inhalation	Unknown	119 cases and 108 controls were classified as being potentially exposed to DCM. The risk was reported to increase with the probability of exposure and duration of employment. The result should be viewed with caution because the exposure information is weaker	Case-control study 300 cases with hospital diagnosis of astrocytic brain cancer and 320 control matched age, year of death an geographical area	Heineman et al., 1994
Sprague-Dawley Rats	6h/d, 5 /week for 2 years	Inhalation	0,1770, 5300 or 12400 mg/m ³	Increased CO-Hb levels, increase in benign mammary gland tumours and tumours in mid-cervical region		Burek et al., 1984
Sprague-Dawley rats	6h/d, 5d/week for 20, 24 months	Inhalation	0,177, 710, 1770 mg/m ³	No increase in incidence of benign mammary tumours in rats exposed to 177 or 710, increased incidence of benign mammary tumours in females at 1770 NOAEL 710 mg/m ³		Nitsche et al., 1988
Fischer-344 rats	6h/d, 5d/week for 102 weeks	Inhalation	0, 3500, 7100, 14100 mg/m ³	Dose-dependent increase in benign mammary tumours		NTP, 1986 Mennear et al., 1988
Sprague-Dawley rats	4h/day, 5d/week for 7 weeks then 7h/d, 5d/week for 97 weeks	Inhalation	350 mg/m ³	No statistically significant increase in total malignant tumours		Maltoni et al., 1988
B6C3F1 Mouse	6h/d, 5d/week up to 104 weeks	Inhalation	7100 mg/m ³	Mice exposed for more then a year showed an excess of lung and liver tumours		Kari et al., 1992
Syrian Golden Hamster	6h/d, 5 d/week for 2 years	Inhalation	0,1770, 5300, 12400 mg/m ³	No significant increase in incidence of benign tumours		Burek et al., 1984
Rats (Spragu1e- Dawley)	6h/d, 5d/week for 20 month (male) 24 months (female)	Inhalation	0, 177, 885, 1770 mg/m ³	Increase in number of benign mammary tumours/ tumour bearing female rat exposed to 1770. No effect on salivary gland tumours in males		Nitschke et al., 1982

Species	Duration/h(hours)/ d(days)	Route	Concentration	LC50/LD50/LOAEL/ NOAEL/Effects	Comments	Reference
Rat	2 years	Drinking water	0, 5, 50, 125 or 250 mg/kg bw/day	Treatment related histological alterations to the liver were evident at nominal doses of 50 mg/kg/day or higher. The low nominal dose of 5 mg/kg/day was the NOAEL	Note: may be the same study as of Serota et al., 1986	NCA, 1982, as cited in US EPA IRIS Substance File (1993)
Rat F344 male and female	104 weeks	Drinking water	0, 5, 50, 125 or 250 mg/kg bw/day	No increase in incidence of neoplasms. Survival and other findings not affected by DCM. Significant decrease in bodyweight gain at 125 and 250 mg/kg/day and evidence of liver damage at doses above 50 mg/kg/day		Serota et al. 1986
Rat F344 Male and Female	6h/d, 5d/week for 102 weeks	Inhalation	0, 3540, 7080, 14160 mg/m ³	Dose-dependent increase in benign mammary neoplasms		National toxicology Program (TR306)
Mouse B6C3F1, Male and Female	6h/d, 5d/week for 103 weeks	Inhalation	0, 7080, 14160 mg/m ³	Dose-dependent increase in alveolar/bronchiolar adenomas		National Toxicology Program (TR306)

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Appendix 4: A summary of the classification and (in)formal standards for DCM in different countries (IPCS, 1996; OECD, 1994; EPA substance file; RIVM, 1988)

Country	Occupational exposure		Occupational exposure Exposure general population		Max. Water conc. (μg/l)	Max. Air conc. (μg/m³)	Max. Soil Conc. (μg/kg)	Classification	Comments		
	8 hr TWA STEL (15 min		TEL 5 min)	Long- term	Short- term						
	Ppm	Mg/m ³	Ppm	mg/m ³							
Austria	100	350	-	-				240 (max ground level)		Potentially carcinogenic. Harmful with possible risk of irreversible effect Schedule 5 poisonous substance	In one state the TLV is lowered to 50 ppm (TWA). In the future DCM will be classified as a hazardous substance
Austria	100	360	500	1800			30 (dw)				Phase out of use a marketing of DCM. Max. level in water is the sum of 14 halogenated hydrocarbons incl. DCM
Belgium	50	174	-	-						Dangerous substance CEPA toxic (Canadian Environmental Protection act)	
Canada COSH	50	175	500	1740			50 (dw) 50 (sw)		1	Toxic substance suspected to be hazardous to the environment	
Czech republic	-	500	-	2500							
Denmark	50	174	-	-						Carcinogenic substance	
Finland	100	350	250	870			20 (dw)			Carcinogen third category	
France	50	174	500	1800							

Country	Occupational exposure		Occupational exposure Exposure general Max. Water population conc. (μg/l)		Occupational exposure Exposure general population			Max. Air conc. (µg/m³)	Max. Soil Conc. (μg/kg)	Classification	Comments
	8 hr	TWA	STEL (15 min)		Long- term	Short- term					
	Ppm	Mg/m ³	Ppm	mg/m ³							
Germany	100	360	500	1800			0.1 (dw)		50-250	Suspected being carcino- genic. Eye irritant, Skin irritant, Harmful to aquatic organism. May cause long-term adverse effects in the aquatic environment Possible risk of harm to the unborn child Avoid release to the environment	Max. air and soil level is total sum of highly volatile chlorinated hydrocarbons
Italy	50	174	-	-							
Japan	100	350	-	-			0.2 (dw) 0.2 (sw)		0.2		
The Netherlands	100	350	500	1750	Oral: 0.06 mg/kg bw/day Inhal- ation: 1.7 mg/m ³	Advice of RIVM to Ministry of Environ- ment: 7 mg/m ³	10 (dw)	20	0.05	No carcinogenic hazard to man, no mutagenic effects	The 24-h TWA and the 5- min STEL for the exposure limit for general population is based on a NOAEL of 173 mg/m ³ . A safety factor of 100 is assigned (RIVM, 1988)
Norway	35	125	500	1750						Harmful by inhalation Low potency carcinogenic	
Portugal	50	174	-	-							
Sweden	35	120	70	250				350		Low potency carcinogenic	Phase out of use an marketing of DCM

Country	Occupational exposure		Occupational exposure Exposure general population			e general Ilation	Max. Water conc. (μg/l)	Max. Air conc. (μg/m ³)	Max. Soil Conc. (μg/kg)	Classification	Comments
	8 hr	TWA	S ⁻ (15	TEL min)	Long- Short- term term						
	Ppm	Mg/m ³	Ppm	Mg/m ³							
Switzerland	100	360	500	1800			0.25 (dw) 0.05 (sw)			Poison class 4 (acute toxicity)	Max. water conc. is the sum of volatile halogenated compounds Maximum concentration in sw is measured as Cl
United Kingdom	100		300							No carcinogenic hazard to man No hazard to the environment	
United states OSHA EPA NIOSH CPSC ATSDR ACGIH	25 25 50	82 125 174	-	-	Oral Rfd: 0.06 mg/kg bw/day Inhalatio n 1.4 mg/m ³ (MRL)		0.05 (0 mg is goal)			Probable human carcinogen (group B2) Potential occupational carcinogen Possible human carcinogen Toxic substance	The NIOSH has set the IDL (immediately dangerous to life or health) level at 5000 ppm. The 24-h TWA and the 5- min STEL for the exposure for the general population is based on a NOAEL of 5.85 and 6.47 mg/kg bw/day. The LOAEL is 52.85 and 58.32 mg/kgbw/day. A safety factor of 100 and 1000 resp. is assigned
European commission										Harmful Carcinogen third category	

Dw= drinking water; Sw= surface water

Appendix 5: Overview of organisations contacted

Company or Organisation	Country	Remarks
General	*	
Data Shop Eurostat	Luxembourg	
European Chlorinated	Belgium	
Solvent Association (ECSA)		
Conseil Europeen de	Belgium	
L'indutrie Chimique (CEFIC)		
Euro Chlor	Belgium	
The Dutch Chemical	The Netherlands	
association (VNCI)		
DCM producers		
ICI Chemicals	UK	
AKZO NOBEL	The Netherlands	
Aragonesas Industrias	Spain	
Dow Europe	Switzerland	
Elf Atochem	France	
Erkimia	Spain	
LII Europe	Germany	
Solvay SA	Belgium	
Erkimia SA	Spain	
EniChem Spa	Italy	
Paint remover		
Conseil Européen des	Belgium	
Industries des Peintures,		
des Encres d'imprimerie et		
des Couleurs d'Art (CEPE)		
The Dutch society of paint	The Netherlands	
and ink producers (VVVF)		
Workers association of Real	The Netherlands	
estate maintenance		
Henkel	UK	
MEBO environmental	The Netherlands	
consultancy bureaus		
Consumentenbond	The Netherlands	
Fa. Hendriks	The Netherlands	
Fa. Gravenbaars	The Netherlands	

Adhesives		
Association of European Adhesives Manufactures (FEICA)	Germany	Through the FEICA several national members have been contacted.
Asociatcion Espanola de Fabricantes de Colas y Adhesivos (ASEFCA)	Spain	
The Dutch Adhesive Association (VNL)	The Netherlands	Have contacted its members
Central union of Furniture producers (CBM)	The Netherlands	
SABA	The Netherlands	
Ato Findley (Int)	The Netherlands	
Scholten lijmen	The Netherlands	
Turco adhesives	The Netherlands	
Several furniture &	The Netherlands	
mattresses producing		
companies		
Aerosols		
European Aerosol	Belgium	Through the EEA we have contacted
Ederation (FEA)	Deigidin	several national members
		(Osterreichische Aerosol Vereingung.
		Asociation Belge Des Aerosols.
		Aerosol industriens Brancheforening
		(DK), Finnish Aerosol Association,
		Comite Francais Des Aerosol,
		Industrie Gemeinschaft Aerosole E.V.,
		Aerosol, Associazione Italiane Aerosol,
		Associacao Portuguesa De Aerosols,
		Asociacion Espanola De Aerosoles,
		Swedisch Aerosol Vereniging, British
		Aerosol Manufacturers Association)
Dutch Aerosol Associations	The Netherlands	
(NAV)		
Bayer Agro (Int)	The Netherlands	
Beiersdorf AG	Germany	
TROST Group	The Netherlands	
BASF	Germany	
Eurofill	The Netherlands	
Overloop gewas – en	The Netherlands	
beschermingsmiddelen		