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INTEGRATED CRITERIA DOCUMENT DICHLOROMETHANE

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SUMMARY

This document contains data on sources and distribution patterns (soil, water, air, biota) of dichloromethane (DCM), on risks considering its concentrations in the environment and the exposure routes on the one hand and its harmful levels for man, ecosystems and materials on the other, and the technical possibilities and business economic consequences with regard to reduction of these risks. Based on these data, several possible policy scenarios have been worked out. This information serves as a scientific basis for the formulation of the effect-oriented standard setting policy.

Because of its considerable solubility and its low boiling point, DCM is widely used. In 1984 almost 7,000 tons were emitted into the environment in The Netherlands, for the greater part into the air (> 97%). Industrial and diffuse sources contribute equally. The major industrial sources are the chemical and pharmaceutical industries. DCM is distributed diffusely by the use of spray-cans and paint strippers.

The average concentrations, which may be calculated on the basis of the emissions mentioned and which were measured in the same order of magnitude, neither pose a threat to man nor to ecosystems. DCM is considered non-carcinogenic for experimental animals. Insufficient data are available to assess its carcinogenicity for man.
A safe value of 1.7 $mg.m^{-3}$ for air is determined on the basis of no-effect levels in chronic rat experiments, with a safety factor of 100. The annual average, nationwide, is approximately 0.6 $\mu g.m^{-3}$. For aquatic ecosystems a similar difference is observed between the value considered acceptable, 0.5 $mg.l^{-1}$, and the annual average, nationwide, of less than 5 $\mu g.l^{-1}$. It is assumed that the current exposure levels do not pose a threat to terrestric ecosystems either.

Locally a few problems may arise, however. It may be possible that people are exposed to slightly higher concentrations than 1.7 $mg.m^{-3}$ per 24 hours. Measures are possible, costing less than Dfl. 30.- per kg DCM removed, which, it is expected, will result in concentrations exceeding the safe value in at most 2 or 3 localities and during only a few days per year.
Industrial discharges may also lead to (incidentally) high concentrations in water. Preventive measures are also available in these circumstances.

Furthermore, people, when using spray-cans with DCM or paint stripper (also in the working environment) are exposed for short periods to values, which, depending on the ventilation, may increase to many hundreds of $mg.m^{-3}$ as a 5 minutes average. This may be tested by a value derived from the 24-hour value. The entire intake over 24 hours being concentrated in 5 minutes, it would result in 490 $mg.m^{-3}$. Here, a certain risk is involved. Although there are substitutes for DCM in spray-cans, there is still little known about their applications.

INTRODUCTION

The environmental policy in The Netherlands is in the first place aimed at achieving and maintaining an environmental quality, which guarantees the health and well-being of people and the preservation of animals, plants, goods and patterns of utilization in a general sense (IMP Milieubeheer 1986 - 1990). Adequate knowledge lacking it will, however, not be possible for some time to fully define the general environmental quality aimed at. Therefore, attention is concentrated first on factors which may present great risks, such as substances hazardous to the environment. A selection has been made of the many substances that are important because of emission or usage and a priority list has been drawn up. For most priority substances socalled Integrated Criteria Documents are written.

Arranged by substances or groups of substances, Integrated Criteria Documents contain data on sources and distribution patterns (soil, water, air, biota), the risks of present concentrations for man, (parts of) ecosystems and materials, and the technical and economical possibilities of reducing these risks. This information serves as a scientific basis for the formulation of the effect-oriented environmental policy. Environmental quality requirements and a general term of reference for the emission reductions per type of source may result from this.

Dichloromethane (DCM) deserves further attention in view of its widespread applications as a solvent and cleaning agent and also because of the fact that it is emitted at a large scale.

The document is drawn up by the National Institue of Public Health and Environmental Protection (RIVM). The Dutch Organization for Applied Scientific Research (TNO) and the Institute for Environmental Problems (IvM) have contributed to this document.

For various sections, such as control techniques and the costs involved, valuable information has been obtained from several chemical concerns and other companies. The appreciated co-operation has been obtained through the Department of the Environment and Environmental Planning of the Council of the Dutch Employers' Unions VNO and NSW.

The content of this document has been checked by a Review Committee of the RIVM. Support in the preparation of this document was rendered by a Counselling group consisting of staff members of the Ministry of Public

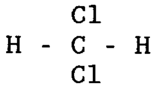
Housing, Physical Planning and the Environment (VROM), the Department of Inland Waterways (DBW/RIZA) and the Ministry of Agriculture and Fisheries (L&V).

The deliberate aim was to keep this document as concise as possible. As a result considerable background information, although useful, has not been included. Such information has been recorded, however, in reports dealing with emissions and emission reduction (not publicly), effects as well as business economic consequences.

1. PROPERTIES AND EXISTING STANDARDS

1.1. PROPERTIES

1.1.1. Structural formula and molecular formula



$$\begin{matrix} & Cl & \\ H - & C & - H \\ & Cl & \end{matrix}$$

CH_2CL_2

1.1.2. Registration numbers

Chemical Abstracts Service (CAS) registration number: 75-09-2 (000075092). Registry of Toxic Effects of Chemical Substances (RTECS) registration number: PA 8050000.

1.1.3. Nomenclature and synonyms (Hommel, 1980)

Dutch nomenclature: dichloormethaan, methyleenchloride (KNCV, 1977). IUPAC name: dichloromethane.

German	English	French
Dichlormethan	Dichloromethane	Dichlorométhane
Chlormethylchlorid	Methane dichloride	Chlorure de méthylène
Methylenbichlorid	Methylene bichloride	
Methylenchlorid	Methylene chloride	
Methylendichlorid	Methylene dichloride	
Methylenum chloratum	Solaesthin	

1.1.4. Physical properties (Kirk-Othmer, 1978; Solvay, 1985)

1 $mg.m^{-3}$ = 0.28 ppm (20°C, 101.3 kPa) (Verschueren, 1977)
1 ppm = 3.57 $mg.m^{-3}$
molecular weight : 84.92
boiling point : 39.8
freezing point (101.3 kPa), °C : -96.7
density (20°C), $kg.m^{-3}$: 1315.7
vapour pressure (20°C), kPa : 46.5
(10°C), kPa : 31

refractive index (20°C) : 1.4244
viscosity (20°C), mPa.S : 0.43
surface tension (20°C), N.m^{-1} : 0.02812
evaporation heat (20°C), kJ.kg^{-1} : 329.23
combustion heat, MJ.kg^{-1} : 7.1175
critical density, kg.m^{-3} : 472
critical temperature, °C : 245
critical pressure, MPa : 6.171
solubility in water (20°C), g.kg^{-1} : 13.2
(10°C), g.kg^{-1} : 14.4
water solubility in DCM (20°C), g.kg^{-1} : 1.4
n-octanol-water partition coefficient
(20°C) : log K_{OW} = 1.25 (EPA, 1982)
Henry constant (10°C) : 0.08
(25°C) : 0.13

Dichloromethane (DCM) is a clear, colourless, volatile liquid with a slight etherical smell. Although it is only slithtly soluble in water, the substance is completely mixable with other chlorinated solvents, diethyl ether and ethyl alcohol. DCM is an excellent solvent for resins, (paraffin) waxes and fats. Because of this property the substance is applied in industry on a large scale.

1.1.5. <u>Chemical properties</u> (Kirk-Othmer, 1978)

DCM is a relatively stable organic chlorine compound with an initial thermic decomposition temperature in dry air of 120°C. For higher moisture contents the decomposition temperature is lower. Hydrochloric acid and, to a lesser degree, phosgene are formed as decomposition products. Degradation may be prevented by adding traces of phenol, hydrochinon, p-cresol or resorcinol.

Stability is also increased by adding small quantities of amines or a mixture of nitromethane and 1,4-dioxane.

During long-term contact with water DCM hydrolyzes slowly, forming hydrochloric acid as a primary product. Heating at 140-170°C, during a longer period, in a closed vessel in the presence of water, leads to the formation of formaldehyde and hydrochloric acid. At 180°C formic acid, chloromethane, methanol, hydrochloric acid and carbon monoxide is formed.

Under normal conditions, anhydrous DCM does not react with metals. However, addition of small quantities of other halogenated solvents or aromatic solvents may initiate a reaction with aluminium. Iron catalyzes this reaction, which is important in storage, transfer and product formulations (e.g. aerosols in aluminium containers).

In the gas phase DCM reacts with nitrogen dioxide at 270°C forming a gas mixture with carbon monoxide, nitrogen monoxide and hydrochloric acid being the major products. The corresponding reaction with chloroform produces phosgene.

DCM is easily reduced to chloromethane and methane by alkali metal-ammonium compounds in liquid ammonia. When the vapour is led over reduced nickel at 200°C in the presence of an excess of hydrogen, hydrochloric acid and elementary carbon is formed. Heating with alcoholic ammonia at 100-125°C results in hexamethylene tetramine, a heterocyclic compound. With aqueous ammonia at 200°C hydrochloric acid, formic acid and methylamine are formed.

In the presence of chlorinating catalysts DCM may be chlorinated to chloroform and carbon tetrachloride. Bromochloromethane is produced by reaction of an excess of a mixture of DCM and bromine with aluminium at 26-30°C.

1.1.6. Storage and transport

Because of its low boiling point (40°C), DCM should be stored in a cool place away from direct sunlight. Storage containers may be constructed of galvanized or differently coated sheet metal.

It is not advisable to use alumium for bulk storage. Bulk storage reservoirs should be provided with a dryer packed with a drying agent like calciumchloride in order to prevent moisture absorption. Dry, inert gas with a degasing valve may also be used.

DCM is transported in drums, by lorry, rail, flat-bottomed boats or seaworthy vessels. The International Regulations on Railtransported Dangerous Goods, the European Agreement concerning Roadtransported Dangerous Goods, the Regulations on Rhine-transported Dangerous Substances and the Intergovernmental Advisory Maritime Organization place DCM in class of risk 6.1. Each organization specifies the measures to be applied and labels to be used in storing and transporting this substance. DCM is liable for labelling under AGS.

1.2. EXISTING STANDARDS AND GUIDELINES

1.2.1. Soil

For the evaluation of the concentration levels in the soil a testing frame is given in the "Leidraad Bodemsanering" (VROM, 1983). The concentrations mentioned are not to be considered standards, but a frame for assessment; the concentrations are to be considered in connection with the utilization of the soil and the local pollution situation (see table 1.1. and 1.2.).

Table 1.1. *Framework for the evaluation of the concentration levels of alifatic chlorinated hydrocarbons in soil and sludge (VROM, 1983) in* $mg.kg^{-1}$ *dry substance*
A= reference value, B= trigger value for further inquiry and C= trigger value for research on sanitation

Component	*A*	*B*	*C*
Individual alif. hydrocarbons	*0.1*	*5*	*50*
Total alif. hydrocarbons	*0.1*	*7*	*70*

Table 1.2. *Testing frame for the evaluation of the concentration levels of alifatic chlorinated hydrocarbons in groundwater in* $\mu g.l^{-1}$ *(see table 1.1. for explanation)*

Component	*A*	*B*	*C*
Individual alif. hydrocarbons	*1*	*10*	*50*
Total alif. hydrocarbons	*1*	*15*	*70*

1.2.2. Surface water

For the basic quality of surface water (IMP 1985-1989, 1985) the median value for volatile halogen compounds is VOX < 5 $\mu g.l^{-1}$ (as for chlorine). The EPA has formulated criteria for halogenated methanes in surface water and in organisms, used for human consumption, inhabiting it. Assuming a life-time exposure, concentration levels are presented for various risk estimates.

1.2.3. Air

Table 1.3. Quality of the air at work places: MAC-values (8-hour time weighted averages (TWA) in $mg.m^{-3}$

Country	*Conc.*	*Remarks*	*References*
The Netherlands	*350*		*Nat. MAC list (1986)*
USA	*350*	*- ACGIH, 1985*	*IARC (1986)*
	1740	*15 min. TWA*	
	261	*- NIOSH, 1985*	
	1740	*max. value*	
	1750	*- OSHA, 1985*	
	3500	*max. value*	
	7000	*15 min. TWA*	
West Germany	*350*		*Deutsche Forsch. Gemeinschaft (1981)*
East Germany	*500*		*ACGIH (1981)*
	1500	*15 min. TWA*	
Rumania	*500*		*ACGIH (1981)*
	700	*max. value*	
Yugoslavia	*500*		*ACGIH (1981)*
Czechoslovakia	*500*		*ACGIH (1981)*
Sweden	*250*	*1984*	*IARC (1986)*
	500	*max. value*	
USSR	*50*		*ACGIH (1981)*

Table 1.4. *Air quality standards for outdoor air in mg.m^{-3} (IDC, 1977)*

Country/Province	*Concentration*	*Remarks*
West Germany	*20*	*annual average*
	50	*daily average*
	150	*1/2-hour average*

1.2.4. Food and drinking water

In The Netherlands there are no limit values for DCM-residues in foodstuffs. However, DCM is prohibited for the fumigation of products. The following limit values are in force abroad: 5 mg.kg^{-1} (Belgium) and 10 mg-.kg^{-1} (USA) in decaffeinated coffee and 30 mg.kg^{-1} (total solvents) for herb extracts (USA) (Staarink and Hakkenbrak, 1985). The Scientific Comittee of the EC proposed a tentative limit value of 10 mg.kg^{-1} for foodstuffs (Staarink and Hakkenbrak, 1982).

In drinking water in The Netherlands the value for halogenated hydrocarbons (except pesticides), 1 μg.l^{-1} per individual compound (EEC, 1980), may only be exceeded in particular cases, as described in the Water Board Resolution (1984).

2. PRODUCTION, APPLICATIONS, SOURCES AND EMISSIONS

2.1. APPLICATIONS

Most applications of DCM are based on its considerable solubility and its low boiling point. The main applications are:

- solvent in spray cans
- in paint stripper
- in varnish stripper
- degreaser in surface treatment (metals)
- extracting agent (foodstuff industry)
- solvent/reaction medium in the chemical/pharmaceutical industry
- cleaner in the synthetics processing (polyester, polyurethane)
- in the production of fibres
- in the surface treatment of synthetics
- solvent for lacquers and glues

2.2. PRODUCTION

The world production of DCM in 1980 amounted to appr. 570 tons, of which the United States and Western Europe each produced almost half (SRI, 1982; Edwards et al., 1982). A recent study of the EPA shows that the production in the United States has scarcely increased since (EPA, 1985). The world production for 1984 is estimated at appr. 600 ktons, of which 270 ktons produced in the United States, 230 ktons in Europe and appr. 100 ktons in other countries. A very slight increase in the world production is expected.

In table 2.1. data on the capacity of the West European countries are presented, as per 1 January 1982 (SRI, 1982).

For The Netherlands a production capacity of 15 ktons per year is given. This may, however, be slightly adjusted to the demand; in the installations concerned DCM and chloroform are manufactured (27 ktons per year in total). It is evident, from applications for environmental permits, that the total capacity in the future will be extended to 47 ktons per year. The proportion between DCM and chloroform produced may be varied.

Table 2.1. Production capacities in Western Europe (SRI, 1982)

Country	*Number of plants '82*	*Total capacity 1982*	*(Ktons per year) 1985*
West Germany	*3*	*153*	*183*
Italy	*2*	*23*	*12*
The Netherlands	*1*	*15*	*15*
Belgium	*1*	*16*	*16*
France	*2*	*67*	*67*
Spain	*1*	*14*	*12*
Great Britain	*1*	*100*	*100*

A mass balance for The Netherlands has been made up (fig. 2.1.) on the basis of:

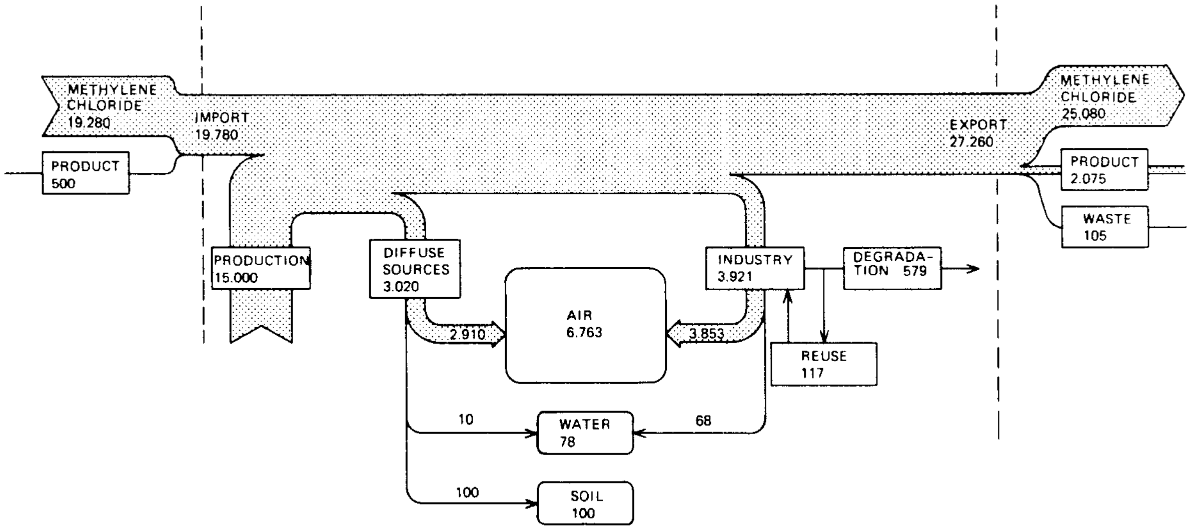
- information on the production capacity
- the import and export of DCM (CBS, 1984)
- information on the quantities processed in various products provided by industrial organizations (SRI, 1984)
- a revies of the emission into air and water
- waste obtained from industrial plants
- supplemented with data from registration systems (emissieregistratie 1974-1979; Meldingenbestand chemisch afval, 1985) and information on diffuse source (Feenstra and Van der Most, 1985).

It should be noted that the inaccuracy in the quantities of DCM, which are imported or exported with products, is as much as 30%. No accurate data are available on production either. Therefore the above-mentioned capacity data are used.

It is not possible therefore to use this balance to determine the emission into the environment from the difference between production and import on the one hand and the total export on the other. However, the various data obtained independently appeared to be mutually consistent to the extent that the order of magnitude could be confirmed. The balance was finally equalized by adjusting the figure for the export of DCM in products (by appr. 5%).

For the import and export in products, aerosols, paint strippers and glues are relevant. The import of DCM with aerosols, however, is negligible. It is estimated that, in The Netherlands, 3,000 tons was put in spray cans in 1984, of which only one third was actually used in The Netherlands. This is presented in the mass balance as emission into air. For paint strippers a use of 2,000 tons is assumed. Various authors have postulated that this use may be higher. Quite insignificant in comparison, import and export are estimated at 300 tons and 70 tons, respectively. Finally, the use of glue, with DCM as a solvent, results in slight diffuse losses. The import is estimated at 200 tons, of which 10% is used by private individuals.

Fig. 2.1. Mass balance of dichloromethane in The Netherlands in 1984 (in tons per year), trans-frontier emissions excluded



2.3. SOURCES AND EMISSIONS

2.3.1. Industrial and diffuse sources

A summary is presented in 2.2. The contribution to the total emission into the environment varies considerably among the various applications. In table 2.2. a summary is given of the emission per industrial activity, while the diffuse sources are given in table 2.3.

Table 2.2. Summary of the emission into the environment by industrial activities in The Netherlands in 1984

Activity	*Number of plants**	*Emission (tons per year)*		
		Total	*Air*	*Water*
Chemical industry	*7*	*1,332*	*1,317*	*15*
Pharmaceutical industry	*5*	*1,106*	*1,065*	*41*
Electrotechnical industry	*9*	*385*	*385*	
Synthetics processing	*16*	*341*	*341*	
Paint and lacquer industry	*8*	*192*	*192*	
Production aerosols	*3*	*38*	*38*	
Storage and transfer	*1*	*42*	*42*	
Other	*8*	*485*	*473*	*12*
Total		*3,921*	*3,853*	*68*

** Additional smaller plants contribute less than 5 tons per activity per year to the emission*

The emission per source (plant) varies from a few kg to more than 800 tons. This will be discussed further in chapter 7.

Table 2.3. Summary of the emission into the environment from diffuse sources in The Netherlands in 1984

Source	*Emission (tons per year)*			
	Total	*Air*	*Water*	*Soil*
Paint stripper	*2,000*	*1,890*	*10*	*100*
Spray cans	*1,000*	*1,000*		
Glue	*20*	*20*		
Total	*3,020*	*2,910*	*10*	*100*

2.3.2. Emissions into soil

Of the DCM discharged with domestic waste water, which does not pass a sewage water treatment plant, an estimate of 1 ton per year is emitted into the soil. Little or none is found in sewage sludge. It has not been determined to what extent DCM, used by private individuals, passes straight into the soil. It is likely, however, that, with the use of paint strippers, this emission is not to be neglected. A load of 100 tons per year from this source is postulated in the mass balance. In only 1% of the soil reconstruction cases known from 1983, DCM was present.

Emissions into the soil by industry are rare. Deliberate emissions into the soil have not been observed. Recent research shows that DCM may be formed by percolation of chlorinated water through the soil under anaerobic conditions at low water temperatures (Hrubec, 1986).

2.3.3. Emissions into water

A mass balance of a process or plant gives little information on the load discharged, the quantity of DCM, which is discharged by a plant, being only a fraction of the emission into the air. Therefore, measurements are necessary. A study was carried out by the RIZA and the data obtained were incorporated (Van Luin and Van Starkenburg, 1982).

As in most cases no measurements were carried out, estimates based on a solid understanding of the process need to be used. The data are therefore fairly inaccurate. In comparing measured values with estimates based on process data (also done by the companies concerned), the latter tend to be higher.

In table 2.2. a summary is given of the data divided into the various branches of industry. In a number of cases waste water is treated in biological treatment plants (anaerobic and aerobic), the efficiencies of which have not been determined in all instances. In the above-mentioned RIZA report an efficiency of 95% is mentioned for one aerobic cleaning. In sewage water treatment plants 19 to 99% DCM is removed, as stated by a later publication (DBW/RIZA, 1985), the highest values being attained at considerably high and constant influent concentrations. The removal is probably carried out mainly by stripping of DCM during aeration. Occasional influent and effluent concentrations of several hundreds of $mg.l^{-1}$ were observed during this study.

The loads reported, which are passed into water, are those after treatment (also in the instance of a sewage water treatment plant).

For the determination of DCM in domestic water an emission factor may be used. Until recently a value of 24.6 g per inhabitant per year was used (Feenstra and Van der Most, 1985). Recent measurements show, that this value is more likely te be 2 g per inhabitant per year (DBW/RIZA, 1985). It originates mainly from paint strippers, of which an estimate of 10 tons per year is eventually emitted into the water. An insignificant amount passes into the soil and is decomposed. The remainder is lost into the air.

2.3.4. Emissions into air

- Industrial emissions

Various industrial sources may be distinguished:

* production process emissions (2095 tons), which mainly occur when DCM is used as a solvent in processes or is processed in products,
* emissions resulting from cleaning processes, degreasing, varnish stripping or cleaning of appliances (953 tons),
* losses during reloading of DCM and losses through leakage and evaporation in pumps and valves (323 tons),
* undetermined and other emissions e.g. losses which occur during aerating in water treatment plants (383 tons).

The division over these four types of sources may only slightly reflect the actual division, as, in a great number of plants, it is not well possible to distinguish the emission sources.

In table 2.4. the emissions into air are presented, broken down by the sources mentioned and the main branches of industry. In the chemical and pharmaceutical industry DCM is mainly used as a solvent and as a reaction medium. Most processes in the (bulk) chemistry are continuous, whereas the preparation of pharmaceutical products is carried out batchwise. The product needs to be separated from the reaction medium and especially during this separation losses occur, despite the fact that the equipment is kept closed as much as possible.

During the processing of DCM in products such as paint strippers and spray cans a slight proportion may be vented into the air through ventilators or it may pass into the air during destruction of rejected spray cans.

Further process emissions also may occur during surface treatment of synthetic foil as well as during extraction in the foodstuff industry. In all branches of industry mentioned above, part of the total emission may be attributed to vent and dislodgment losses or leakage of pumps and valves. These also occur during the production of DCM.

Table 2.4. Summary of the emissions of dichloromethane into the air from industrial sources (in tons per year) in The Netherlands in 1984

Branch of industry	*Total*	*Production processes*	*Cleaning*	*Loading leakage*	*Remainder unknown*
Chemical industry	*1,317*	*745*		*228*	*344*
Pharmaceutical industry	*1,065*	*950*		*30*	*85*
Electrotechnical industry	*385*	*10*	*373*		*2*
Synthetics processing	*341*	*93*	*229*		*19*
Paint and lacquer industry	*192*	*187*		*5*	
Production aerosols	*38*	*25*		*10*	*3*
Storage and transfer	*42*			*42*	
Other	*473*	*85*	*351*	*8*	*29*
Total	*3,853*	*2,059*	*953*	*323*	*482*

Emissions as a result of cleaning processes occur in various branches of industry. In the electrotechnical industry it is part of the processing. In the production of printing plates it is used as a photo-resist stripper. In the synthetics processing, particularly plants producing polyester products, it is used for the cleaning of spray heads. DCM is very effective as a varnish stripper and is used as such in various plants (also for private individuals).
In most plants it was possible to derive the emission from the amount of DCM purchased. Only in a few instances it was possible to use the results of measurements. Losses during loading were mainly calculated. In a few cases emission factors were used for the losses through valves and pumps. In the formulation of paint strippers, the emissions, if not determined, were estimated at 5 to 10% of the amount of DCM processed. This value is based on rather dated observations, and it may be slightly lower at present.

- Non-industrial emissions

Diffuse emissions are of importance as well, as is apparent from table 2.3. When spray cans are used, practically all the DCM present (up to 35 weight %) is emitted into the air. Because of the high volatility of DCM a considerable amount of paint stripper (DCM-content 50-85 weight %; Cohen et al., 1980; Otson et al., 1981) ends in the air, whereas an insignificant amount passes into domestic waste water (see fig. 2.1.).

2.3.5. Dichloromethane in waste

A large number of plants that use DCM have waste flows in which DCM is present. An insignificant amount finds its way into other countries. The possibilities for processing in The Netherlands are incineration at sea, incineration on land and distillation. In some cases the waste producer takes back the distilled product, in other cases it is put on the market by the processing company. In table 2.5. a summary is given of waste flows per industrial activity. The greater part of it is incinerated. It is apparent that regeneration often poses practical problems. Reasons are: the composition of the contaminated product, which renders the processing more difficult, and the fact that many companies (need to) prefer a new product for qualitative reasons.

During incineration DCM is destroyed, but is partly converted into HCl.

Table 2.5. Summary of quantities of dichloromethane in industrial waste (in tons per year) in The Netherlands in 1984

Industrial	*Total*	*Load DCM in waste with processing method*		
		Incineration	*Distillation*	*Export*
Chemical industry	*103*	*38*	-	*65*
Pharmaceutical industry	*270*	*230*	-	*40*
Electrotechnical industry	*99*	*58*	*41*	-
Synthetics processing	*69*	*63*	*6*	-
Paint and lacquer industry	-	-	-	-
Production aerosols	*10*	*10*	-	-
*Storage and transfer**	-	-	-	-
Other	*194*	*124*	*70*	-
Total	*745*	*523*	*117*	*105*

** remains of load not determined*

2.3.6. Expectations for the near future

The use and consumption of DCM is considerably stable at the moment. For most major applications there is no distinct alternative and no reason to switch over to an alternative either. For a number of processes the companies concerned expect that DCM, or the entire process in which it is used, will be substituted in the near future. However, it is expected that a number of new processes, in which DCM is used, will be introduced.

2.4. INFLUENCE FROM ABROAD

It is to be expected that DCM from abroad will find its way into The Netherlands particularly through the air (see section 3.3.). As the emission takes place in a great variety of activities, it is realistic to assume an emission rate per inhabitant for the countries surrounding The Netherlands.

The emissions in The Netherlands is appr. 0.45 kg per inhabitant per year. This factor is roughly the same in the surrounding countries. Few data are available on the loads in water, such as the large rivers. They are probably slight.

2.5. SUMMARY AND CONCLUSIONS

Because of its considerable solubility and its low boiling point, DCM is widely used. In 1984 the world production amounted to appr. 600 ktons, of which 230 ktons was produced in Europe and 15 ktons in The Netherlands. For a mass balance reference is made to fig. 2.1. In The Netherlands a total of 6,940 tons was emitted into the environment, of which the greater part (> 97%) into the air. Industrial and diffuse sources contribute equally. The main industrial sources are the chemical and pharmaceutical industries (> 60%), the main diffuse sources being paint strippers and spray cans. As yet, a clear-out trend in the use and consumption of DCM cannot be ascertained.

3. DISTRIBUTION AND TRANSFORMATION

3.1. BEHAVIOUR IN SOIL

3.1.1. Distribution

The extent of adsorption of DCM in soil may be worked out on the basis of the adsorption coefficient k_d. Calculations may be as follows (Giger et al., 1983): $\log k_d = 0.72 \log K_{ow} + 0.5$, in which K_{ow} is a standard for the lipophilous characteristics of the substance (for DCM $\log K_{ow} = 1.25$) and f_{oc} the content of organic carbon in the soil (assumed to be 1%). This results in a value of 0.25 for k_d, showing that the adsorption will be very slight (Zoeteman et al., 1981; Matthess, 1983).

Because the solubility of DCM in water is 1 to 2% and its density and vapour pressure are high (see section 1.1.), the substance can dissolve in humid soil and be integrated in the hydrologic cycle. During infiltration of surface water DCM will reach the groundwater practically inhindered, because of its limited retention in soil (EPA, 1985). If concentrations are low, distribution in groundwater occurs according to the laws of groundwater flow (see dispersion models: van Duijvenbooden et al., 1981; Matthess, 1984). If concentrations are high, an increased flow downwards may occur (density flow; Kruijtzer, 1980). The liquid will gather at the bottom of the water bearing layer, while on the way down some DCM will dissolve and some horizontal transport and diffusion will take place (Schwille, 1984). In one case a horizontal distribution of appr. 200 m was mentioned, however, without any hydrologic foundations having been given (Baldauf, 1981). Engesser (1983) states, however, that no distribution has taken place near another pollution source; DCM disappears after a short transport period. This difference may be explained by the fact that biological decomposition may or may not occur (toxicity: see 3.1.2.).

Depending on the DCM concentration in surface water, the substance will penetrate the soil and the groundwater during artificial infiltration and bank infiltration (Schwarzenbach et al., 1983). A few data concerning artificial infiltration, using treated waste water, are presented by Nellor et al. (1985): in lysimeter experiments the DCM concentration decreased by appr. 90% over 2.5 m (from 18 to 1.9 $\mu g.l^{-1}$), probably mainly as a result of aerobic, microbic decomposition. Considerable decrease in DCM concentrations also occurs in other experiments on filtration of waste water. With regard to air in soil it may be stated that evaporation from groundwater will be limited (Giger et al., 1983). In soil which is well pervious DCM vapour will sink rapidly; in the unsaturated zone a considerable amount of vapour will be retained in the granular structure. Concentrations of chlorinated hydrocarbons are generally higher in air stored or trapped in soil than in the atmospheric air (Neumayer, 1983).

3.1.2. Transformation

The main decomposition process in soil is biodegradation. Considerable experimental research has been carried out (table 3.1.); field research is hardly possible because of lack of conditions of equilibrium. It was concluded that the process depends among other things on the acidity, the Cl-concentration and the temperature of the groundwater. Furthermore the micro-organisms in the soil generally need a considerable time for adaptation before the decomposition process gets fully started. A great number of experiments were carried out at room temperature rather than soil temperature (appr. 10^oC). The decomposition process stops at DCM-contents of more than 430-1800 $mg.l^{-1}$ (Stucki, 1982). It has not been studied to what extent this decomposition will occur in natural soil under continuously varying conditions. An indication is, however, that no extensive distribution of DCM has so far been found in soil. It may be concluded that DCM, dissolved in water, at concentrations which are not too high (< 430 $mg.l^{-1}$), will be rapidly decomposed microbiologically after an acclimatization period of appr. 1 week, under aerobic as well as anaerobic conditions and usually through co-metabolic processes (the half-life is estimated at a few weeks to several months).

3.2. BEHAVIOUR IN SURFACE WATER

Documents on DCM have recently been published by the WHO (1984) as well as by the EPA (1985). In the Environmental Health Criteria Document (WHO, 1984) the following summary for the behaviour in surface water is given: "In surface water, volatilization is the major process of removal, hydrolysis and photodegradation being insignificant. The solvent is readily biodegradable aerobically." This conclusion is consistent with further data presented below.

Table 3.1. Experimental data concerning decomposition (and sorption) of dichloromethane in soil

Initial concentr. (mg.l^{-1})	Acclimatization	Final concentration (mg.l^{-1})	Species of bacteria	Reference	Remarks
1.8-3.7	-	n.d.*		Stucky et al., 1980	anaerobic
25	-	1	-	Rittman et al., 1980	anaerobic, sorption
< 430	8	n.d.	Pseudomonas DM 1	Brunner et al., 1980	sorption aerobic pr.
-	-	-	Hyphomicrobium	Stucky et al., 1981	aerobic pr.
				Brunner et al., 1980	sorption
50	-	after 6 h. 4	Actinobacter Alcaligenes, Flaviobacterium Rhodotorula	Davis et al., 1981	
5-10	< 7	4 days, n.d.		Tabak et al., 1981	
appr. 1100	4	appr. 100	Pseudomonas, Agrobacter, Arthrobacter	Jahveri and Mazzaca, 1983	aerobic pr. probably co-metabolism
< 10	1-3	5-20% in a few hours	Pseudomonas LP	LaPat-Polasko et al., 1984	co-metab. sorption
0.018	-	after 2 1/2 m infiltration 0.002	-	Nellor et al., 1985	probably aerobic
1.10 and 100	-	after 9-11 days continuously	-	Klecka, 1982 Rittman et al. 1980	acclimatization nec. aerobic pr.
132	5	n.d.	-	Halbert-Schlager et al., 1984	

* n.d. = not demonstrable

3.2.1. Distribution

The Henry constant amounts to 0.13 at 25°C and 0.08 at 10°C; the half-life for evaporation to the air (containing no DCM) is therefore 3 hours per meter water depth (Lyman et al., 1982). In air containing DCM the half-life is longer and is considerably influenced by water movement, wind and the like. Adsorption to particles is slight (see 3.1.). Sherb (1978) found a half-life of 1.07 hour (depth of water 0.3 m).

3.2.2. Transformation

- Abiotic transformations

Hydrolysis of DCM is expected to be an extremely slow process. The half-life by hydrolysis at pH=7 and at 25°C is estimated at 700 years (EPA, 1979).

Absorption of sunlight by surface water may result in the transformation of DCM by OH-radicals and hydrated electrons (e^-_{aq}). The rate constant for reaction with e^- is estimated at $5x10^9$ $m^{-1}.s^{-1}$ based on data for chloroform and 1-chlorobutane (Ambar and Neta, 1967). Recent measurements of the near surface steady state concentrations of hydrated electrons indicate a concentration of $5x10^{-17}$ M as an annual average for The Netherlands (Breugen et al., 1986). The pseudo-first order reaction constant of this process amounts to $25x10^{-8}$ s^{-1}; the half-life appr. 33 days.

The rate constant for reaction with $OH^\bullet$ is estimated at $6x10^{-7}$ $M^{-1}.s^{-1}$ (section 4), assuming it to be equal to that in air (Klöpffer, 1980). The near surface concentration of $[OH^\bullet]$ is 4.10^{-16} M (Mill et al., 1980; Russie et al., 1982; Hoigné et al., 1985). The pseudo-first order reaction constant of this process amounts to $24x10^{-9}$ s^{-1}. The half-life is appr. 400 days.

The e^-_{aq} is responsible for 90% of the transformation. Reaction products are probably formaldehyde and hydrochloric acid.

The total rate constant for the sunlight-induced transformation in surface water with a depth of 2.5 m, a DOC-content of 4 $mg.l^{-1}$, a chlorophyll-a content of 10 $\mu g.l^{-1}$ and a suspended matter content of 40 $mg.l^{-1}$ will be $2.8x10^{-5}$ day^{-1} (half-life 68 years). The $OH^\bullet$ causes 90% of the transformation.

- Biotic transformation

After adaptation, DCM was dehalogenated to carbon dioxide and chloride by aerobic micro-organisms obtained from active sludge from a domestic waste water treatment plant and by a Pseudomonas species, at concentrations of below 425 $mg.l^{-1}$ (Brumer et al., 1980; Rittman et al., 1980). The substance was toxic for the process at concentrations higher than 1,000 $mg.l^{-1}$ (Klecka, 1982). This proves that DCM is biodegradable in water. The half-life in surface water is estimated at a few weeks to a few months.

3.3. BEHAVIOUR IN AIR

3.3.1. Distribution

In the calculation of DCM concentrations (at ground level) in The Netherlands a distinction is made between:

- distribution on a national scale (maximum area diameter a few hundreds of kilometres)
- distribution on a regional scale (near industrial point sources; maximum area diameter a few dozens of kilometres)

- Distribution on a national scale

In 1984 the emission of DCM into the air in The Netherlands amounted to more than 6,600 tons (appr. 3,750 tons from industrial sources and 2,900 tons from diffuse sources, see fig. 2.1.). From large-scale calculations (Van Egmond and Huygen, 1979) it may be concluded that these sources contribute 0.33 $\mu g.m^{-3}$ to the DCM concentration on a national scale. The contribution of sources outside The Netherlands was estimated, assuming a characteristic residence time of half a year ($1.58x10^7$ s). The emission from Belgium and Western Germany was calculated using an emission of 0.45 kg y^{-1}, equal to that in The Netherlands, and a population of $70x10^6$. Based on this emission (31,500 tons per year) it was found that the contribution to the DCM concentration is 0.08 $\mu g.m^{-3}$ (R1=100 km, R2=300 km). The rest of Western Europe is estimated to contribute equally. According to measurements (see 6.1.) it may be concluded that the world wide contribution is 0.10 - 0.15 $\mu g.m^{-3}$. On this basis the total large-scale concentration in The Netherlands is appr. 0.6 $\mu g.m^{-3}$. In order of magnitude, this result is consistent with the concentrations measured (see 4.3.).

- Distribution on a regional scale

The concentrations near a source are linearly related with the emission figure. In the case of DCM a great number of sources are involved. Therefore, it was decided to study a model situation with a source at a height of 15 m and air with a temperature of 25°C emitted from it. The emission figure was conveniently put at 100 tons per year. Calculations for the distribution on a slightly larger scale were made first, at distances from the source varying from a few hundred metres to several kilometres.

The results are presented in fig. 3.1. to fig. 3.5. Calculations, using this national distribution pattern may be applied for distances greater than ten times the height of the building. Actually, a chimney stack is considered to be the source. DCM, however, is hardly ever emitted through chimney stacks. Diffuse losses mainly occur from buildings and installations. In many cases other buildings (sometimes residential areas) are found at short distances, which renders it necessary to determine the concentrations at shorter distances from the source than is possible with the model used. Recently, a model was developed for the determination of the annual average levels and maximum hour concentrations occurring at distances of less than three times the height of the building from which the emission takes place (Baars and Van Melle, 1985). The concentrations of DCM at distances of between three and ten times the height of the building may be calculated by means of interpolation of results from both models. An example worked out with this model is presented in fig. 3.5. It may be concluded, that, per 100 tons emission per year, a 60x30x20 m building contributes 10 mg.m^{-3} to the maximum hour concentration and 0.22 mg.m^{-3} to the annual average near the source. An evalutation of these results, together with data from various sources obtained from practice, as well as the possibilities for emission reduction are discussed in chapter 9.

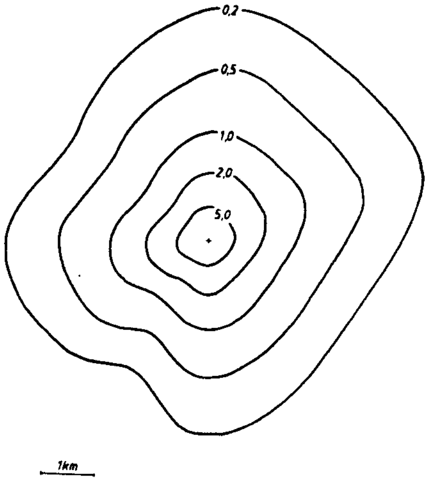


Fig. 3.1. *Annual average concentrations (in µg.m^{-3}) of DCM in the vicinity of a source with an emission of 100 tons. year^{-1} (continuous) at a height of 15 m; climatology Schiphol; scale 1 : 50,000*

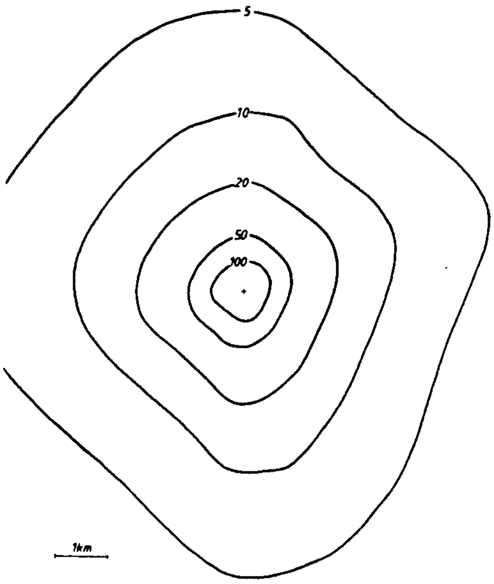


Fig. 3.2. 99.5-percentiles of hourly average DCM-concentrations (in $\mu g.m^{-3}$) in the vicinity of a source with an emission of 100 tons.year^{-1} (continuous) at a height of 15 m; climatology Schiphol; scale 1: 50,000

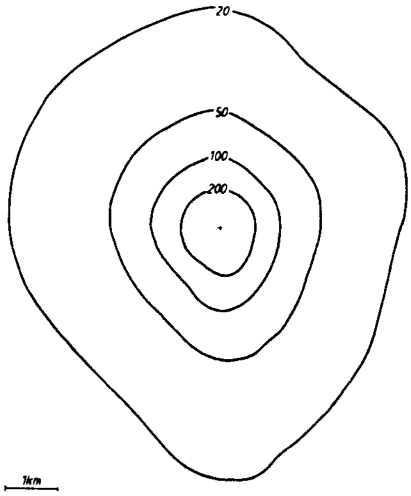


Fig. 3.3. 99.99-percentiles of hourly average DCM-concentrations (in $\mu g.m^{-3}$) in the vicinity of a source with an emission of 100 tons.year^{-1} (continuous) at a height of 15 m; climatology Schiphol; scale 1: 50,000

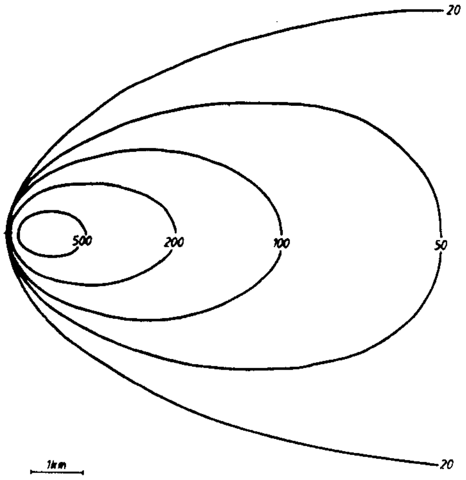


Fig. 3.4. Hourly average DCM-concentrations (in µg.m^{-3}) at the lee side of a source with an emission of 100 tons.year^{-1} (continuous) at a height of 15 m, in the least favourable situation (Pasquil-stability class F, wind velocity 1 m.s^{-1}); scale 1 : 50,000

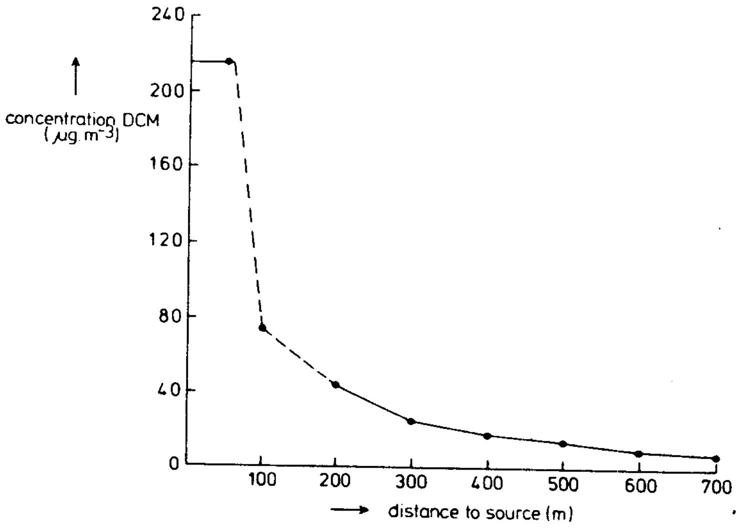


Fig. 3.5. Distribution of DCM near a fictitious source of 100 tons.year^{-1} in the form of a 60x30x20 m building, climatology Eindhoven (1977-1986)

- Deposition

At an estimated concentration of 0.6 $\mu g.m^{-3}$ in the outdoor air (see 3.3.1.) and a Henry constant of 0.8 (Lyman et al., 1982), the equilibrium concentration in rainwater will amount to 7.5 $\mu g.m^{-3}$. Consequently, the annual rainfall in The Netherlands being 760 mm, the amount of DCM removed by wet deposition is 230 kg per year. The half-life for removal by wet deposition amounts to appr. 550 years ($k_v = 4x10^{-11}$ s^{-1}), according to the method of Cupitt (1980).

The dry deposition rate towards DCM-free surface water may be calculated from the air-water partition coefficient and the evaporation rate from the water. It amounts to 0.05 $cm.s^{-1}$. Assuming a near-existing air/water equilibrium partition, the actual dry deposition rate towards surface water will certainly be 1 to 2 orders of magnitude smaller and even more so towards soil. At an estimated average concentration of 0.6 $\mu g.m^{-3}$ in the outdoor air, the load in The Netherlands by dry deposition amounts to 4-40 tons per year maximally. The actual load may, however, be considerably smaller.

3.3.2. Transformation

In the atmosphere, DCM is mainly decomposed by hydroxyl radicals. The reaction rate constant (k_{OH}) has been determined by various authors. By means of absolute methods Howard and Evenson (1976), Perry et al. (1977) and Davis et al. (1976) found $k_{OH} = 230 \pm 50$, 215 ± 10 and 170 ± 10 $ppm^{-1}.min.^{-1}$ respectively. Cox et al. (1976) determined the relative rate constant (with respect to methane) and found $k_{OH} = 160$ $ppm^{-1}.min^{-1}$ (all values at $T = 298$ K). These values are mutually consistent. For the determination of the life span of DCM in the atmosphere the reaction constant determined by Davis et al. (1976) is the most practical, as these authors have determined the temperature dependence: $k_{OH} = 4.27x10^{-12}e^{-2174/RT}$ $cm^3.molecule^{-1}.s^{-1}$. Over The Netherlands ($T = 288$ K) $k = 140$ $ppm^{-1}.min^{-1}$ en $[OH^\bullet] = 5x10^{-8}$ ppm (Van Aalst and Diederen, 1981). The half-life time amounts to 70 days. In the non-polluted troposphere with $T = 265$ K and $[OH^\bullet] = 2x10^{-8}$ppm (Singh, 1983) the half-life is 235 days.

As a consequence of the low transformation rate it is not possible to determine right away which products were formed in smogrooms or in the atmosphere. After irradiating 20 ppm DCM in the presence of 5 ppm Cl_2, Spence et al. (1976) observed that transformation was practically complete after 5 minutes, resulting in 5 ppm CO, 38 ppm HCl, 2 ppm $COCl_2$ and 12 ppm CO_2. The authors suggest a mechanism, in which chlorine radicals initiate the decomposition of DCM, while chlorine radicals originating from the DCM molecules further contribute to the decomposition. The circumstances in the atmosphere being different from those in the experiment mentioned above (considerably lower precursor concentrations and the presence of different hydrocarbons and NO), the decomposition is expected to differ as well. A plausible mechanism is as follows:

$$\begin{array}{lllll}
 & CH_2Cl_2 & + \dot{O}H & \rightarrow & \dot{C}HCl_2 + H_2O \\
 & \dot{C}HCl_2 & + O_2 & \rightarrow & \dot{O}_2CHCl_2 \\
 & \dot{O}_2CHCl_2 & + NO & \rightarrow & \dot{O}CHCl_2 + NO_2 \\
 & \dot{O}\text{-}CHCl_2 & + O_2 & \rightarrow & H\dot{O}_2 + COCl_2 \text{ (phosgene)} \\
\text{or} & \dot{O}CHCl_2 & & \rightarrow & CHOCl \text{ (formylchloride)} + \dot{C}l \\
 & CHOCl & & \rightarrow & CO + HCl
\end{array}$$

The chlorine radical will transform e.g. methane in the atmosphere, yielding HCl, formaldehyde and H_2O. Through both reaction routes regeneration of the OH-radical occurs (through $H_2O + NO \rightarrow OH + NO_2$. Therefore, products from DCM may possibly be CO, HCl and phosgene. The latter substance is stable in the atmosphere (Snelson et al., 1978). Removal takes place by wet deposition and dry deposition over water surfaces. Because of the uncertainty as to this mechanism, it is impossible to state whether DCM contributes to the occurrence of phosgene in the atmosphere.

3.4. BEHAVIOUR IN BIOTA

For details see Chapter 5.
DCM is readily absorbed through the oral and respiratory route. Absorption in the liquid phase through the skin is slow. DCM spreads through the entire body and is not bio-accumulative. In most cases a considerable amount will be degraded into CO and CO_2 (liver, kidneys, lungs).

3.5. MULTICOMPARTMENTAL DISTRIBUTION

Based on the preceding data the distribution of DCM over water, soil and air compartments may be estimated by means of the fugacity model developed by MacKay (1985). For the situation in The Netherlands the following model parameters have been used:

- total area : 40,000 km^2 (90% soil, 10 % water)
- height air column : 800 m
- height water column (fresh) : 2.5 m
- height soil column : 0.15 m
- residence time of air (Ta) : 0.8 or 2.3. days
- residence time of water : 43 days

Because of the uncertainty as to the residence time in air two calculations were carried out using the values mentioned. Besides, two values for the Henry coefficient were used (0.13 and 0.08) in association with different temperatures (appr. 25°C and 10°C, respectively).
In table 3.2., the distribution in the environment at equilibrium is given, assuming a contribution from abroad of 0.1 $\mu g.l^{-1}$ via water and 0.16 $\mu g.m^{-3}$ via air.

From these data it is evident that:
* DCM mainly occurs in the air compartment
* removal mainly takes place through the air phase, and
* transport is the main removal mechanism.
Besides, it may be concluded that temperature has little influence. The susceptibility to the residence time in the air compartment is greater.

Table 3.2. Distribution of DCM in The Netherlands over environmental compartments at equilibrium based on emissions in The Netherlands and trans-frontier emissions

H = 0.13 Ta = 0.8 days	Air (in $\mu g.m^{-3}$)	Water (in $\mu g.l^{-1}$)	Soil (in $ng.kg^{-1}$)	Groundwater (in $\mu g.l^{-1}$)
Concentration	0.63	0.030	1.9	0.03
Distribution (%)	98.6	1.3	0.1	
Removal (%)				
- advection	99.2	0.02		
- reaction	0.8	0.02		
H = 0.07 Ta = 0.8 days				
Concentration	0.63	0.035	2.5	0.017
Distribution	98.3	1.6	0.1	
Removal (%)				
- advection	99.2	0.03		
- reaction	0.8	0.02		
H = 0.07 Ta = 2.3 days				
Concentration	1.48	0.047	4.3	0.029
Distribution (%)	98.9	1.0	0.1	
Removal (%)				
- advection	97.7	0.05		
- reaction	2.3	0.04		

3.6. SUMMARY AND CONCLUSIONS

Since emission of DCM mainly takes place into the air and as a result of its behaviour in the environment, the greatest amount is found in the atmosphere (almost 98%). Removal also occurs mainly in the air compartment (more than 99%), particularly by transport. The contribution to the outdoor air concentration in The Netherlands from abroad amounts to appr. 50%. The composition in the atmosphere mainly takes place by reaction with hydroxyl radicals (half-life appr. 70 days). Removal by deposition is slight; wet deposition amounts to 230 kg per year.

In the soil (particularly humid soil) DCM will especially reside in groundwater. If concentrations are low, dispersal will be limited because DCM is decomposed microbiologically, after an adaptation period (half-life a few weeks to several months). If concentrations are higher (> 400 mg-.l^{-1}) decomposition is slowed down by occurring toxicity and the flow downwards may increase.

In surface water abiotic (photolysis: half-life 68 years; hydrolysis: half-life 700 years) as well as biotic (half-life a few weeks to several months) transformation occurs. Evaporation is, however, the main removal process.

DCM is hardly bio-accumulative. During biotic as well as abiotic transformations (intermediate) products (phosgene, chloromethane, etc.) are formed which may be potentially hazardous to health. It is not possible, however, to give a rough estimate of the quantities formed.

4. CONCENTRATIONS IN THE ENVIRONMENT AND EXPOSURE LEVELS

4.1. BACKGROUND CONCENTRATIONS

No natural sources of DCM are known, which is made plausible by Singh et al. (1983) who demonstrated the association between the outdoor air concentrations measured and anthropogenic emissions. Consequently the lowest concentration levels have been found in areas at great distances from anthropogenic sources. Considerably higher concentrations have been found in urban areas where DCM is applied. A considerable number of research results have been summarized by Egle et al. (1982). In table 4.1. the values measured for large-scale concentrations (mainly in the United States) are presented; from these it may be concluded that the background concentration of DCM is 0.10-0.15 $\mu g.m^{-3}$. No literature data are available on background concentrations in soil and water.

Table 4.1. Measured background concentrations of dichloromethane

Area	*Average concentration ($\mu g.m^{-3}$)*	*References*
Wiltshire, UK	*0.12*	*Cox et al. (1976)*
Continent, USA	*0.13*	*Pierrotto and Rasmussen (1976)*
Atlantic Ocean, N	*0.11*	*Cronn et al. (1976)*
Atlantic Ocean, N	*0.12*	*Robinson (1978)*
Southern Hemisphere (4 loc.)	*0.12 - 0.14*	*Robinson (1978)*
Panama	*0.12*	*Cronn and Robinson (1979)*
Washington, USA	*0.12*	*Rasmussen et al. (1979)*
California, Nevada, Kansas (6 loc.)	*0.17*	*Singh et al. (1979)*
Arctic Ocean	*0.26; 0.29*	*Hov et al. (1984)*
Northern hemisphere	*0.13*	*Singh et al. (1983)*
Southern hemisphere	*0.05*	*Singh et al. (1983)*

4.2. OCCURRENCE IN SOIL AND GROUNDWATER

Although DCM may occur in soil and air trapped in soil, no data are available on this matter. During 1980-1983, groundwater was sampled at 41 measuring points (distributed all over the country, at depths of roughly 10, 15 and 25 m below ground level) and analyzed for DCM as part of the groundwater quality monitoring system of the RIVM. With the analysis method used, all observations were below the detection level (10 $\mu g.l^{-1}$). In a number of cases further analysis was made, of which the results are summarized in table 4.2. In the United States concentrations of < 0.2 to 8.9 $\mu g.l^{-1}$ were observed in 67 groundwater samples (Nellor, 1985).

Table 4.2. DCM concentrations ($\mu g.l^{-1}$) in groundwater in The Netherlands

Observation site Groundwater Measuring System	*10 m below ground level*	*15 m below ground level*	*15 m below ground level*
62	*3.2*	-	-
67	-	*2*	*1*
73	-	-	*0.30*
294	-	-	*26*

(- = not analyzed)

A finding of 3,000 $\mu g.l^{-1}$ near a garbage dump was reported by Zoeteman et al. (1981). No further data on The Netherlands are available; a number of times DCM was found in concentrations varying from 90 $\mu g.l^{-1}$ to more than the solubility limit in places near garbage dumps and in calamitous situations (table 4.3.) (Baldauf, 1981; Kelly et al., 1981; Page, 1981; Schuckrow et al., 1981; Engesser, 1983; Schwarzenbach, 1983; Craun, 1984). The geohydrologic conditions were inadequately described if at all; it is expected that DCM will mainly reside in the upper waterbearing zone.

Concentrations found in ground water are higher than those in surface water (Page, 1981; Christman, 1982; Craun, 1984). This may be explained by assuming non-turbulant flows causing an evaporation decrease from the water; the evaporation from soil is probably involved as well.

4.3. OCCURRENCE IN SURFACE WATER

Very few data are available on concentrations of DCM in surface water. The analysis of DCM is not included in the quality survey programme of state waters. In view of the conclusions concerning its behaviour in water (see 3.2.) concentrations are expected to be low. According to multicompartmental distribution models (see 3.5.) concentrations in surface water are 30-50 ng.l^{-1}. Higher concentrations will occur in the close proximity of sources. In the Rhine river concentrations of 1-2 μg.l^{-1} (Bauer, 1978) and 5 μg.l^{-1} (Zoeteman et al., 1980) have been reported, being the lowest detection limit of the method used. Occurrence in the Meuse from source to mouth was studied in September 1982 (RIWA, 1982). The concentrations amounted to 1.7 μg.l^{-1}- < 0.1 μg.l^{-1}. In surface water in Hilversum concentrations of 0.3 μg.l^{-1} have been observed (KIWA, 1981/1982). Recent studies on the North Sea showed concentrations of appr. 100 ng.l^{-1} in the coastal area and concentrations of appr. 5 ng.l^{-1} in the central part of the North Sea.

4.4. OCCURRENCE IN AIR

4.4.1. Indoor air

- Occupational exposure

A review article on occupational exposure was recently published (WHO, 1984). The major part of DCM is used in the paint stripper production. Small objects are either brushed with stripper or submerged in tanks containing this agent. Time weighted average concentrations (TWA) of DCM, during stripping of furniture, ranging from 70 to 250 mg.m^{-3}, were reported by Markel (1982). Considerably greater TWA's, of 630-1,020 mg.m^{-3}, have been reported from other studies (Chrostek, 1980). Concentrations of DCM sometimes increased to 4,900 mg.m^{-3} for short periods (appr. 1 hour). During stripping of large objects (planes, trains) the stripper is being sprayed. Cohen et al. (1980) observed a TWA of 50-930 mg.m^{-3}(average: 220 mg.m^{-3}). Hartle (1980) mentioned a TWA of 350-440 mg.m^{-3}. In the latter study the air concentrations measured ranged from 300-1,450 mg.m^{-3}. For exposure to DCM during paint stripping in homes reference is made to the next subsection.

Not only the removal of paint, but also the actual painting may result in exposure to DCM. However, in painting systems DCM is only applied on a limited scale to reduce the drying time. An exposure of up to several $mg.m^{-3}$ was observed during mixing c.q. stirring as well as during spraying in paint cabins (Pryor, 1981; Chrostek and Levine, 1981; Whitehead et al., 1984). An 8-hour TWA of 140 $mg.m^{-3}$ was observed during spraying of walls, ceilings etc. (Chrostek and Levine, 1981). DCM is also used in several kinds of adhesives to accelerate drying. Spraying with DCM-containing adhesives results in an average TWA of 130 $mg.m^{-3}$ with a maximum of 430 $mg.m^{-3}$ (Whitehead et al., 1984). DCM is sometimes used as an "adhesive", e.g. in the assembly of plastic parts. Tharr and Donohue (1980) mention a TWA of 50-650 $mg.m^{-3}$ for this application, whereas Markel and Slovin (1981) reported 15-330 $mg.m^{-3}$.

Exposure may also occur in the synthetics industry. Cohen et al. (1980) mention a TWA ranging from 105-1,050 $mg.m^{-3}$, at an outdoor air concentration of 1,420-3,380 $mg.m^{-3}$. Ott et al. (1983) observed TWA's of 170-2,400 $mg.m^{-3}$ with an average of 490-1,650 $mg.m^{-3}$, depending on place and activity.

In addition, DCM is used as a solvent for cleaning engine parts in the production of polyurethane foam.

Exposures of 100 $mg.m^{-3}$ or less were found by Almaguer et al. (1982) and Reisdorf and Haggerty (1980); 7-1,080 $mg.m^{-3}$ by Burroughs and Moody (1982).

DCM is applied in the foodstuff industry as an extraction agent for natural substances such as fats, cacao and caffeine. Cohen et al. (1980) carried out a study in a decaffeinating installation; the TWA for workers amounted to 1-115 $mg.m^{-3}$ with a geometric mean of 10 $mg.m^{-3}$. In the literature relatively low concentrations of DCM were reported in the graphic industry, with a maximum TWA of 130 $mg.m^{-3}$(NIOSH, 1980; Lewis and Thoburn, 1981; Johnson, 1982).

Only one article has been found presenting exposure data on DCM during degreasing of metals; the values observed amounted to 140 $mg.m^{-3}$ maximally (Ruhe et al., 1981).

In laboratories DCM is applied as a multipurpose extraction agent. Hertlein (1979) reported concentrations of up to 75 $mg.m^{-3}$ (4h-TWA). Salisbury (1981) observed an ambient air concentration of 380 $mg.m^{-3}$ during extractions, resulting in an 8 h-TWA of about 100 $mg.m^{-3}$. In the pharmaceutical industry DCM is applied as a solvent; concentrations of up to 510 $mg.m^{-3}$ are reported, resulting in an 8h-TWA of 360 $mg.m^{-3}$(Watanebe et al., 1982).

The above-mentioned data are all from foreign studies. Data concerning the situation in The Netherlands are not available.

- Non-occupational exposure

A number of houses in the US were examined by Gupta et al. (1984) on the occurrence of DCM in indoor air. This study, carried out during the winter, produced an average concentration of 14.3 $\mu g.m^{-3}$ with a standard deviation of 9.4 $\mu g.m^{-3}$ ($n = 13$), whereas another study (EEC, 1984) showed concentrations of < 5 - 5,000 $\mu g.m^{-3}$. No explanation was given for the higher concentrations.
During paint stripping high concentrations were observed in houses. In a non-ventilated testroom an 8h-TWA of 460-2,980 $mg.m^{-3}$ was observed by Orsen et al. (1981), whereas in a ventilated room it ranged from 60 to 400 $mg.m^{-3}$.
Spray-cans constitute yet another source of DCM emission in houses. Because its atmospheric half-life is short in comparison with that of freones (Sigh et al., 1983) some producers show an ever increasing preference for the use of DCM. It concerns spray-cans for various purposes, such as paint, insecticides, shampoos and hair sprays. According to the NVA (Van Diesen, 1986), appr. 90% (900 $tons.year^{-1}$) of spray-cans are used indoors. Roughly calculated, this amount, averaged over 14 million rooms of 40 m^3 each, results in an annual average concentrations of appr. 200 $\mu g.m^{-3}$. Recently the RIVM (Bloemen and Eerens, 1987) carried out indicative measurements on the peak concentrations of DCM to be expected in the use of hair sprays. Six spray-cans of four different brands were tested in two different ways. In the first case by using the spray-can round the head for appr. 10 seconds, in the second case by directing it only at the back and the sides of the head. The concentrations of DCM near the mouth were determined every 11 seconds under normal ventilation conditions of the room. In the first case the concentrations over an average of 5 minutes ranged from 500 to 1,600 $mg.m^{-3}$, with an average of 800 $mg.m^{-3}$, and in the second case from 15 to 200 $mg.m^{-3}$, with an average of 90 $mg.m^{-3}$. Concentration measurements were started immediately after spraying. With maximum ventilation (door and windows open, a ventilator in the room and a clearly perceptible draught) the 5-minute average concentrations were reported to be 100 $mg.m^{-3}$ and 20 $mg.m^{-3}$, respectively.

In addition to the above-mentioned applications, DCM is used in a number of adhesives, cleaning products and pens, the uses of which may also result in increased indoor air concentrations.
Another source of DCM in houses is smoking; Harsch (1977) observed that the smoking of one cigarette raised the concentration in a room from 7 $\mu g.m^{-3}$ to well over 70 $\mu g.m^{-3}$.

4.4.2. Outdoor air

Knowledge on large-scale concentrations in The Netherlands is limited; they are estimated at 0.6 $\mu g.m^{-3}$ (see 3.3.1.).
In Delft, on 11 out of the 138 measuring days, during the period from 22/9/77 to 23/5/78 concentrations found ranged from 0.04 to 0.8 $\mu g.m^{-3}$(Keijzer et al., 1981). The average concentrations in background areas (see 4.1.). According to Guicherit and Schulting (1985), the concentrations will be higher and range from 1.4 $\mu g.m^{-3}$ (Terschelling) to 14 $\mu g.m^{-3}$ (Delft, Vlaardingen), depending on the area. The concentrations are of the same order of magnitude as those found in urban areas in the United States of America (see table 4.3.).
A considerable amount of data are available on the USA (table 4.3.). Measurements in Cambden, Newark and Elisabeth have been reported several times, by mostly the same authors. It is remarkable, however, that the concentrations reported differ by appr. a factor 2, which is possibly the result of the application of different correction factors for break-through during sampling on Tenax. It is evident from these values measured that, whereas the concentration of DCM may average a few $\mu g.m^{-3}$ over long periods, it may be considerably higher for short periods.

No data are available on concentrations in rainwater. The estimated concentration amounts to appr. 5 $\mu g.m^{-3}$ (see section 3.3.1.).

Table 4.3. Outdoor air concentrations of DCM measured near sources abroad

Area	*Average concentration ($\mu g.m^{-3}$)*	*Duration cq. period of sampling*	*References*
Upland (California)	*42*	*48 h*	*Pellizzari and Bunch (1979)*
Edison (New Jersy)	*1270*	*11 min*	*Pellizzari and Bunch (1979)*
States Island (New York)	*194*	*75 min*	*Pellizzari and Bunch (1979)*
Front Royal (Virginia)	*247*	*7.25 hr*	*Pellizzari and Bunch (1979)*
Houston (Texas)	*3,5*	*3 hr*	*Pellezzari and Bunch (1979)*
Los Angelos (California)	*13*	*2 weeks*	*Singh et al. (1981)*
Phoenix (Arizona)	*3,2*	*2 weeks*	*Singh et al. (1981)*
Oakland (California)	*1,5*	*2 weeks*	*Singh et al. (1981)*
Cambden (New Jersey)	*5.4*/2.5***	*6 weeks (summer)*	*Lioy et al.* (1983)* *Harkov et al.** (1983, 1984)*
Newark (New Jersey)	*2.3*/1.2***	*6 weeks (summer)*	*Lioy et al.* (1983)* *Harkov et al.** (1983, 1984)*
Elisabeth (New Jersey)	*1.7*/0.8***	*6 weeks (summer)*	*Lioy et al.* (1983, 1984)* *Harkov et al.**(1983)*
Cambden (New Jersey)	*8.9*/4.2***	*6 weeks (winter)*	*Lioy et al.* (1983)* *Harkov et al.**(1984)*
Newark (New Jersey)	*6.2*/2.4***	*6 weeks (winter)*	*Lioy et al.* (1983)* *Harkov et al.**(1984)*
Elisabeth (New Jersey)	*6.9*/3.1***	*6 weeks (winter)*	*Lioy et al.* (1983)* *Harkov et al.**(1984)*

4.5. OCCURRENCE IN FOOD AND DRINKING WATER

DCM may be used for the isolation of valuable components or raw materials from foodstuffs and for the removal of components which are particularly undesired. Examples of the former application are the isolation of components from hop, spices or oils and fats by extraction with DCM. Decaffeination of coffee has a dual purpose, producing decaffeinated coffee and caffeine. DCM is also used for the fumigation of wheat and citrus fruits. It is difficult to say to what extent the target values mentioned in chapter 1 are exceeded in practice. Very few data are available on this matter. One study on oleoresins, carried out in 1975, shows that 15 out of 17 samples studied contained concentrations of DCM ranging from 1 to 83 $mg.kg^{-1}$ (Page and Kennedy, 1975). In two studies on the concentration of DCM in drinking water carried out by the KIWA, 3.7% of the samples contained more than 0.1 $\mu g.l^{-1}$ and 4.1% more than 1 $\mu g.l^{-1}$, respectively. Chlorination of drinking water may result in the presence of DCM, but the concentrations are usually below 1 $\mu g.l^{-1}$ (Bauer, 1981; IARC, 1979). An average of 3 to 10 $\mu g.l^{-1}$ was observed in a Canadian study (30 waterworks). Concentrations in summer were slightly higher than those in winter, the highest value observed amounting to appr. 50 $\mu g.l^{-1}$ (Otson et al., 1982).
Until 1983 a temporary acceptable daily intake (ADI) for DCM was put at 0.5 $mg.kg^{-1}$ body weight. However, in view of the possibly carcinogenic properties of DCM the ADI has been withdrawn by the Joint FAO/WHO Expert Committee on Food additives (1983). According to the same committee (JECFA), the use of DCM as an extraction agent for foodstuffs should be limited in order to reduce residues of the substance in foodstuffs as much as possible. In particular cases liquid CO_2 might possibly be an alternative for the use of DCM as an extraction agent.

4.6. EXPOSURE LEVELS

Based on the above-mentioned concentrations (see table 4.5.) exposure levels may be estimated.
In view of the environmental DCM concentrations, the main route of exposure for man is through the respiratory tract. A rough estimate of the exposure to DCM in The Netherlands is presented in table 4.4. assuming a 3 to 1 ratio in the residence times in indoor and outdoor air. The remaining exposure routes (oral, dermal) are considered negligible, whereas absorption

at working places, by smoking and the use of paint stripper or spray-cans is not included. Recent levels may therefore be considerably higher for particular (temporary) population groups.

In aquatic ecosystems the exposure level may be considered to be equal to the concentrations in surface water. In terrestrial ecosystems, however, there may be considerable interspecies variance, depending on the living habits.

Table 4.4. Rough estimate of the exposure to DCM of the population in The Netherlands listed by residential area

Number of people	*Conc. indoor air ($\mu g.m^{-3}$)*	*Conc. outdoor air ($\mu g.m^{-3}$)*
900	*100*	*50 - 100*
9,000	*50*	*20 - 50*
10,000	*25*	*11 - 20*
40,000	*20*	*5.6 - 11*
160,000	*15*	*2.6 - 5.6*
300,000	*10*	*1.6 - 2.6*
appr. $14x10^6$	*10*	*0.6*

4.7. SUMMARY AND CONCLUSIONS

In table 4.5. a summary is presented of DCM concentrations in various environmental compartments. These concentrations are based on measurements which may sometimes be inaccurate (see chapter 6); model calculations and estimates should therefore be considered indicative. Although data on concentrations in the range of food are not available, they are estimated to be negligible.

The concentrations in indoor and outdoor air determine, to a considerable extent, the exposure level for man; the daily amount of DCM absorbed per inhabitant in The Netherlands ranges from appr. 100 to 1000 μg, depending on the distance between residences and sources. By smoking, use of paint stripper and/or spray-cans and by working in particular work places the absorption may be considerably higher. In studies on spray-cans, concentrations (5-min average) of many hundreds of mg.m^{-3} were measured, depending on the ventilation.

Table 4.5. Summary of DCM levels estimated and measured in various environmental compartments in The Netherlands

Soil		
- *groundwater*	*< 10*	$\mu g.l^{-1}$
- *soil material*	*negligible*	
Surface water		
- *fresh*	*< 0.1 - 5*	$\mu g.l^{-1}$
- *salt, coastal area*	*0.1*	$\mu g.l^{-1}$
- *salt, central North Sea*	*0.005*	$\mu g.l^{-1}$
Air		
- *outdoor air*		
background area outside The Netherlands	*~ 0.1*	$\mu g.m^{-3}$
nationwide	*~ 0.6*	$\mu g.m^{-3}$
local	*10 - 100*	$\mu g.m^{-3}$
wet deposition	*~ 5*	$\mu g.m^{-3}$
- *indoor air*		
living environment	*~10*	$\mu g.m^{-3}$
living environment, in which is being smoked	*10 - 100*	$\mu g.m^{-3}$
living environment, use of spray cans (peak values)	*90 - 800*	$mg.m^{-3}$
living environment with other sources (8h-TWA)	*60 -3000*	$mg.m^{-3}$
work places	*idem*	
Food and drinking water	*not available*	

5. EFFECTS

This chapter comprises a summary of data on the effects of DCM and includes a risk evaluation. Detailed information is given separately in the appendix (Van Apeldoorn, 1987).

5.1. HUMAN TOXICOLOGY

DCM vapour is rapidly absorbed through the lungs and gastrointestinal tract, uptake being directly proportional to exposure. Its absorption increases with exercise and with the amount of body fat. The absorbed compound, which is distributed to all body tissues, crosses the placenta and blood-brain barrier. Absorption of liquid DCM via the skin is slow. At current exposure levels, most of the DCM taken up is metabolized to carbon monoxide and carbon dioxide, mainly in the liver, kidneys, and lungs. With high or repeated exposure, the microsomal cytochrome P-450 enzyme system becomes saturated and unmetabolized DCM may occur in fat.

Exposure to DCM will result in elevated carboxyhaemoglobin levels in blood. Even at relatively low (i.e. beneath levels saturating the cytochrome P-450 system) exposure levels, carboxyhaemoglobin levels in the blood can be sustained for many hours after exposure, because of conversion of DCM released from fat. Blood carboxyhaemoglobin levels may lead to an erroneous estimation of exposure when either exercise or smoking is involved.

Exposure to DCM can be roughly estimated by the determination of its levels in blood or expired air.

The oral LD50 for rat and dog amounted to 3,000 $mg.kg^{-1}$ body weight and the LC50 for mouse and rat ranged from 49,000-79,000 $mg.m^{-3}$ of air.

Liquid DCM causes severe skin irritation and moderate, reversible eye irritation in rabbits.

Short-term studies showed at oral doses > 133 $mg.kg^{-1}$ body weight and at exposure levels > 347 $mg.m^{-3}$, changes in liver (fatty changes) and kidneys (tubular damage) in mammals.

In long-term drinking water studies with mice and rats no significantly increased tumour incidences were observed.

In a carcinogenicity study with mice by inhalation exposure increased incidences of lung tumours (adenomas and carcinomas) and liver tumours (adenomas and carcinomas) in male and female animals were found at levels of 6,940 and 13,880 $mg.m^{-3}$. Two carcinogenicity studies with Sprague Dawley rats by inhalation exposure were conducted. In one of these studies (exposure levels: 0; 1,730; 5,200 and 12,100 $mg.m^{-3}$) the number of benign mammary tumours/rat was increased in a dose-related manner at both sexes but not the number of rats with a benign mammary tumour. In the other study (exposure levels: 0; 173; 694 and 1,730 $mg.m^{-3}$) only in females at the highest exposure level an increased multiplicity of benign mammary tumours was found. It should be noted that Sprague Dawley rats exhibit a high incidence of spontaneous mammary tumours.

In a third carcinogenicity study with rats (F344 strain) exposed by inhalation (exposure levels: 0; 3,470; 6,940 and 13,880 $mg.m^{-3}$) increased incidences of benign mammary tumours in both males and females were observed. Despite the high levels of exposure, in none of the rat studies a shift from benign to malignant mammary tumours was found.

In a long-term carcinogenicity study with hamsters exposed by inhalation no increased tumour incidences were seen.

Distinct hepatotoxicity in rats was observed at levels > 59 $mg.kg^{-1}$ body weight and > 694 $mg.m^{-3}$, respectively, in long-term oral and inhalation studies.

According to a recent re-evaluation by IARC (1986) DCM has sufficient evidence for carcinogenicity in experimental animals. The same position was recently taken by EPA (1985). However, in view of the available data, the weight of evidence for the possible carcinogenicity of DCM is very weak. In one study with rats an increased incidence of benign mammary tumours was observed. The relevance of this finding is not clear, although the exposure levels were very high there was no shift to malignancy; moreover in three other rat studies no such increase occurred. In one experiment with mice a distinct treatment-related increase in tumours (liver and lung tumours) was found at exposure levels that are hepatotoxic. In particular, enhancement of liver and lung tumours in mice, without clear positive results in other species, is not regarded as adequate evidence for carcinogenicity to experimental animals (IARC, 1982). Therefore, in spite of uncertainties there is not sufficient ground to consider DCM as a potential human carcinogen.

DCM is mutagenic in bacteria; there is some evidence that DCM has mutagenic activity in fungi. Contradictory results were obtained in tests with Drosophila. In two tests with mammalian cells in vitro chromosomal aberrations were induced. No gene mutations were detected in mammalian cells in

vitro. DCM did not reveal mutagenic activity in in vivo studies with mammals for chromosomal aberrations and micronuclei.
A weak increase in the induction of SCEs in mammalian cells in vitro was found. No induction of unscheduled DNA repair synthesis by DCM in mammalian cells in vitro was observed. The inhibition of DNA synthesis found in one test with mammalian cells in vitro was reversible and suggested to be caused by a metabolic block of synthesis. Positive results were found in two cell transformation assays, a third assay was found to be negative.
No DNA-alkylation was observed in in vitro and in vivo studies.
In conclusion, DCM has mutagenic properties in several in vitro systems, both in the absence and the presence of a metabolic activation system; in vivo mammalian studies showed negative results.

In fetuses of mice and rats DCM induced dilated pelves and extra sternebrae. These findings are not considered as evidence for teratogenic activity.
No reproductive impairment in rats was found, neither in a one generation reproduction study at 125 $mg.l^{-1}$ in the drinking water administered during 13 weeks before mating, nor in a two generation reproduction study at exposure levels up to 5,200 $mg.m^{-3}$.

In view of the very weak evidence for a carcinogenic activity in experimental animals, the conflicting results of the mutagenicity studies and the absence of DNA alkylation by DCM, it seems appropriate to establish a no-effect level based on the long-term toxicity studies. The key criterion is the hepatotoxic effect of DCM. The oral no-effect level is derived from a long-term drinking water study with rats and amounts to 6 $mg.kg^{-1}$ body weight (NCA, 1982). The no-effect level for inhalation exposure is derived from a long-term inhalation study with rats and amounts to 173 $mg.m^{-3}$ (Nitschke et al., 1982).
Acute toxicity in man is low. The predominant effects on human beings are elevated carboxyhaemoglobin levels of the blood and central nervous system depression. These effects are reversible. Blood carboxyhaemoglobin levels exceeded control values after exposure to 350 $mg.m^{-3}$ for 8 hours in non-smoking, sedentary individuals. The lowest-observed adverse acute effect level, for inhalation exposure of non-smoking, healthy individuals, is appr. 690 $mg.m^{-3}$. Some neuro-behavioural changes become measurable at this

exposure level. Impairment of psychomotor performance after 4 hours exposures to 2,610 $mg.m^{-3}$ was observed. Narcosis occurred following exposure to 69,000 $mg.m^{-3}$ for 30 minutes.

Individuals with heart disease may be at increased risk if exposed to high levels of DCM; this may particularly occur during the use of paint removers. One case of acute renal tubular damage after exposure to a tile remover containing DCM has been described.

The vapour is moderately irritating to the eyes and respiratory tract while the liquid is irritating to the skin.

The predominant long-term effects in humans are nervous system depression and an elevated carboxyhaemoglobin level of the blood. However, no exposure related subjective symptoms, neurobehavioural effects, motor nerve conduction velocity changes, changes in electrocardiograms, or clinical effects were reported in workers exposed to 260 to 347 $mg.m^{-3}$ when compared with age matched controls. It has to be noted that this study showed some deficiencies.

Two cases of permanent damage to the central nervous system in high long-term occupational exposures have been reported. In spite of many reports of fatty degeneration in the liver and tubular degeneration in the kidneys of animals, there is no clear evidence of liver or kidney damage in human beings after long-term exposure to DCM.

In two epidemiological mortality studies, there was no excess mortality due to cancer when compared with control populations. The data from human studies, carried out so far, are not yet adequate for evaluation of the carcinogenicity of DCM to man.

5.2. ECOTOXICOLOGY

Acute effects (EC50, LC50) to aquatic organisms may be expected at concentrations $\geq$ 100 $mg.l^{-1}$. Data on chronic effects after long-term exposure are lacking. The embryonic development of some amphibians is clearly affected at concentrations $\geq$ 1.0 $mg.l^{-1}$.

The Electron Transport System activity in sediment from fresh water is significantly stimulated at concentrations of 1.3 $g.kg^{-1}$ sediment and higher. Although experimental data are lacking, DCM is considered to have little potential for bioaccumulation (BCF of 4 calculated from the octanol/water partition coefficient log Pow = 1.25).

There are insufficient data on ecotoxicity and bioaccumulation in terrestrial organisms (invertebrates and plants). In an acute filterpaper toxicity test DCM was very slightly toxic to earthworms (LC50 > 1,000 μg-.cm^{-2}; soil concentrations > 1000 mg.kg^{-1}). For mammals the acute LC50 and LD50 are 49-79 g.m^{-3} and 3 g.kg^{-1} body weight, respectively. After single exposure of mammals to concentrations $\geq$ 2,600 mg.m^{-3} effects on the central nervous system were seen.

5.3. EVALUATION

5.3.1. Human toxicology

In animals the main target organs for DCM toxicity are the liver and the central nervous system. The predominant effects on human beings are elevated carboxyhaemoglobin levels in the blood and central nervous system depression. The weight of evidence for a carcinogenic effect in experimental animals is very weak. DCM has mutagenic properties in in vitro systems; in vivo mammalian studies showed negative results. Data from human studies, carried out so far, are not yet adequate for evaluation of the carcinogenicity of DCM to man.

Human data are considered inappropriate to estabilish a limit value. Based on the available data, it is considered appropriate to establish a limit value for DCM based on long-term animal studies using a safety factor.

The most relevant study to calculate a limit value for oral uptake, is a long-term drinking water study with rats (NCA, 1982). In this study a no-effect level of 6 mg.kg^{-1} body weight was found. Making use of a safety factor of 100, a limit value for daily oral uptake of 0.06 mg.kg^{-1} body weight is derived.

The most relevant study to calculate a limit value in the air, is a long-term inhalation study with rats (Nitschke et al., 1982). In this study a no-effect level of 173 mg.m^{-3} in the air was found. Making use of a safety factor of 100, a limit value of 1.7 mg.m^{-3} is derived.

Since no studies are available from which directly a health limit value for short-term peak exposure can be derived, the following procedure has been used. Based on the proposed limit value of 1.7 mg.m^{-3} as a 24 hour time-weighted average, a value for intermittent short-term air concentration is calculated according to the formula peak value (t min) = limit value (24 h) x 60 min/t x 24 h/1 h

For an exposure of 5 minutes a peak value of 490 $mg.m^{-3}$ is allowed as long as the 24 hour time-weighted average concentration is not exceeded.

5.3.2. Ecotoxicology

Two extrapolation methods have been proposed that may be used to arrive at a "safe" concentration in the aquatic environment based on acute toxicity data. Applying the method of Slooff et al. (1986) on the lowest LC50-value observed (193 $mg.l^{-1}$) 1.78 and 0.48 $mg.l^{-1}$ may be proposed as "safe" concentrations for species and ecosystems, respectively. Application of the method of Kooyman (1985) on the median LC50 (310 $mg.l^{-1}$; 7 toxicity data only) results in the calculated LC50 among 1,000 species of 1.26 $mg.l^{-1}$. Based on the results of these two extrapolation methods 0.5 $mg.l^{-1}$is proposed as a "safe" level for the aquatic environment.

Since there are insufficient data on ecotoxicity and bioaccumulation of DCM in terrestrial organisms, a limit value for the soil ecosystem cannot be established.

6. MEASURING METHODS AND MEASURING STRATEGIES

6.1. MEASURING METHODS

6.1.1. General analytical remarks

Due to its great volatility DCM easily escapes during taking, transportation, storage and processing of water, soil and biota samples. It may also cause the samples to be easily contaminated through the atmosphere in laboratories where DCM is being handled.

The retention volume in various absorbents will be small, limiting the size of air samples. If DCM is isolated by extraction or elution with pentane (boiling point 36.2 °C), or carbon disulphide (boiling point 46.3 °C), these solvents having a comparable volatility, the peak of the extraction agent may interfere with gas chromatography. Extracts cannot be evaporated, which unfavourably affects the lowest possible detection limit that can be reached. Trials on the use of slightly volatile extraction agents have not been described in the open literature. Chlorinated hydrocarbons cannot be used for extraction, causing too much interference, particularly when using an ECD.

In table 6.1. the order of magnitude is presented of the minimum detectable amounts of DCM which can be measured by several GC-detectors, under optimal gas chromatographic separation conditions (sharp, well-separated peaks).

Table 6.1. Order of magnitude of the minimum detectable amounts of DCM which can be measured with three different detectors under optimal GC-conditions

Flame ionization detector	*(FID)*	*appr. 0.1 ng*
Electron capture detector	*(ECD)*	*appr. 0.05 ng*
Mass selective detector	*(SIM)*	*appr. 0.005 ng*

It is important that, because of its relatively low sensitivity, the ECD offers fewer advantages than the FID for the determination of DCM than for e.g. chloroform and tetrachloroethane. An advantage of the ECD is its considerable insensitivity to n-pentane. Based on the data mentioned in table 6.1., the lower limit for the determination of DCM in air and water has been calculated for various determination methods and sample sizes (table 6.2.).

The GC-retention time of many substances is practically the same as for DCM. The only way to detect the substance specifically is to apply a mass selective detector adjusted at m/z 49, 51, 84, 86 and 88 if necessary, taking into consideration the right isotope ratio and the retention time (Markens, 1985).

Summaries, presenting data on the determination methods for DCM, were published by WHO (1976, 1984), Nakamura (1977), Baggen et al. (1983), Halliday (1983), the EPA (1982) and the Expert Study Group of the National MAC-Committee (1983).

On the determination in soil and biota very little has been published.

Few publications deal specifically with the determination of DCM. The substance usually occurs by chance in a variety of other volatile (halogen) compounds that receive more attention. Only those publications that mention DCM explicitly, are discussed in this summary.

6.1.2. Determination in soil

- Soxhlet-extraction

Akkerhuis (1985a) describes the following method. The soil is dried with anhydrous sodium sulphate and subsequently extracted in a Soxhlet-extractor with carbon disulphide. Losses through drying are supposed to be extremely limited. The extract is analyzed by gas chromatography. The lowest determination limit for DCM is in the order of 0.1 $mg.kg^{-1}$.

- Static headspace-analysis

Langelaan (1984) compared two methods for the determination in soil of a number of volatile, organic compounds, including DCM. His study concerns Soxhlet-extraction with carbon disulphide and a direct headspace method. With the latter method 50 g of soil is put in a 350 ml headspace jar. For sandy soil a satisfactory compromise between the two methods was found. The headspace method was observed to be distinctly unsuitable for clay soils, from which it is difficult to evaporate organic compounds (Slingerland and Luijten, 1985). The lowest determination level for DCM in soil is reported to be 0.2 $mg.kg^{-1}$.

Table 6.2. Sample sizes and order of magnitude of the lowest detection limit, assuming the sensitivity for DCM of the three different GC-detectors mentioned in table 6.1. and the optimal separation conditions (which are not always reached in practice; see table 6.3.)

Method	*Sample size*	*Lowest detection limit* *FID*	*ECD*	*MS (SIM)*	
Soil					
Extraction with 100 ml acetone; carry into 5 ml hexane; 50% recovery; 5 μl injection	*50 g*	*4*	*2*	*0.2*	$\mu g.kg^{-1}$
Purge and trap; 50% recovery; thermic desorption	*10 g*	*0.02*	*0.01*	*0.001*	$\mu g.kg^{-1}$
Water					
Direct injection	*25 μl*	*4*	*2*	*0.2*	$\mu g.l^{-1}$
Headspace (measured)	*10 ml*	*0.1*	*0.05*	*0.005*	$\mu g.l^{-1}$
Purge and trap; thermic desorption	*5 ml*	*0.02*	*0.01*	*0.001*	$\mu g.l^{-1}$
Extraction in 1 ml followed by injection of 5 μl; 10% recovery	*1 l*	*0.04* *(extr. with n-decane)*	*0.02*	*0.002* *(extr. with n-pentane)*	$\mu g.l^{-1}$
Air					
Direct injection in the gas chromatograph	*2 ml*	*50*	*25*	*2.5*	$\mu g.m^{-3}$
	20 ml	*5*	*2.5*	*0.25*	$\mu g.m^{-3}$
Cold trap or adsorption, followed by thermic desorption	*0.5 l*	*0.2*	*0.1*	*0.01*	$\mu g.m^{-3}$
	5 l	*0.02*	*0.01*	*0.001*	$\mu g.m^{-3}$
Adsorption; elution with 1 ml CS_2; injection of 5 μl	*0.5 l*	*40*	*20*	*2*	$\mu g.m^{-3}$
	5 l	*4*	*2*	*0.2*	$\mu g.m^{-3}$
	20 l	*1*	*0.5*	*0.05*	$\mu g.m^{-3}$

- Purge and trap analysis after suspension in water

Nowicki and Devine (1980) put 1 to 1.5 g of soil into an 8.5 ml screw cap bottle, which is closed after having been filled with pure water. Deuterium-marked 1,2-dichloromethane is injected into the bottle as an internal standard. After homogenization of the contents, 4 ml of the suspension is put in a liquid sample concentrator (LSC), by means of which a normal purge and trap analysis is carried out. The GC is connected to a

MS. The lower limit of the determination level is appr. 1 μg.kg^{-1}, for DCM as well.

- Vacuum evaporation, purge and trap analysis

Hiatt (1981) observed that the headspace methods recommended by the USEPA for the analysis of soil and biota, produce unacceptable results, because of the fact that detection limits are insufficiently low, whereas recoveries are too low. The following method is recommended by Hiatt to isolate substances from soil. The sample is placed in a vacuum and the volatile components are collected in a condensation vessel kept at -196 ^{o}C. After placing this condensation vessel in a normal purge and trap design, the contents are analyzed by means of a modified method 624 (US-EPA). With 10 g samples, to which 0.25 μg of various volatile halogen hydrocarbons had been added, recoveries were found of appr. 100% (for DCM no data were given, the samples being useless through laboratory contamination with this substance!). The method is not affected by the moisture content of the sample and has a recovery of 126 ± 22% for DCM (!) from sample of sediment-free water. Consequently the recovery of DCM from sediment has not been determined.

6.1.3. Determination in water

- Direct injection in the gas chromatograph

An automatic and continuous determination of halogenated hydrocarbons has been described by Grandi et al. (1984). The GC is equipped with two columns, in one of which water is retained, whereas in the other one the organic compounds are separated. By means of a valve-system the water is automatically removed from the first column, in counterflow, for DCM the lowest detection limit is 0.5 mg.l^{-1}, using a FID and a packed column.
Fujii (1977) injected 100 μl of a water sample directly into a GC-MS-system, of which the GC is equipped with a precolumn with diglycerol as a stationary phase, in which water is retained. The detection limit with the MS in the SIM-mode is 0.2 μg.l^{-1} for DCM.
Simmonds and Kerns (1979) applied direct analysis of 1 - 20 μl water samples, in which water is removed selectively by means of diffusion through a membrane placed before the injection gate of the GC. A detection limit of only 100 μg.l^{-1} is achieved for DCM, due to the relative insensitivity of the ECD.

Boos et al. (1985) injected the water sample into a short column, filled with calcium carbide which is situated before the GC column. As the water is converted into acetylene it cannot interfere with the ECE. Due to the slight sensitivity of the ECD for DCM a lowest detection limit of only 0.4 mg.l^{-1} is achieved.

- Static headspace analysis

This technique, in an automatized form, as applied by Akkerhuis (1985b) is recommended by Baggen et al. (1983). The instrument used is a Carlo Erba Mega 5360 gas chromatograph, equipped with a headspace automatic. A 25 meter fused silica column is used and flame ionization as well as electron capture detection are applied. The size of the sample is 10 ml. A salt is added to the sample. For DCM a lowest determination limit is reached in the order of 0.1 μg.l^{-1}.

Mieure (1980) reported a limit of 25 μg.l^{-1} (flame ionization detection; 1 ml samples) for the headspace determination of DCM.

Gruber (1984) described a headspace analysis in which, by double injection, a relative standard deviation of 0.5-5% with a detection limit of 0.1-1 μg.l^{-1} is reached in water samples (see Comba and Kaiser, 1983).

- Purge and trap technique; thermic desorption

This method has been described as the EPA Test Method 601, Purgeable Halocarbons (1982) and as the EPA Test Method 624, Purgeables (1982). In the former a GC with a EC-detection or a microcoulometer-detector is used, in the latter a GC-MS-system. The detection limits for DCM are reported to be 0.25 μg.l^{-1} and 2.8 μg.l^{-1}, respectively. Dreisch and Munson (1983) used the EPA method 624, with fused silica capillary columns instead of packed columns. DCM concentrations in the range of 1 to 20 μg.l^{-1} may be observed; the sample size is 5 ml. Practically identical results were obtained by Olynyk et al. (1981) and Trussell et al. (1981). The purge and trap method has also been applied in the studies to determine DCM in Meuse water (RIWA, 1983), mentioned in chapter 4.

- Solvent extraction

Although this method is frequently applied for the determination of e.g. trihalomethanes, it has not been described in the literature on DCM (Otson and Williams, 1981).

- Membrane permeation techniques

* Membrane permeation, and subsequent mass spectrometry

Mieure (1980) described how a mass spectrometer in the SIM mode can be connected to a water stream, using a membrane to separate the vacuum of the spectrometer from the water to be analyzed. Thus a lowest detection limit of 4 $\mu g.l^{-1}$ for DCM is obtained (spectrometer set at 49).

* Membrane permeation and subsequent carbon adsorption and carbon disulphide elution

A dynamic as well as a static design of this method were described by Blanchard and Hardy (1984). The organic substances diffused through the membrane are retained by active carbon and subsequently eluted with carbon disulphide followed by a gas chromatographic analysis. The authors used a concentration of 10 $mg.l^{-1}$ water for DCM. The use of rubber plugs in this design may result in DCM losses.

6.1.4. Determination in air

- By means of test tubes

The firm "Draeger" introduces tubes for the determination of DCM in air (measuring range 50-3,000 $mg.m^{-3}$). The relative standard deviation amounts to 15-10%. The colour change is from greenish brown to brownish green. In addition to DCM other halogenated hydrocarbons, hydrocarbons (petrol) and carbon monoxide are determined. Consequently, the method not being sufficiently selective, it is unsuitable for the determination of DCM in an environment where DCM is not the dominating contaminant.

- By means of infrared spectrometry

The DCM concentration in air may be immediately determined by using a gas cell with a variable optical range of 20 m maximally and by measuring at a wavelength of 13.3 μm. The detection limit as reported by the manufacturers (Wilks, Norwalk, USA) is 0.2 vpm wavelength (0.76 $mg.m^{-3}$). Other components in air that adsorb at the same wavelength (including chloroform, vinylchloride and (chlorinated) aromatics) may interfere with the measurements. The method should therefore generally be considered unsuitable if the presence of interfering components cannot be excluded.

- By means of gas chromatography

* Direct GC analysis without preconcentration

The lowest detection limit to be reached is presented in table 6.2. Publications, mentioning the actual reaching of this limit, are not available. Leveson et al. (1981) described an air analyzer for the detection of a wide range of air pollutants at concentrations of $< 4\ \mu g.m^{-3}$. The air, without preconcentration, is immediately being led, as a carrier, into a GC with a photo-ionization detector (PID) and subsequently analyzed. The data supplied by the manufacturers show that the lowest detection limit for DCM is in the order of magnitude of $10\ \mu g.m^{-3}$. The PID is not specific for DCM and the sensitivity for benzene, for instance, is ten times higher. The applicability of the instrument therefore depends highly on the contaminants, which are present in the air in addition to DCM. Interferences caused by these contaminants may also be limited by using a column with a greater separating capacity.

* GC-analysis

Freezing

Rasmussen et al. (1977) applied a method with which traces of halogenated hydrocarbons with a low electron capture absorption-coefficient are determined quantitatively at the $ng.m^{-3}$ level; 500 or 1000 ml of air is led through a thin tube, chilled at - 196 ^{o}C. After completely freezing out the pollutants, the tube is put in water of 95 ^{o}C and the components are injected into the column, kept at - 10 ^{o}C, after which the temperature of the column is programmed to 70 ^{o}C. EC or MS detection is used with the ECD and a sample size of 500 ml, the lowest detection limit for DCM is 15 $ng.m^{-3}$. From table 6.1. it may be stated that using the MSD the detection limit will be lower than 1.5 $ng.m^{-3}$.

Adsorption and liquid elution

The principle of adsorption to active carbon, desorption with carbon disulphide and GC analysis for DCM are described in the NIOSH handbook for analytical methods under method No. S 329 (1974) and in the "Nederlandse Voornorm" NVN 2794 (Bayense, 1985). In one evaluation study Kring et al. (1984) demonstrated several inadequacies in the NIOSH protocol: care should be taken in sampling humid air and laboratory validation of carbon tubes is highly recommended. DCM, however, was one of the substances tested for which the method met the NIOSH accuracy requirements. The NIOSH method is also discussed in the book of Halliday (1983): NIOSH method No. P&CAM 127. The sample size may be between 0.5 and 3.8 1. Measurements are carried out in the vpm-range and have a lowest detection limit of appr. 0.5 $mg.m^{-3}$.

Adsorption and thermic desorption
Parkes et al. (1976) apllied this technique for DCM, using a commercially available flash heater. A lowest detection limit of appr. 3 $\mu g.m^{-3}$ is reached (adsorbent: Chromosorb 101; detector: FID).

Adsorption, thermic desorption and cryo-focussing
Sparacino (1979) applied thermic desorption at 270 ^{o}C by means of a helium flow, collecting the desorbed components in a cold trap at -196 ^{o}C and injecting the trapped vapours into a glass capillary column, connected to a continuously scanning mass spectrometer. This combination of thermic desorption and cold trap has been developed and described by Pellizzari et al. (1975). A similar system has been described by Talman and Lakwijk (1979), for the analysis of air with volatile organic compounds containing 1 to 6 carbon atoms per molecule. The adsorption tube contained a combination of Tenax-GC and Ambersorb XE 340. The GC was equipped with a 50 m capillary system enabling analysis in the $ng.m^{-3}$ range.

6.1.5. Determination in biota

- Vacuum evaporation, freezing, purge and trap analysis

The method mentioned above (Hiatt, 1981) has also been used for samples of fish. Laboratory contamination of these samples with DCM was also observed. Based on results with the other substances the recovery may be estimated at 75%.

- Dynamic headspace analysis

In the dynamic headspace analysis, a gas flow is passed over rather than through the sample to be analyzed and subsequently through an absorbent. Foaming of the samples and other inconveniences are prevented, whereas the detection limits reached are considerably lower than with the static headspace method. Michael et al. (1980) (see Pellizzari, 1975) recommended this method for the determination of DCM in urine, blood, milk and adipose tissue (the analysis of fat samples was very difficult). The samples were suspended in water. The recoveries were determined by means of compounds marked with C14. The following data were obtained for DCM (an average of four determinations):

urine	(appr. 0.2 $\mu g.g^{-1}$)	80 ± 12%
blood	(appr. 0.3 $\mu g.g^{-1}$)	110 ± 8%
adipose tissue	(appr. 0.3 $\mu g.g^{-1}$)	48 ± 30%

The method is applicable to a content of up to 10 $\mu g.g^{-1}$.

6.1.6. Sample taking and handling, calibration and validation

From the following facts it may be evident that the reliablitiy of the determination of DCM in water and soil needs further studies.

- In The Netherlands DCM is occasionally found in groundwater, usually in concentrations lower than those for e.g. tri- and tetrachloroethane (Akkerhuis, 1985). Kobus (1985), however, considers DCM, along with trichloroethane, tetrachloroethane and 1,1,1-trichloroethene, to be one of the major chlorinated hydrocarbon contaminants in German groundwater.
- In a study on volatile chlorinated hydrocarbons in the Rhine and the Elbe the substance was not found (RIWA, 1984; ARGE-ELBE, 1983/4). In 1982, however, concentrations of < 0.1 $\mu g.l^{-1}$ to over 7 $\mu g.l^{-1}$ were observed in the Meuse (RIWA).
- An extensive study on the occurrence of volatile halogenated hydrocarbons in groundwater was carried out by the (then) RID and RIV (Trouwborst, 1981). Although DCM was found in several samples, it was not included in the study. One reason for it not being included was the use of an EC-detector with which DCM might not be distinguished from freons that could possibly be present. Another reason was the inadequate sensitivity of the detector for DCM in the low concentration ranges at which measurements were carried out (0.01 - 10 $\mu g.l^{-1}$) (Slingerland and Luijten, 1985). DCM was not included either in a multi-centre study on the determination of 15 volatile halogenated hydrocarbons in water. One multi-centre study, carried out in 1984 on the determination of halogenated hydrocarbons (trichloroethene and tetrachloroethene) in sandy soil, showed dissimilarities of up to a factor 100 in the results from the participating laboratories, and up to a factor 40 in the third round (Slingerland and Luijten, 1986). No data are available on ring assays in which DCM was one

of the substances to be determined. However, its great volatility is likely to give rise to greater problems than those occurring in assays of trichloroethene and tetrachloroethene. As volatile halogenated hydrocarbons may remain adsorbed very persistently to e.g. clayey soil, the purge and trap technique is rendered very time-consuming, necessitating it to be carried out at high temperatures (Slingerland, 1985). Daft (1985) observed the presence of traces of DCM in various laboratory-reagents, while another author observed the occurrence of laboratory contamination (Hiatt, 1981).

The control and guarantee of quality are applied only occasionally through the use of internal standards, with or without the method being tested with marked compounds (Michael et al., 1980; Hiatt,1981; Nowicki et al., 1980). In the field, internal standards are only rarely incorporated. Useful guidelines for the sampling of water and soil are not available. For water, techniques are applied which are commonly used for the determination of volatile components but the reliability for DCM has not been tested. The testing of methods on soil samples by means of a ring assay produced poor results (Slingerland and Luijten, 1986). Methods for air in the expected measuring range have not been tested.

6.2. MEASURING STRATEGIES

Measuring strategy aims at the drawing up of a measuring plan which should provide the desired results with as little effort (cost) as possible while the results should be acceptably accurate. A distinction may be made between measuring in order to establish the levels in the environment (local, regional and nationwide) and measuring in order to establish the origine (source-oriented). The choice of the measuring plan and the interpretation of the data collected are largely determined by what is known about the sources (ch. 2), their distribution and the resulting exposure levels (ch. 4), as well as the risks to be expected for man and ecosystems (ch. 5).

The accuracy of the measuring results depends on the number of samples over time and space, the variability over time and space of the variable to be determined (averages, percentiles) and on the measuring methods.

6.2.1. Soil

DCM is only found in soil and groundwater in relation to local sources of pollution such as industrial zones and garbage dumps. No indications have been found for diffuse distribution in groundwater and dry soil (see sections 3.1. and 4.2.). The measuring strategy should therefore be restricted to local pollution situations. It is not possible, however, to define a general strategy as all parameters of importance for dispersal will differ from place to place. The following points may be mentioned, however:

- Pollution will mainly take place in the form of a (dissolved) liquid, infiltrating through the unsaturated zone into the groundwater; depending on the density and the quantity, a density flow will occur. Therefore attention should be focussed on groundwater, in a number of cases necessitating drilling as deep as into the impermeable zone of the waterbearing stratum.
- However, to get a first impression of the extent of the pollution a cheaper exploration method may be applied, such as the sampling of air trapped in soil (semiquantitative; Neumayer, 1983).

The frequency of sampling (years) depends mainly on the flow rate of the groundwater (several tens of metres per year). The flow pattern may be changed drastically by environmental engineering measures.

6.2.2. Surface water

Changes in DCM concentrations occur as a result of changes in the way and to what extent it is used and through occasional changes in the emission (calamities). It is not to be expected that the use of DCM will increase (ch. 2). The present concentrations (0.005-4 $\mu g.l^{-1}$; ch. 4) are far below the level at wich harmful effects (500 $\mu g.l^{-1}$; ch. 5) are to be expected. An extensive measuring programme is therefore not essential. The fact that DCM is heavier than water has to be taken into account with regard to calamities.

6.2.3. Air

- Outdoor air

Considering the difference between the estimated, average, large-scale concentration (section 4.4.2.: < 1 $\mu g.m^{-3}$) and the toxicological limit value (section 5.5.1.: 1.7 $mg.m^{-3}$) it has been decided not to include a measuring strategy for this purpose. a measuring strategy for DCM near point sources will be discussed, however. Methods for the calculation of DCM concentrations near point sources are mentioned in chapter 2. The accuracy of the DCM concentrations thus determined is limited, near buildings deviations of up to a factor 10 from the actual concentration may occur. If the limit value is approximated, a more accurate estimate of the level may be called for. Annual average levels in the vicinity of reasonably constant, isolated point sources may be determined with an accuracy of 10% if several hundreds of 24-hour samples are taken and analyzed according to the Van Fett-Lahman scheme. The measuring effort required will practically double if a number of emitting sources are situated closely together. The presence of structures in the vicinity of sources will further affect the results considerably.

- Indoor air

In a number of cases (little or no ventilation) the use of paint strippers and spry-cans, as well as smoking may result in fairly high concentrations in indoor air. A measuring strategy would in that case have to be adapted to control measures (e.g. product requirements).

6.3. SUMMARY AND CONCLUSIONS

Depending on the analysis techniques used, the detection limits amount to 1 $\mu g.kg^{-1}$ in soil material, 0.1 $\mu g.l^{-1}$ in water, 1 $ng.m^{-3}$ in air and 10 $\mu g.kg^{-1}$ in biota. There are doubts as to the accuracy of the determination. However, the determination methods for air appear to be fairly reliable. In table 6.3. a summary is given of the processing methods, analysis techniques and detection limits for DCM in soil, water, air and biota. Concerning measuring strategies it may be stated that they are not essential for the environmental compartments in view of the great differences between the concentration levels (ch. 4) and the toxicological limiting values (ch. 5). However, attention should be paid to the use of products with DCM and to large emittents of the substance.

Table 6.3. Summary of measuring methods with corresponding concentration ranges and detection limits

Method	Sample size	Concentr. range	Detection limits	References
Soil				
Extraction, followed by GC			0.01-0.1 $mg.kg^{-1}$	Akkerhuis (1985)
headspace-GC	50 g		0.2 $mg.kg^{-1}$	Langelaan (1984)
purge and trap after susp. in water	1-1.5 g		appr. 1 $\mu g.kg^{-1}$	Nowicki (1980)
vacuumextraction	10 g		25 $\mu g.kg^{-1}$	Hiatt (1981)
Water				
direct analysis	4 μl		0.5 $mg.l^{-1}$	Grandi (1984)
	100 μl	1-50 $\mu g.l^{-1}$	0.2 $\mu g.l^{-1}$	Fujii (1977)
	1-20 μl	1-50 $\mu g.l^{-1}$	< 1 $\mu g.l^{-1}$	Simmonds (1979)
	appr. 1 μl		0.4 $mg.l^{-1}$	Boos (1985)
purge and trap	5 ml	10-200 $\mu g.l^{-1}$	0.25 $\mu g.l^{-1}$	EPA (1982)
	5 ml		2.8 $\mu g.l^{-1}$	EPA (1982)
	25 ml		1 $\mu g.l^{-1}$	Trussel et al., (1981)
head space	1 ml	10-100 $\mu g.l^{-1}$	0.1 $\mu g.l^{-1}$	Gruber (1984)
			25 $\mu g.l^{-1}$	Mieure (1980)
cell permeation		0.01-20 $mg.l^{-1}$	10 $mg.l^{-1}$	Blanchard (1984)
			4 $\mu g.l^{-1}$	Mieure (1980)
Air				
- test tubes		180-10800 $mg.m^{-3}$		Dräger (1985)
- infra red spectrometry			760 $\mu g.m^{-3}$	Wilks (1978)
- gas chromatogr. direct analysis	1 μl-1 ml	0.4 $\mu g.m^{-3}$ 400 $mg.m^{-3}$	10 $\mu g.m^{-3}$	Leveson (1981)
preconcentr. freezing out	100-500 ml	appr. 150 $ng.m^{-3}$	15 $ng.m^{-3}$	Rasmussen (1977)
adsorption therm. des.	100 ml-10 l	10 $\mu g.m^{-3}$ 100 $mg.m^{-3}$	2.7 $\mu g.m^{-3}$	Parkes (1976)
ads./therm des./cryofocussing	10 l	10-200 $ng.m^{-3}$	1 $ng.m^{-3}$	Sparacino (1979) Pellizzari (1975) Talman (1979)
Biota				
vacuumextr.	10 g		30 $\mu g.kg^{-1}$	Hiatt (1981)
dyn. headsp.	5-25 g		10 $\mu g.kg^{-1}$	Michael (1980)

7. POSSIBILITIES AND COSTS OF EMISSION REDUCTION

The possiblities to reduce the emission of DCM in the environment, as presented in chapter 2, are discussed in this chapter. The measures may vary from replacement of DCM with other substances, or replacement of the processes in which DCM is used with other processes, to keeping storage systems and process installations more closed, and the purification of effluents, with or without the possibility of recycling. Although a great number of these measures are not specifically aimed at concentration reduction in air, water or soil, they result in an overall reduction. Other measures are initially aimed at preventing the effluent from reaching one specific environmental compartment. However, they influence other flows to such an extent, that they may also be considered to be integrated. The presentation of the possibilities has therefore been worked out for total reduction of the emission into the environment. Subsequently, the effects of the various technical variants on the emission into the various environmental compartments are presented in totals.

7.1. REPLACEMENT OF DICHLOROMETHANE

A distinction may be made between the replacement of DCM with another substance in an existing process (which should hardly change, or not at all, as a result of the replacement) and replacement of processes (in which DCM is an important component) with other processes. The fact that the distinction is not quite clear is not essential in this context. However, the costs of the replacement of these processes are of another order of magnitude. The replacement of a substance or a process will result in the emission of other substances. Generally, it cannot be indicated whether this is more favourable from an environmental point of view. It has not been taken into consideration in describing the replacement possibilities given below.

7.1.1. Replacement of DCM as a solvent in chemical processes

In the chemical industry it appears possible to replace one or several processes, in which DCM is used as a solvent, with a completely different process. The extent to which this is pursued and the financial consequences this may involve is not known. As to the pharmaceutic industry there also may be possibilities to replace DCM in several processes. In particular cases DCM is a replacement for other solvents (e.g. of chloroform). It is not likely, however, that replacement with a compound other than from the group of organochlorine compounds will be effectuated in the immediate future. A considerable amount of research will need to be carried out before such a substitute can be put into practice.

7.1.2. Replacement of DCM as a cleaner and remover

Cleaning and removing of lacquer for which DCM is used, may be carried out in various ways, without using DCM or any other organochlorine compounds. Cleaning may take place as follows:

- in an aqueous environment (alkaline, steam)
- emulsion cleaning
- non-chemical (mechanical, air-blowing)
- with other organic solvents
- pyrolytic

Cleaning in an aqueous environment offers a great number of applications. Limiting factors may be e.g. the base material and the shape of the object to be treated. The presence of a considerable amount of cavities will render drying more difficult. Because of the fact that a vapour degreasing installation is not suitable for degreasing in an aqueous environment, replacement is rendered necessary, involving considerable costs. The replacement of the process of cold lacquer removing is easier and may be realized in a plant within 12 weeks (EPA, 1982). A limited emission reduction as a result of such replacements is to be expected in the near future (appr. 100 tons per year).

Emulsion cleaning and non-chemical cleaning pose more problems. In emulsion cleaning an "oily" layer remains on the object. In non-chemical cleaning it is difficult to achieve the same standard.

Pyrolysis as a cleaning technique has been put into practice in The Netherlands. However, its applicability is only limited, depending on the nature of the base material, the quality and shape of the object to be treated.

A great number of the above-mentioned problems do not occur in cleaning with organic solvents not belonging to the group of organochlorine compounds. Therefore studies on replacement with these substances are carried out in various places. Acetone, for example, would present a good alternative for the cleaning of, for instance, tools and equipment in polyester processing plants and is used for that purpose in a number of concerns. However, the use of acetone and other suitable organic solvents results in an increased fire hazard. Plants having been completely adjusted to an increased fire hazard may be able to carry out the above-mentioned replacement without much additional cost. For other plants, however, it may involve the need for drastic changes at considerable costs.
Studies are being carried out on the replacement in paint strippers for use by private individuals. Because of the fact that a great number of alternatives is less user-friendly, only a number of the above-mentioned alternatives is suitable. A measure not involving replacement c.q. emission reduction is the addition of particular substances to the paint stripper, which inhibit evaporation of DCM and consequently decrease exposure levels during usage. This may offer possibilities for future applications.

7.1.3. Replacement in aerosols

Through its unique properties, DCM is applicable as a solvent, decreasing the pressure of the propellant mixture at the same time. It may, in principle, be partly or completely replaced in particular applications. However, according to the EPA (1982) it is as yet still irreplaceable in at least 10% of the applications. It has not been determined whether this percentage is the same in The Netherlands. Each replacement involves cost of research, according to the EPA varying from 15 to 160 hours per product (Dfl. 1,000-10,000) bearing in mind there are a great number of different products. For some products costs may be considerably higher, however. New labelling may cost up to 20,000 guilders per product (EPA, 1982). Considering, however, the fact that new labels are frequently made, the costs will be slight.

7.2. EMISSION REDUCTION TECHNIQUES

7.2.1. Waste water treatment techniques

DCM is fairly soluble in water resulting in waste water flows with DCM in various plants. In many cases the purification will in practice start with a volatilization sometimes not aimed at. The following technologies are more consciously applied:

- Stripping with air
  This technology is very effective for reasonably concentrated waste flows, as the amount of air needed may be limited. This air flow can/needs to be retreated, for instance with active carbon. The concentrations may be decreased to below 1 $mg.l^{-1}$ (Oranjewoud, 1983). This implies that waste water flows with concentrations of several $mg.l^{-1}$, being treated in aerobic purification systems, are already being stripped of a considerable amount of DCM during aerating.

- Steam stripping
  Results, similar to those with air stripping, are obtained. In this case retreatment is necessary by way of phase separation following condensation and consequently recycling. Steam stripping is applied in The Netherlands in several places, particularly integrated in recycling systems. Further reduction of the total emission into the environment by appr. 200 tons per year (incl. Dfl. 0.50-1.00 per kg yield) is possible by means of steam stripping at costs varying from 1 to 25 guilders per kg DCM.

- Adsorption to active carbon
  Less concentrated flows are also purified with this technique, which is usually the last one in a series of purification phases. It is, for instance, applied in the drinking water production. However, it is also applied in the industrial waste water treatment in The Netherlands, where DCM is removed as one of the components. The efficiency of the installations concerned has not been determined. For installations in the United States an average efficiency of 70% (with considerable variation) has been observed (EPA, 1981).

- Biological purification with oxygen

  For aerobic purification processes generally, data on solvents such as DCM are no more readily available than those on the total removal. The extent to which it either concerns decomposition or transition into air during aerating may depend on the influent concentration and the sludge composition (see: Stripping with air). Laboratory tests at rather high and constant influent concentrations have shown that over 99% of DCM was removed, while only 5% was being stripped (Stover, 1983). In various instances in The Netherlands, total removal percentages of 95% (Van Luin and Starkenburg, 1982) and 90% were measured.

- Biological purification without oxygen

  DCM may inhibit anaerobic decomposition when its concentrations in waste water are too high. In such cases it will not be decomposed, although part of it may pass into the biogas and subsequently be burnt.

7.2.2. Techniques for emission reduction into air

The emission into air may be reduced by the application of purification techniques, by the implementation of processes in more enclosed installations and, to a certain extent, by improved monitoring and work tidyness. The following purification technologies may be considered:

- Condensation

  This may only be applied on very high concentration flows (low flow rates). It is applied frequently in the chemical and pharmaceutical industry, following vapourisation, drying or distillation processes. It may also be applied in the ventilation of storage tanks, reactors or vacuum pumps. Apart from initial and final temperatures, the efficiency is determined by the initial concentration. In The Netherlands, one example has been recorded of process-integrated condensation during the application of a photosensitive film, where DCM was used as the solvent (Stemerding, 1984). It is estimated that appr. 200 tons of DCM may be condensed annually, at (net) costs varying from 0 to 30 guilders per kg (inclusive of a benefit of Dfl. 1 per kg recycled DCM).

- Adsorption to active carbon

In several localities in The Netherlands adsorption to active carbon is applied. Recycling is the major consideration in these cases. Regeneration with steam is a possibility, although this results in the decomposition of a small percentage of DCM. It may be implemented with small, fairly concentrated, flows (for example after condensors), but in principle also with more diluted flows (source or even space exhaustion). The costs do increase considerably with the outflow. For the cleansing of air and water flows originating from baths for the removal of lacquer a combination of active carbon and stripping may be selected (Kohler and Halbartschlager, 1984). At a total (net) expenditure of between 0 and 30 guilders per kg DCM 1,500-2,000 tons may be removed from effluent air flows annually (inclusive of a benefit of Dfl. 0.50-1.00 per kg recycled DCM).

- Afterburning

During burning of DCM, HCl is formed. Afterburning should be followed by washing with water or alkaline solution. The discharge of washing water is only allowed after it having been neutralised, which renders this approach rather complicated. In The Netherlands this technique is not applied for DCM, although it may be suitable fo small air flows with high concentrations of various organic components. In order to prevent the formation of other substances hazardous to health the combustion conditions should be optimal.

- Biofiltration

This technique may be expected to be used for DCM in the near future. Experiments do suggest, however, that the decomposition capacity of (expecially inocculated) filters is as yet rather low. This suggests that this technology may not be suitable for considerable loads of DCM. The application of source exhaustion (with a restricted output and various components) seems to offer the best prospects. The contribution to a possibly comprehensive cleansing is as yet estimated at several tens of tons per year.

- Washing

In view of the high volatility of DCM washing seems hardly suitable as a technique for the reduction of emission. In fact, the substance is diluted in the water phase. The prospects for this technique are limited to situations where water purification may be undertaken adequately at low cost. One could think of the availability of large quantities of steam, or of a purification plant with excess capacity. In one plant in The Netherlands this technique is applied, in combination with steam stripping.

7.2.3. Measures concerning installations or processing

The emission of DCM into the environment may be reduced by measures aimed at keeping processing installations and storage systems more closed. Examples of this are:

- application of duplicate mechanical seals in pumps (cleansing of abstruction fluid)
- vapour balance systems
- isolation of storage tanks
- storage of DCM-containing waste in closed systems
- The use of a layer of water to cover baths containing DCM (this is already being applied in various places)

The latter two measures call for tidyness. Generally speaking, process management may be an important factor in determining the emission. One aspect of importance in this respect is the frequency of inspection and maintenance of installations. It has not been assessed to what extent the above-mentioned measures have already been applied. Therefore, hardly any indication can be given of possibilities for the further reduction of emission.

Cleansing of abstruction fluid may reduce the emission of DCM by 100 tons. In connection with the storage of chemical waste, in particular of polyester processing plants, emission into air might be reduced by 30 tons per year.

7.3. COST OF EMISSION REDUCTION

The possibilities for reduction of the total emission of DCM have been considered for the major industrial emittents or groups of emittents. Specific industrial situations of relevance for the determination of technical possibilities and/or their costs were taken into account as much as possible. Several dozens of specific sources were examined and worked out. For other sources, data from comparable situations were utilised to estimate the emission reduction and the corresponding costs. In determining the annual costs, only those fixed and variable costs connected with the measure were taken into account. An interest rate of 6% is used to determine depreciation. This rate was decided upon for the sake of unambiguity, even though it differs from those used in the cost accounting of a number of companies that balance the investments involved against profitable investments. Measures already considered for implementation (e.g. specific requirements as part of permit regulations, investments already decided upon) have been included without additional costs.

In table 7.1. the results of these elaborations are summarized, given per company activity. In table 7.2. it is indicated to what extent the discharge of DCM into water may be reduced and how much effort this may require. It is assumed that this will not lead to a replacement by emissions into air. The costs of stripping of DCM in particular instances are lower than those presented in table 7.2.

It is obvious that large sources and concentrated flows may be cleansed with relatively the least effort. After the implementation of measures listed in table 7.1., the purification of diffuse sources and residual emissions remaining in the chemical and pharmaceutical industry is considerably more difficult. In the synthetics processing and the production of aerosols, where emissions are mainly related to space exhaustion, the reduction of emission is very expensive; up to several hundreds of guilders per kg DCM removed.

The effect of a certain effort upon emissions into air of individual concerns was determined as well, in this case expressed in guilders per kg DCM prevented. The extent of an emission from a point source and the number of point sources with a certain emission may be of interest in estimating the number of people exposed to a certain concentration of DCM in air.

7.4. SUMMARY AND CONCLUSIONS

The replacement of either DCM by other compounds in existing processes or of such processes by other ones has only limited scope for the time being; more extensive research in this area is probably desirable. The treatment of effluent water flows containing DCM is possible. This may result in unintended vapourisation of DCM. Emissions into air may be reduced by the application of purification techniques, the implementation of processes in more enclosed installations and, to a certain extent, by improved checking and greater tidyness.

Table 7.1. Summary of the possible reduction of the total emission into environment (in tons per year) in connection with various industrial activities and the related cost

Industrial activity	*Total emission in 1984*	*Reduction of emission and cost in guilderd per kg DCM removed*								
		autonomous	*< 1*	*%**	*1-3*	*%**	*3-10*	*%**	*10-30*	*%**
Chemical industry	*1332*	*7*	*724*	*55*	*23*	*56*	-	*56*	*60*	*61*
Pharmaceutical ind.	*1106*	*40*	*281*	*26*	*88*	*35*	*154*	*49*	*130*	*61*
Electrotechnical ind.	*385*	*242*	*10*	*7*	*71*	*57*	-	*57*	-	*57*
Synthetics processing	*341*	-	*19*	*6*	*44*	*18*	*7*	*21*	*57*	*37*
Paint and lacquer ind.	*192*	-	*20*	*10*	*72*	*48*	*40*	*69*	-	*69*
Aerosols production	*38*	-	-	-	-	-	-	-	*6*	*16*
Storage and transit	*42*	-	-	-	*11*	*26*	*6*	*40*	-	*40*
Others	*485*	-	-	-	*20*	*4*	*229*	*51*	*49*	*61*
Total	*3921*	*289*	*1054*	*29*	*329*	*38*	*531*	*53*	*302*	*61*

** cumulative of residual emission after autonomous development*

Table 7.2. Reduction of DCM discharges in effluent water

Industrial activity	*DCM discharges in tons per year*				
	situation 1984	*Autonomous*	*Costs of cleansing in guilders per kg DCM*		
			1-3	*3-10*	*10-30*
Chemical industry	*15*	*7*	-	-	-
Pharmaceutical industry	*41*	-	*9*	-	*27*
Others	*12*	-	-	*6*	-

Table 7.3. provides an overview of the current distribution and the distribution after a given effort. Only those concerns were taken into consideration which under current conditions have an emission of more than 20 tons of DCM per year.

Table 7.3. *Results of the introduction of emission reduction measures on the emissions into air of plants which in 1984 had an emission of more than 20 tons per year*

Emission per concern (tons per year)	*Number of concerns before and after sanitation*					
	Situation in 1984	*Autonomous*	*Cost of sanitation in guilders per kg DCM*			
			< 1	*1-3*	*3-10*	*10-30*
< 20	-	*3*	*7*	*11*	*14*	*17*
20 - 50	*11*	*10*	*9*	*8*	*6*	*4*
50 -100	*8*	*6*	*5*	*2*	*1*	*1*
100-200	*2*	*2*	*1*	*1*	*2*	*1*
200-500	*2*	*2*	*3*	*3*	*2*	*2*
> 500	*2*	*2*	-	-	-	-

On account of autonomous developments an emission reduction of 289 tons per year is to be expected (mainly in the electrotechnical industry). Against costs of < 1, 1-3, 3-10 and 10-30 guilders per kg of DCM prevented, reductions of respectively 1,054; 329; 531 an 302 tons of DCM may be achieved. Diffuse sources and residual emissions may be difficult to control against considerably higher costs.

8. BUSINESS ECONOMIC CONSEQUENCES OF EMISSION REDUCTION

8.1. GENERAL

This chapter will dwell on the business economic consequences of the measures proposed in chapter 7. In view of the vast diversity in characteristics and the environmental measures to be taken it will be necessary to treat each branch of industry separately. For each branch of industry, an outline of its nature, size and composition (structural outline) will be given. In cases where only a few companies within one branch of industry utilise DCM, such a structural outline will be too general. In such cases an indication will be given of the proportional contribution of such firms to the total volume of the branch of industry concerned. As reliable data are lacking, rough estimates of this proportional contribution will be given for very heterogeneous branches of industry, such as the chemical industry.

In order to gain an insight into the functioning of a given branch of industry, the MIOW method ('t Gilde et al., 1986) is used. In this method, three key variables are being distinguished: the market situation, the international competition, and the resilience. In the respective paragraphs, the values of these key variables will be determined on the basis of a number of specific characteristics of the branches of industry concerned. Viewed in the context of their mutual interdependency, the three variables characterize the conditions prevailing in each branch of industry rather succinctly. These conditions determine the possibilities of industry to respond to measures imposed from outside.

Two restrictions still need to be pointed out. In the first place, no estimate will be obtained of the maximum feasible effect of measures aimed at emission reduction. This is due to the fact that (very) expensive measures have not been taken into consideration in chapter 7. In the second place, it is possible that other substances emitted in a given branch of industry, in addition to DCM, may require additional measures. This chapter does not cover the cumulative business economic consequences of several measures that may need to be taken concurrently. CBS statistics (1984) and other sources of data were used. More details may be found in the note of the IvM (1986).

8.2. CHEMICAL INDUSTRY

The chemical industry forms a very heterogeneous branch of industry. Broadly defined, it also encompasses the pharmaceutical and paint industries which will be treated separately in 8.3. and 8.5. Leaving these sectors aside, in The Netherlands this branch of industry counts 206 companies with more than ten employees each. In 1984 they employed a total of 64,600 people and attained a turnover of more than 37 billion guilders. The use of DCM as a solvent and as a reaction medium is limited to only a few manufacturing processes, that are applied by some companies. More specifically, this relates to petro-chemistry, the production of synthetics and the production of inorganic raw materials. These belong to the so-called basic chemical industry, which produces chemical commodities and semi-finished products.

The basic chemical industry consists mainly of large-scale plants with a rather weak market position. The international competition is substantial and the companies exhibit a reasonable resilience. In summary, one may characterise the basic chemical industry as a sector operating at the international level in search of a new market equilibrium after several years of severe difficulties.

According to table 8.1. 64% of the emission may be prevented at a cost of 1.5 million guilders annually. Another 1.2 million guilders may be instrumental in the reduction of current emission levels by an additional 5%.

Table 8.1. Measures for the reduction of emissions in the chemical industry

Emission (tons per year)		*Cost (millions of guilders per year)*
1,338		
480	*(36%)*	*1.5*
420	*(31%)*	*2.7*

The annual costs will, therefore, remain below 3 million guilders. This is slightly more than 0.3% of the one billion guilders turnover and one percent of the added value. It definitely does not constitute a drastic cost increase. For this reason one may expect that the measures proposed will not essentially affect the relevant concerns. It is not to be excluded, however, that they may lead to considerations to discontinue certain processes. In view of the low degree of labour intensity, the impact on employment will be negligible.

Finally the effects of emission-reducing measures on the sales of DCM may be mentioned. The consequences for the producers have not been estimated.

8.3. PHARMACEUTICAL INDUSTRY

In the pharmaceutical industry drugs are being manufactured, along with the necessary basic ingredients and semi-finished products. This branch of industry also produces substances with additional applications, such as enzymes. DCM is applied as a solvent and as an extraction medium.

In The Netherlands, 50 companies with more than 10 employees each are involved in the pharmaceutical industry. The average volume of these concerns is large. Some 94% of the total production takes place in plants with more than 50 employees. The five largest ones, which have an annual turnover of over 250 million guilders each, share 90% of the production capacity between them.

The most important companies are large and their resilience ranges from reasonable to fair. They are faced with an unstable market situation and substantial international competition. In summary, this branch of industry comprises a group of reasonably healthy concerns with good possibilities for coping with setbacks.

According to table 8.2. 58% of the emission may be prevented at a cost of 2.1 million guilders annually. A further reduction of 17% of the present emission will cost the three companies involved 3.7 million guilders per year. The total costs of the proposed measures is appr. 6 million guilders per year. That represents 0.5% of the turnover and almost one percent of the added value in the three companies. The costs will therefore not rise drastically. Hence, it may be expected that the pharmaceutical industry will not suffer any essential loss of competitiveness.

Table 8.2. Measures for the reduction of emissions in the pharmaceutical industry

Emission *(tons per year)*	*Costs* *(in millions of guilders per year)*
1,094	
465 (42%)	*2.1*
277 (25%)	*5.8*

8.4. ELECTROTECHNICAL INDUSTRY

The electrotechnical industry produces a wide variety of capital goods as well as commodities. These products utilise electricity either as a source of power or energy (power current) or as a data carrier (low-voltage current). Within this branch of industry the sectors for power current and low-voltage current products are of about equal importance. DCM is used in the surface treatment of metals, which forms only a small part of the total production process. The use is not limited to a certain sector.

In 1984 the turnover in the electrotechnical industry amounted to 21,320 million guilders. It offered employment to 111,000 people, i.e. 11,400 fewer than in 1974.

Within the electrotechnical industry a few very large firms operate alongside a large number of middle-sized and small ones. The market situation is unstable and international competition is strong. In summary, the electrotechnical industry may be characterised as a vulnerable branch of industry.

As the surface treatment of metals constitutes only a small part of the total production process, one should not expect large cost effects from additional environmental measures. According to chapter 7, 84% of the emission may be prevented at a cost of 0.3 million guilders annually. This amounts to less than 0.1% of either turnover, or added value. The proposed measures are therfore not expected to result in noticeable effects on the electrotechnical industry.

8.5. PAINT INDUSTRY

The paint industry forms part of the chemical end-products industry. In this branch of industry, chemical treatments do not take place. By means of physical processes, chemical products procured from elsewhere, such as solvents, thickeners, pigments and filling materials are converted into paints, lacquers, varnishes, fillers, etc. DCM is one of the less important solvents (in 1979 constituting 3% of the total solvents usage). It also forms the basis for stripping compounds.

In 1984 the total turnover of the paint industry amounted to 1,346 million guilders. The total number of employees was appr. 5,800 which is considerably below the number of 7,300 recorded for 1972.

The paint industry is characterised by middle-sized firms with, in general, a low resilience. The market situation is weak and international competition is strong for the middle-sized firms. In summary, the paint industry may be characterised as a vulnerable branch of industry that (with the exception of the two largest concerns) has few possibilities to cope with setbacks.

In chapter 7 it appeard that 69% of the emission of DCM may be prevented at a cost of 0.2 million guilders annually. This amount is less than 0.1% of the added value and the turnover. Despite the weak position of this branch of industry, these modest amounts are not expected to result in far-reaching effects on competitiveness or employment.

8.6. SYNTHETICS PROCESSING INDUSTRY

In this branch of industry semi-finished products emanating from the chemical industry are subjected to various treatments. These involve the use of a variety of techniques, such as injection moulding, pressing and extrusion. Most concerns apply a combination of these techniques. DCM is used as a cleansing agent for tools, in particular in polyester processing plants. Within this branch of industry, these plants constitute a distinct group, about which only few data are available. Polyester processing companies are mostly small and their market position is weak. They experience little international competition and they are probably reasonably resilient.

The possibilities for a drastic reduction of the emission with affordable measures appear to be limited. A reduction of the emission by 34% will cost

1.3 million guilders annually. This represents approximately 1% of the added value, or 0.5% of the relevant turnover (300 million guilders per year). In spite of the fact that key variables are not unequivocally healthy, it is not to be expected that measures of this order of magnitude will worsen the prospects of the firms concerned in an essential way. Nevertheless, prudence is called for.

8.7. SUMMARY AND CONCLUSIONS

In table 8.4. the most important data on the five branches of industry considered have been listed. The increase in cost, expected as a result of the measures proposed are indicated as well.

Table 8.4. Overview of branches of industry considered

Branch of industry	*Structure (company size)*	*Market situation*	*International competition*	*Resilience*	*Cost increase (% of added value)*
Chemistry	*large*	*weak*	*strong*	*reasonable*	*1*
Pharmacy	*large*	*unstable*	*strong*	*reasonable/ fair*	*1*
Electro-technical	*large/ small*	*unstable*	*strong*	*weak*	*< 0.1*
Paint	*medium-sized*	*weak*	*strong*	*weak*	*< 0.1*
Synthetics processing	*small*	*weak*	*weak*	*reasonable*	*1*

Considering the values of key variables, in the pharmaceutical industry these are better than average, while for the paint industry they are worse. In the remaining three branches of industry relatively good values alternate with relatively bad ones. Considering the cost increase to be expected, a clear-cut dichotomy may be distinguished: for the chemical, pharmaceutical and synthetics processing industries this increase will be noticeable, but not drastic. For the electrotechnical and paint industries the cost increase is negligible. The conclusion is drawn that the business economic consequences of the measures proposed are very minor. The greatest influence will be felt by the synthetics processing industry, to be followed in order of declining severity by the chemical, pharmaceutical, paint and electrotechnical industries. Finally, it should be noted that no attempt was made to determine whether the environmental costs concerned may affect those sectors of industry where DCM is being used.

9. EVALUATION

9.1. RISKS AND GROUPS AT RISK

9.1.1. Risks for man

For the time being, DCM is not considered carcinogenic for man; the data available do not permit for an assessment of this aspect. As epidemiological data are also insufficient, the limit values have been determined on the basis of no effect levels in chronical animal experiments, applying a safety factor of 100: orally 0.06 $mg.kg^{-1}$ body weight per day and by inhalation 1.7 $mg.m^{-3}$ as a 24 hr time-weighted average. Based on these figures a limit value of 490 $mg.m^{-3}$ has been calculated for exposure of short duration (5 min). If these values are compared with exposure levels in the environment (4.2 $mg.day^{-1}$ compared with a few $\mu g.day^{-1}$ orally; 20.4 $mg.day^{-1}$ compared with a maximum of appr. 1 $mg.day^{-1}$), it may be generally postulated that the contemporary DCM concentrations do not pose a threat to human health. However, situations round industrial sources and indoors in connection with the use of spray-cans or stripping compounds require further analysis.

Averages per hour and per year have been calculated for industrial sources. The 24 hr averages may be estimated on the basis of experiences with similar situations, where these are in the order of approximately half the hourly averages. The emissions from one source resulting in DCM concentrations of respectively 1,700; 170 and 17 $\mu g.m^{-3}$ at distances of 60; 100 and 500 meters from that source have been determined. The results are summarized in table 9.1.

Thus, a comparison can be made with source intensities found in The Netherlands (table 7.3.). It needs to be pointed out that differences may occur in specific situations, especially at short distances. This is, for instance, true for companies with several sources scattered over an industrial park. The comparison shows that, at distances of 500 meters or more, values of 1,700 $\mu g.m^{-3}$ are never exceeded while values of 170 $\mu g.m^{-3}$ are, under current conditions, only exceeded near a few plants. The value of 17 $\mu g.m^{-3}$ is, at that distance, probably exceeded near some 20 plants. After the implementation of measures at a cost of up to Dfl. 30 per kg, this number will have decreased to appr. 5 plants. The situation at shorter distances from the source is quite different. Whether any people will be exposed to the concentrations at this distance, and how many, depends on the presence of residential structures in the immediate vicinity. Indeed, several situations exist where rather large sources are placed in or near residential areas.

Table 9.1. Source intensities (in tons per year) leading to concentrations of 1,700; 170 and 17 $\mu g.m^{-3}$ at various distances from the source

Distance	*1.700*		*170*		*17*	
(meters)	*Hour**	*Year*	*Hour**	*Year*	*Hour**	*Year*
60	*17*	*780*	*1.7*	*78*	*0.2*	*8*
100		*2,180*		*218*		*22*
500	*1,700*	*34,000*	*170*	*3,400*	*17*	*340*

** at 60 m maximum values; at 500 m 99.5 percentiles*

On the basis of these data it may be assumed that the value of 1,700 $\mu g.m^{-3}$, as a 24 hr average (99.5 percentile), is being exceeded in 10 to 20 places in close proximity to the source (60 meters), and a few places also at 100 meters. The indicated measures of up to Dfl. 30 per kg will reduce the occurrence of excess values in residential areas to a few days per year in two or three places.

The values of 170 and 17 $\mu g.m^{-3}$ are exceeded in many places. The measures specified in this report will be insufficient to cope with these.

For peak loads (5 min) a limit value is proposed of 490 $mg.m^{-3}$. As the 24 hr average of 1.7 $mg.m^{-3}$ is maintained in addition, the load should be zero for the remaining part of the day. In many instances this cannot be expected to happen, if only for the fact that the use of spray-cans or stripping compounds often leads to exposures of well over five minutes. Both with paint stripping and with the use of spray-cans, 5 min concentrations were found to exceed the limit value mentioned.

In principle, possibilities exist to (partially) replace DCM in many types of spray-cans, but probably not (yet) in all of them. A combination of DCM replacement and the provision of recommendations concerning ventilation with products containing DCM, will probably be sufficient to avoid exceeding the recommended maximum peak loads in most instances.

Risk groups are pregnant women, persons with a cardiac disease and smokers.

9.1.2. Risks for ecosystems

Whereas DCM concentrations in water vary around 0.1 $\mu g.l^{-1}$, the level where ecotoxicological effects may be expected was estimated at more than 500 $\mu g.l^{-1}$. In view of this difference, DCM does not present a threat to the aquatic environment at the national level. Locally, however, some problems may occur in connection with the high volumes of a number of known industrial discharges and incidentally high effluent concentrations from sewage treatment plants. Technical measures are feasible. In addition, monitoring may be crucial.

In respect of terrestrial ecosystems, insufficient data are available to arrive at a limit value. It may be postulated that current concentrations do not pose a threat to terrestrial ecosystems either, for the following reasons: (1) the vast differences between the acute toxic values for earth worms (LC50 > 1,000 $mg.kg^{-1}$) and mammals (LC50: 49-79 $g.m^{-3}$; LD50: 3 g-$.kg^{-1}$ body weight), (2) the low exposure levels in the environment (groundwater < 10 $\mu g.l^{-1}$, soil material appr. 2 $ng.kg^{-1}$, air 0.6 $\mu g.m^{-3}$ nationally and 10-100 $\mu g.m^{-3}$ locally) and (3) the limited capacity of DCM for bio-accumulation.

In view of the possibility of cumulative aspecific effects of compounds with a similar mode of action, a further reduction of the emission levels could be taken into consideration, certainly if the costs would be low and the business economic effects probably modest. For this reason, a rough estimate is given of environmental DCM concentrations in a state of equilibrium (according to the method described in 3.5.), following autonomous developments and the implementation of measures. If the fact that rather intangible diffuse sources produce 44% of the total emission is taken into account, it appears that an emission reduction of 34% of the total may be achieved against reasonably low cost (less than 30 guilders per kg of DCM). this will, at the national level, lead to a reduction of DCM concentrations in water and air of up to 25-30%; locally the effect may of course be greater.

9.1.3. Other risks

Neither global effects nor effects on materials are to be expected of current concentrations. Insufficient data are available for an assessment of transformation products of DCM.

9.2. CONCLUSIONS AND RECOMMENDATIONS

Conclusions

- Current DCM concentrations in the environment do not pose a threat to man, ecosystems or materials, with the possible exception of situations in close proximity to large industrial sources. Global effects are not to be expected either.
- Air concentrations inside human habitations may exceed the toxicological limit value (490 $mg.m^{-3}$) during five minutes as a result of the use of spray-cans and paint strippers. In work places it is not unlikely that the intended MAC-value (TGG of 350 $mg.m^{-3}$ over 8 hours) is being exceeded.

Recommendations

- Further studies on the use of DCM inside buildings, the resulting concentrations and exposure times, the effect of ventilation and the possibilities for the replacement of DCM, particularly in spray-cans.
- Further studies on the occurrence of cumulative effects of DCM and compounds with a similar mode of action, to provide a basis for the consideration of measures to reduce emissions, in view of the low costs and the limited business economic impact.

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ADDENDUM INDUSTRY*

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1. GENERAL REMARKS

When dichloromethane enters the atmosphere, it is broken down by photochemically initiated reactions with OH radicals and has an atmospheric lifetime of 0.7 years. DCM has been shown (see this document 3.3.2.) to have no influence on smog production.

Calculations show that only 2.5 percent of emitted DCM at ground level reaches the stratosphere. On this basis DCM does not contribute significantly to any possible ozone depletion (CEFIC BIT, 1982).

Since DCM is volatile and is also biodegradable, only very low levels are found in the environment (Herbert, 1986).

There are seven animal studies, only one of which, an inhalation study in the sensitive $B_6C_3F_1$ mouse at high dose levels showed tumors in the liver and lung. The other six studies did not show any carcinogenic effects. The carcinogenic response was not found in rats or hamsters. The species differences in the carcinogenic effect of DCM correlates well with the extent to which the various species metabolize DCM by the glutathione-S-transferase pathway (ECETOC, 1987). This pathway is not significant in man. There is currently no evidence for any carcinogenic, mutagenic or teratogenic effect in humans. Epidemiology studies have shown no significant increases for any cause of death, including cancer.

From this document it is clear (4.4.2.) that the ambient concentrations can be estimated at 0.6 $\mu g.m^{-3}$. The no-effect level (NOEL) in rats has been shown to be 173 $mg.m^{-3}$. Allowing for a safety factor of 100, the NOEL for man may be estimated at 1,730 $\mu g.m^{-3}$. Hence, the ambient concentration is

2,000 times lower (ie 3 orders of magnitude). Moreover, in humans the main effect of acute exposure are reversible. Long-term behavioural and neurological studies in animals have shown no significant adverse effects. There is no evidence for the irreversible central nervous system effects sometimes referred to as Danish Painters Syndrome. DCM can be used safely and all hazards avoided if ventilation is adequate to keep exposure below the Occupational Exposure Limit.

The unique combination of properties of DCM, low boiling point, high solvency power, low toxicity and non-flammability has led to its use in a large variety of applications and industries. Since there is no evidence for any adverse effects for man on the environment, we conclude that there is no reason for any restriction in the production of DCM.

2. **COMMENTS PER CHAPTER**

Chapter 4, par. 4.4.1.

Recent investigations have shown that when an aerosol jet is used, peak concentration of DCM of between 105-280 $mg.m^{-3}$ may occur. The conditions were as follows:

- room 2 x 4 x 3.1 m, - no ventilation, door closed;
- time of application 8 seconds;
- two successive applications with 10 minutes interval.

Within 10 minutes the concentration of DCM was again at background level (Battagello, 1984).

Other recent studies in a hairdressing salon have shown that the average concentrations of DCM in the atmosphere are very low and well below the Occupational Exposure Limit. Average values are between 1 - 4 ppm (3.5 - 14 $mg.m^{-3}$) whilst with poor ventilation levels may be 8 - 16 ppm (28 - 56 $mg.m^{-3}$). The highest values for momentary exposure were 18 - 26 ppm (63 - 91 $mg.m^{-3}$).

Chapter 5, par. 5.3.1.

In the evaluation of human toxicology, a method of calculation for a limit value for short-term exposure is used which is poorly documented. Moreover, this method is not generally accepted by the scientific community. The complex metabolism of DCM, which involves two pathways with different enzyme/substrate affinities and saturation levels, can not be adequately described by lineair extrapolation from high to low dose. This can only be achieved by taking into account the metabolic and kinetic constants that describe the behaviour of DCM at different doses in each species. Equally, the marked species difference in the utilisation of the glutathione pathway cannot be described by cross species extrapolations based on body weight or surface area corrections.

Accurate risk assessment should, therefore, be based on the internal dose of metabolites from the glutathione-S-transferase pathway utilising species dependant physiological and pharmacokinetic paramaters to quantify the internal dose. As a result of this recent work, (ECETOC, 1987) it is now possible to undertake this type of risk assessment using the mathematic model developed by Anderson et al. (1987). The glutathione pathway has clearly been identified as the pathway of risk. In vivo pharmacokinetic data is now available at up to five dose levels from 100 to 4,000 ppm, including blood levels of the parent chemical, post exposure elimination of parent chemical and the elimination of CO and CO_2 both during and post exposure and studies to identify the source of CO_2 at different dose levels. Furthermore, this data is available from studies using the same species, strains and exposure conditions used in the NTP cancer bioassay. It is now possible to determine form this data the in vivo metabolic constants K_m and V_{max} for rats and mice and to use the in vitro values of these parameters for scaling to the hamster and human where the same depth of in vivo data is not available. These values, in conjunction with the known and measured physiological parameters, for DCM uptake and distribution will enable significant further development of the PB-PK model presented by Anderson et al. (1987).

Chapter 7, par. 7.1.

In this document a possible replacement of DCM is discussed. The consequences of this possible replacement have been insufficiently discussed. In the short term there is no alternative for many applications as a solvent or as a cleaning agent. Moreover, any replacement must also take into account the possible risk to human health and the environment. The influence of DCM on health and environment is well documented and there is no evidence of any harm to mankind or the environment when DCM is correctly handled.

Chapter 7, par. 7.3.

The calculated costs of emission reduction are under estimated by a factor of about 2. This is due to the way in which investment is calculated into annual usage cost. The cost of capital should be calculated as 13% DCF after tax and before financing (VNO/NCW, 1987).

Chapter 8

The economic consequences of emission reduction: the method used here for cost accounting is not correct. The costs should not be related to total turn-over, but only to the part of the company which uses DCM. These costs are likely to be of considerable importance for the future. A more realistic procedure would be to compare production costs with the cost of additional environmental measures for the specific parts of the company.

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