CEFIC B.I.T. Solvants Chlorés

The occurrence of chlorinated solvents in the environment

March 1987

CEFIC Conseil Européen des Fédérations de l'Industrie Chimique

European Council of Chemical Manufacturers' Federations

250, Avenue Louise–Box 72–B–1050 Brussels–Belgium
Telephone: 02/640.20.95–Telex: 62 498 CEFICB
Telefax:

SL 037114

The review makes the following conclusions:

- the concentrations of these solvents in the atmosphere and in the aquatic environment is generally extremely low (of the order of a few ppt – 1 in 1,000,000,000,000)
- where local higher concentrations are measured, in ground water or in surface water, this is directly due to spillage or indiscriminate waste disposal
- there is no overall trend for the total concentrations in the environment to increase. Whilst atmospheric concentrations of 111-trichloroethane are still growing, the rate of change in concentration is low and is diminishing
- the natural degradative processes in the atmosphere are ensuring that there is no undesirable build up of these products in the environment
- strict observance of current Codes of Practice covering storage, handling and use of these solvents will ensure that problems of limited local contamination are reduced considerably.

SL 037115

Reprinted from Chemistry & Industry, 1986, 861 – 869
by Strange the Printer Ltd., Heathfield, East Sussex TN21 8HX

The occurrence of chlorinated solvents in the environment*

This review covers the occurrence in the environment of the four most widely used chlorinated solvents in industry: methylene chloride (ME); 111-trichloroethane (methyl chloroform) (111-Tri); trichloroethylene (Tri) and perchloroethylene (Per).

Much of the data published on the four solvents is brought together in this review which covers their occurrence in the atmosphere, surface water and ground water. The various degradative processes are discussed, including trends in the concentration levels. The total tonnage of these solvents is declining, partly because of the economic pressures and partly as a result of developments in cleaning process technology and cleaning plant design.

Consumption, use and emission

As an introduction to this review of the occurrence of the title solvent chlorohydrocarbons in the environment, this section deals with their consumption in western Europe, including their pattern of use and estimated emissions into the atmosphere. The data is based on information from the Conseil Européen des Fédérations de l'Industrie Chimique (CEFIC) and other producer estimates.

Consumption–western Europe. Since the mid 1970s the consumption of Tri and Per has declined by 30-50 per cent while the consumption of 111-Tri increased initially, but has remained steady since 1979. The consumption of methylene chloride dropped by around 10 per cent over the same period. These trends are shown in the Table 1 and also in Fig 1.

End-use pattern. While the consumption of Tri and 111-Tri is principally in metal degreasing, Per is used mainly in drycleaning. Methylene chloride is used in

*Prepared by a workshop of the European Chemical Industry Federation, CEFIC: Paul Herbert (ICI, England); P Carbonnier (Atochem, France); L Rivolta (Montedipe, Italy); M Servais (Solvay, Belgium); F Van Mensch (AKZO, Holland) and Ian Campbell of ICI.

Table 1 **Western Europe consumption** (kt)
(Based on information from CEFIC and other producer estimates)

	ME	Tri	Per	111-Tri
1974	222	310	290	92
1975	195	253	275	86
1976	207	277	290	99
1977	203	257	281	109
1978	201	236	304	120
1979	206	210	240	147
1980	208	177	215	145
1981	214	159	187	146
1982	196	154	196	142
1983	191	151	172	140
1984	202	148	180	144
1985	195	147	172	150

111-Tri figures do not include US imports which were around 12-15 kt/a between 1981-5.

Fig 1 Consumption of chlorinated solvents in western Europe

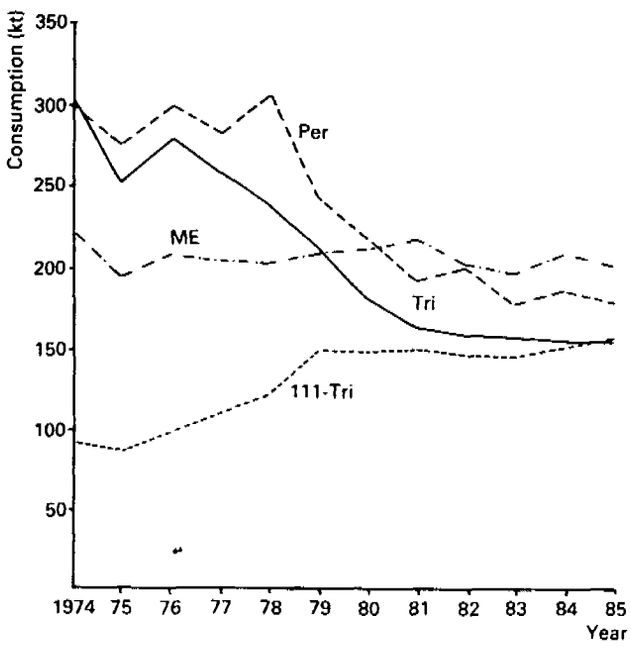

Table 2 **End-uses of title solvents**

Use (%)	ME	Tri	Per	111-Tri
Metal degreasing	★	★★★	★★	★★★
Dry cleaning	–	★	★★★	–
Extraction	★★	★	★	★
Solvent	★★	★	★★	★★
Aerosols	★★	–	–	★
Adhesives	–	★	–	★
Paint Stripper	★★	–	–	–
Intermediates	★	–	★	–

>50% ★★★
10–50 ★★
1–10 ★
<1% –

Table 3 **Estimated emissions in air, kt/year (1984)**
(based on information from CEFIC and other producer estimates)

	ME	111-Tri	Tri	Per	Total
Belgium	10.0	4.0	2.3	3.5	19.8
Denmark	0.9	1.1	0.5	0.8	3.3
Eire	–	–	0.4	0.8	1.2
France	26.1	21.4	21.1	14.7	83.3
FR Germany	56.7	22.0	18.6	23.7	121.0
Greece	1.0	0.6	1.3	0.8	3.7
Italy	27.8	13.9	11.6	18.5	71.8
Netherlands	9.5	3.9	1.8	3.4	18.6
United Kingdom	27.2	21.0	17.8	9.3	75.3
Spain & Portugal	–	3.8	NA	7.0	10.8
Sub total EEC	159.2	91.7	75.4	82.5	408.8
Other western European countries*	14.0	8.7	13.2	7.2	43.1
Total	173.1	100.4	96.4	89.7	459.6

*Includes Austria, Switzerland & the Nordic countries

further solvent applications, including paint strippers, aerosols and, as an extraction solvent. The details are shown in Table 2.

Estimated emissions. Direct emission of chlorinated solvents in air, as a percentage of the total consumption, have been estimated as follows: ME – 86 per cent; 111-Tri – 70 per cent; Tri – 60 per cent; Per – 60 per cent. The total emissions in air in 1984, due to end-use are given in Table 3.

The occurrence of chlorinated solvents in the environment

Atmosphere. The background levels of the title solvent chlorohydrocarbons in the earth's atmosphere, remote from the emissions of the substances range from 0.01 – 0.12 ppb. (0.01 – 0.12 parts in 10^9 by volume). The measured levels in the northern hemisphere are as follows: ME 0.04 ppb; 111-Tri 0.15 – 0.17 ppb; Tri 0.01 – 0.02 ppb and Per 0.06 – 0.09 ppb.
The detailed information is given in table 4 which summarises Table 3 – 1A of the NASA/WHO review[1].

The higher level of all four substances in the northern hemisphere relative to the southern hemisphere, reflects the predominant source of release coupled with the relatively slow inter-hemisphere transfer. In the case of methyl chloroform, neither the inter-hemisphere transfer nor the equilibria of tropospheric oxidative destruction mechanisms, are likely to have reached equilibrium. The trends show that methyl chloroform has increased from approximately 0.1 ppb in 1978 in the northern hemisphere, to approximately 0.15 ppb in 1984. The corresponding levels at the equator are 0.07 – 0.11 ppb and in the southern hemisphere (41° South) 0.06 – 0.1 ppb. However, the rate of increase is slowing down. These trends are summarised in Table 3 – 13 of Ref 1 and information detailed in Table 5.

The lifetimes and levels of methylene chloride, trichloroethylene and perchloroethylene are so short and low respectively that it would not be possible to measure trends of the concentrations in the atmosphere. All three have almost certainly reached a steady state concentration. The lifetimes of methylene chloride and Per are of the order of a few months, while the lifetime of trichloroethylene which is more easily oxidised than Per, is of the order of a week[15]. The lifetime of methylchloroform is longer, being reported to be between 5 and 10 years[16, 17, 18] in earlier work, or 10 years[19], six years[20] or nine years[2] in more recent publications.

The lifetimes of methylene chloride, methyl chloroform and perchloroethylene are shown in Table 5 (extracted from Table 3 – 1B of Reference 1). Slightly higher localised levels are sometimes found in ground level air in industrial areas and in air masses from such countries. Typical levels are as follows: Tri 0.01 – 1.0 ppb; Per 0.01 – 1.0 ppb; and 111-Tri 0.05 – 0.5 ppb. These have been summarised in CEFIC reports and elsewhere.[10, 11, 12, 23]

Degradation. The degradation of the title compounds in the Earth's atmosphere is a complex process essentially consisting of oxidation by the oxygen of the air under the action of ultraviolet light from the sun.[1] The reactions involved in degradation are shown in Fig 2.

Because of the temperature inversion tropopause in the Earth's atmosphere at an altitude of about 8 – 15km (varies with latitude), the atmosphere is divided into an upper layer (stratosphere) and lower layer (troposphere). The ozone layer is formed mainly in the stratosphere, by conversion of diatomic O_2 molecules into triatomic O_3 ozone molecules under the action of short wavelength UV sunlight penetrating into the stratosphere. Less ozone is formed in this way at or below the tropopause because the short wavelength light needed is greatly attenuated by absorption. Ozone is constantly being decomposed and reformed under the action of sunlight, bringing about a steady-state concentration of ozone (the 'ozone layer').

Halogenated organic compounds with relatively short atmospheric lifetimes, such as the title compounds except methyl chloroform, are not able to diffuse easily upwards across the tropopause and into the stratosphere. Instead, they are held down in the troposphere and undergo degradative processes as shown in Fig 1. The lifetime of methyl chloroform is only just long enough for a small fraction of the amount to be emitted, (about 10 per cent) to pass into the stratosphere and so become involved in various stratospheric chemical reactions. This effect is calculated to be small, however, and is less than half of that caused by naturally occurring methyl chloride.[16, 17, 18]

Chloroalkenes (trichloroethylene and perchloroethylene) are oxidised to carbon dioxide, water and hydrogen chloride by both ozone and hydroxyl radical.

Table 4 **Measured distributions of selected halocarbons**

Compound	Date of measure-ment	Concentration +/- standard deviation ppt v/v	Latitude	Northern hemisphere average +/- standard deviation ppt v/v	Southern hemisphere average +/- standard deviation ppt v/v	Global average +/- standard deviation	Ref
Methylene chloride CH_2Cl_2	12/81			38.0	21.0		2
Methyl chloroform CH_3CCl_3	12/81			156.0	116.0		2
	2/81	149.1 +/- 3.0	20				3
	1981	170.4 +/- 9.3	70				4
	11/81	123.0 +/- 0.6	30S-42S				5
	1978			117.0 +/- 4.0	90.0 +/- 3.0		6
	1/80			114.4	83.2	98.4	7
Trichloroethylene C_2HCl_3	12/81			12 0	< 3		2
	1981		71	18.0			4
	1981	16.0 +/- 15.0	70				4
				11.0			8, 9
Perchloroethylene C_2Cl_4	12/81			29.0	5.0		2
	2/81	60.0 +/- 7.0	20				3
	1981		71				4
	1981	87.0 +/- 28.0	70	89.0			4
	11/81	9.0 +/- 1.0	30S-42S		9.0 +/- 1.0		5
	1978			56.0 +/- 11.0	14.0 +/- 3.0	35.0	6
				90.0			9

Methyl chloroform and methylene chloride are oxidised by hydroxyl radical only, again forming the same naturally occurring inorganic breakdown products. Trichloroethylene, perchloroethylene and methylene chloride are destroyed so quickly in the troposphere, with lifetimes of a few months or less, (Reference 1, Table 3-18) that they do not reach levels at which their transfer to the stratosphere is significant.

It has been shown that the contribution of chlorinated solvent vapour degradation to the acidity of the atmosphere is negligible.[21] There is undoubtedly a heavy burden of chlorine, suggested to occur in the form of hydrogen chloride [22], and from other sources including sea salt ($1\text{-}9.10^8$kt/year)[23] and volcanic activity (9.10^6 kt/year).[24] The relative importance of other natural sources of gaseous chloride is unknown. Such sources could include forest and grass fires and acidic soils near coastal areas, which might release hydrogen chloride.[22] Hydrogen chloride has been suggested to enhance the $SO_2 \rightarrow SO_4$ reaction, leading to increased acidity in the atmosphere. However, the reaction energy required (57 kcal/mole), renders this routine extremely unlikely.

Movement of volatile solvents from the atmosphere into rainwater, the oceans and ground water. A study of the relevant partition calculations, according to Henry's Law, clearly shows the driving force for the solvents to be from the aqueous phase into the atmosphere. For example, at equilibrium with a concentration of 25 μg/l (25ppb), the levels of the title compounds in the atmosphere would be: Tri – 2.2 ppm; Per – 3.9 ppm; ME – 1.1 ppm and 111-Tri – 2.7.

The movement of solvents from the atmosphere into rainwater[25] and the oceans[26,27] has been studied, and measurements have been reported.[10,11,12] These show that the maximum levels likely to occur in rainwater, and hence in groundwater from rainfall, are very low and are of the order of 10-100 μg/l (ppb). Where ground water contamination exceeding these levels has been detected, this has invariably been caused by the direct discharge of solvents to the ground surface rather than by transfer of solvent vapour from the air.

Evidence has been published suggesting that levels of solvents in freshly-fallen rainwater are higher than those expected from Henry's Law equilibrium.[28] It has never been possible to repeat this finding, and it is possible that the effect is due to adsorption phenomena similar to those described for fluorocarbons.[29] The washout of solvents from the air by rain following a local emission has been studied, and has been found to be very inefficient.[30]

Conclusion. The concentrations of the title solvent chlorohydrocarbons in the atmosphere are very low, in the range of 0.01-0.1 ppb, and, in general, are not increasing. Whilst atmospheric concentrations of 111-trichloroethane are increasing, the rate of increase in the troposphere is slowing down (2) reflecting the fact that equilibrium has not yet been reached. The rate of change in concentration is low and is diminishing.

Surface water

Concentration. There is a wealth of data on the concentrations of chlorinated solvents found in surface water in Europe. Much of this data covers measurements made of concentrations in the Rhine and it tributaries. The concentrations were measured in the rivers and lakes of Switzerland, in England and in several other European countries.

Reference to Henry's Law has already been made and this shows that fairly rapid evaporation of the chlorinated solvent into the atmosphere can be expected. In general, concentrations are reduced by about 90 per cent within ½-1 hour.[31,32] We can conclude that only a very small proportion of the chlorinated solvent produced and consumed in Europe is traceable in surface water.

There are examples of relatively high concentrations, which can be found within short distances of known sources of contamination. These concentrations tend to fluctuate and are reduced very rapidly by dilution by

Table 5 **Reported trends for selected halocarbon concentrations**

Compound	Date	Increase (per cent/a) +/- standard deviation	Increase ppt (ppt/a) +/- standard deviation	Lifetime (years) +/- standard deviation	Reference
ME	12/81			0.90 +/- 0.3	2
111-Tri	12/81		13.0 +/- 3	9.00 +2/- 1	2
			13.2 +.8/1.2		14
	11/81	"			5
	1/80	8.7	8.6	6.5 to 9	Unref-erenced
Per	12/81			0.6 +/- 0.2	1

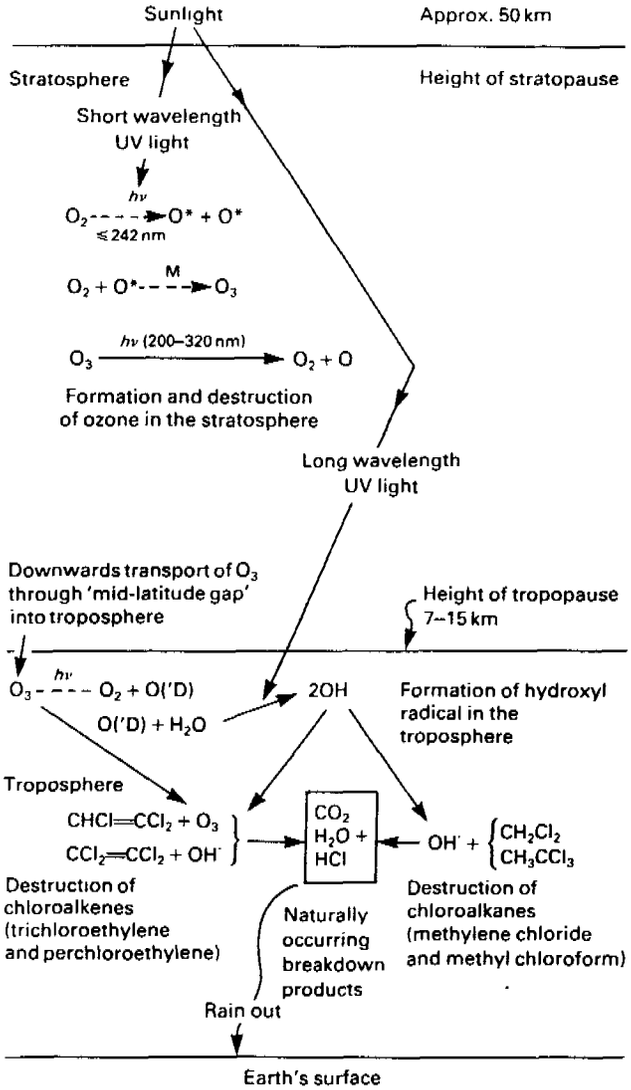

Fig 2 Reaction scheme for the destruction of chloro-organic compounds by oxidation in the lower atmosphere (troposphere).

factors of 10/10,000, depending on the local conditions. The concentrations of chlorinated hydrocarbons measured in European water range from fractions of micrograms/litre to some hundreds of micrograms/litre. The higher levels are caused by local contamination, which are quickly diluted. When the concentration levels are compared over a period of 10-15 years, it can be concluded that there is no overall upward trend. This would also be expected from theoretical consideration, based on Henry's Law, taking into account the rapid evaporation. Details are given in the following tables. The concentrations are micrograms/litre (ppb).

Degradation. The behaviour of the title substances in water varies as a function of their different chemical structures (C_1, C_2 saturated, C_2 olefinic) and depending on the situation of the water (shallow surface water, running surface water, deep surface water, ground water). Only 1,1,1-trichloroethane of the title compounds is known to react with pure neutral deoxygenated water at ambient temperatures, with a half life of 4-10 years, breaking down to HCl, vinylidine chloride and acetic acid.[12] An alkaline pH will enhance this breakdown. Decomposition rates have been measured in aerated water, with and without exposure to light[32], Table 7.

All four compounds will also biodegrade slowly, although experience with ground water pollution shows

Table 6a **Tributaries of the River Rhine**

(Ref)	Tri	Per	111-Tri	ME	Remarks
Main and Lippe (33)	up to 70	up to 70			Industrial effluents
Main at Kostheim (34)	3.20	19.77	2.16	<1	Influence of local industry
Ruhr at Mülheim (35)	0.7-0.9	0.7-1.7	n.d.	n.d.	Household and industrial
Ruhr Lippe (36)	0.3-0.9 2.1-4.1	0.4-1.0 1.5-3.2			Local industrial effluent
Small rivers in central West Germany (37)	0.2-0.9	1.1-2.7	0.05-0.2		Local high emissions
Main at Rüsselsheim (37)	1.2	0.5			Influence of Frankfurt airport
Ruhr at Duisburg (34)	0.45	0.41	0.05	<1	Small industry emissions
Mosel (38)	0.15-0.20	0.8-1.3		1.5-2	
Neckar (38)	0.2-0.4	0.2-0.4		0.6-1.0	
Other rivers in West Germany					
Elbe (38)	0.7-52.3	0.2-9.9		0.7-2.1	Industrial
Weser (38)	0.5-1.5	0.5-1.5			

Table 6b **River Rhine partly under the influence of the tributaries**

(Ref)	Tri	Per	111-Tri	ME	Remarks
Near Koblenz (38)	0.14-1.03	0.22-0.97		5.35-171	Local high emission
Length profile (38)		0.02-0.7		2-5	
At several places (38)	0.2-0.5	0.2-0.9		>1	
From Basel to Duisburg (39)	0.7-3.1	0.3-1.1			Industrial
General (36)	0.1-2.4	0.2-1.3			
At Lobith (34)	1.14	1.53	0.18	1	Industrial
Near Dutch border (40)	1	1		5	Industrial
Near Dutch border (33)	1.1	1.5	0.2	1.0	Industrial
General (41)	0.23		0.2	n.d.	
Near Main mouth (42)	0.75	1.2			Main is more polluted than Rhine

Table 6c **Rivers and lakes in Switzerland**

(Ref)	Tri	Per	111-Tri	ME	Remarks
River Glatt (43)	Max. 80, normally 0.1-1.0				Local industrial effluent
Lake Zurich (44)	0.038	0.14			
Several Lakes (39)	0.1-0.4	0.04-0.1			Remote from industrial activity
Lake Zurich (45)		0.04-0.07			Spills, waste water effluents, rainwater
General (46)	0.058	0.274	0.063		General background only 10% of samples contained more than 1 μ/l with a detection of 0 05. Tri and Per were found in 70% of surface water

Table 6d **England**

(Ref)	Tri	Per	111-Tri	ME	Remarks
Upstream of any industrial activity (47)	0.1-1.4	< 0.1-16	5-41		Special and varying weather conditions
Several rivers (48)	Some	Some			Industrial
Surface water (49)	0.01-1.0	0.01-1.0			Industrial
Sea coast (49)	0.1-1.0	0.1-1.0			Industrial

Table 6e **Other European countries**

(Ref)	Tri	Per	111-Tri	ME	Remarks
Swedish west coast (50)	0.015	0.005	0.046		Anthropogenic source
Surrounding Torino (51)	0-5	0-5	0		Industrial
Danube near Vienna (52)	0.6	0.6	0.2		Dry cleaning spillage and groundwater contamination
Northern Greek coast (53)	0.25-3	0.25-3			Industrial
Surface water Netherlands (54)	0.1-1.5	0.1-1.5			General
General background					
Atlantic (49)	0.001-0.013	0.001-0.013			
Rivers and lakes in urbanized areas (55)	Traces	Traces	Traces	Traces	
Generally sea (coasts) (55)	Traces	Traces	Traces	Traces	

that contamination with methylene chloride is much more localized owing to its relatively ready biodegradation.[56]

However, the above mechanisms are slow compared with the predominant mechanism of transfer to the air.[31,32] The approximate evaporative half-lives of the compounds are as follows: ME 20 mins; 111-Tri 20 mins; Tri 20 mins and Per 25 mins. In all cases 90 per cent had evaporated in less than 1½ hours.

Regulations. There are numerous regulations in Europe for maximal concentrations of the title substances in effluent, surface water and drinking water. It is interesting to note that the legislation is particularly directed at concentrations discharged in the effluent resulting from operations involving chlorinated solvents. The actual concentration in the surface water will ultimately be very dependant on dilution factors and the rate of evaporation into the atmosphere, which has already been mentioned. It is not economic to require all effluent to be of drinking water quality at source.

Drinking water standards are also referred to since in some countries, surface water is a major source of water for domestic consumption. Details of current legislation and recommendations are given in Tables 8a, b and c.

Table 7 **Decomposition rates**

	Half life, months	
	Dark	Illuminated
ME	18	Same
111-Tri	6	Same
Tri	10.7	5
Per	8.8	4

Table 8a **Effluent**

EEC	
Directive (57)	Fresh water, estuarial water, and sea water.
76/464	List I – substances: elimination of pollution
4 May 1976	List II – substances: reduction of pollution intended.
Chlorinated organics are being considered against the criteria for possible inclusion in List 1.	
Switzerland	
Verordnung (58) Abwassereinleitungen, 3 October 1980	Actual limit for all chlorinated compounds together μg/l (as chlorine) for effluents into rivers, lakes and public sewages. Final target (Qualitätsziel): 5 μg/l for individual compounds.
Netherlands	
Law 13 November 1969 (59) and 28 November 1974 (60)	No discharge without permit; Figures can be fixed.
Law 5 June 1975 (61)	Discharge into sea only according to regulation.
Belgium	
Legislation (to be published in 1986) on limits of solvents in effluents.	Total organic halogens in effluents < 150mg/l
FRG	
Baden Württemberg Law 28 June 1978	⩽ 5 mg/l chlorinated solvents (as chlorine)
Recommendation for other 'Länder' of FRG January 1983 (62)	⩽ 5 mg/l chlorinated solvents (as chlorine)
Italy	
Law 319 & 650 (63)	⩽ 1 mg/l total chlorinated solvents
France	No discharge allowed.

Table 8b **Surface water**

FRG	
Recommendation 1981 or earlier (64)	100-200 μg/l total organic chlorine final goal 30 μg/l for individual compounds.
Netherlands	
Planning 1985-1989 (65)	No specific values for Tri and Per. All volatile organohalogens together < 5 μg/l

Table 8c **Drinking water**

Belgium	
Legislation (A.R. 27 April 1984)	< 100 μg/l trihalomethanes
Netherlands	
Recommendation (65)	All organhalogens together < 1 μg/l
Decree Waterworks 2 April 1984	Generally: > 1 μg/l (for each individual chlorinated solvent) not allowed
FRG	
Recommendation (66)	< 25 μg/l for all compounds together 'Richtwert' 1 μg/l (EEC)

Conclusion. The concentrations of the title solvent chlorohydrocarbons in surface water range from fractions of a microgram/litre to some hundreds of micrograms/litre. The higher levels are clearly caused

by local contamination, which are quickly diluted. Evaporation of the title compounds into the atmosphere is rapid with evaporative half-lives in the range of 20-25 mins.

Ground water

Several reports contain data concerning the occurrence of chlorinated solvents in ground waters and a summary is included in Table 9. The maximum levels undoubtedly occur in heavily industrialised areas, while the ubiquitous background levels for all the title compounds are very low (about 0.1 μg/l), (about 0.1 ppb).

The high levels of chlorinated solvent in ground water in industrial areas were found to be caused by a lack of care in handling and the indiscriminate disposal of waste solvent over a period of many years.[67,68,77] Methylene chloride tends to be of considerably less significance in ground water contamination, partly because of rapid evaporation but also because of its relatively ready biodegradability.

Drinking water standards. A publication by the World Health Organisation (WHO) in 1984, deals with guidelines for drinking water quality. The guideline values for Tri and Per are 30 μg/l and 10 μg/l respectively.[69] It must be emphasised that levels recommended in the guidelines are not standards in themselves, but they are intended as recommendations to support both the European standards for drinking water and the international standards, which have been in existence for over a decade.[70,71] The adoption of standards will clearly be influenced by national priorities and economic factors.

In 1980, the EEC directive on the quality of water for human consumption was adopted.[12] The guideline value for organo-chlorine compounds of 1 μg/l was established, but no maximum level was included. The directive now has to be implemented by the member states. In Italy a limit of 30 μg/l is going to be applied by 1990.[73] In West Germany a limit of 25 μg/l has been in practice for several years.[37,66] The fact that the nationally permitted levels are higher than the guideline value has nothing to do with the materials discussed in this paper, and mainly reflects the need to allow for the traces of chloroform produced when drinking water is sterilized by chlorination.

Conclusion. Concentrations of the title compounds in ground water vary quite widely. The ubiquitous background levels are fractions of a microgram/litre (ppb), whilst contaminated water may contain substantial quantities of the title compounds. Where higher concentrations are found, this can be shown to be directly due to spillage or indiscriminate waste disposal, very often over a period of many years.

Clean-up processes for water

Various technologies are available for the removal of trace quantities of the title compounds destined for human consumption. Since chlorinated solvents have a limited solubility in water, and as shown above, a tendency to transfer from water to the air, treatment processes can be designed to take advantage of these physico-chemical properties. Aeration, or the introduction of air into water, has also been widely used to remove other gases.

Another technology available is adsorption involving the concentration of a material at an interface or surface. Activated carbon in granular or powdered form is often used for the removal of the title compounds from drinking water. More recently, adsorption processes based on resins and molecular sieves have been developed. Both aeration and adsorption technologies have been shown to be effective and the technologies can also be applied in series.

It has been reported that bacterial degradation may be possible under certain conditions with the title substances and information on the biological degradation of methylene chloride has been studied. These

Table 9 **Chlorinated solvents in ground waters**

Country	Location	Date	Concentrations (μg/l) Tri	Per	111-Tri	ME	Refs
CH	Zurich	1976		<0.1-82			74
CH	Zurich	1977	0.1-1.9	0.44-236	0.04-4.8		74
CH	Dubendorf	1977		473-954			75
CH	Zurich	1974	0.08	1.85			76
CH	Dubendorf	1978		763			77
CH	Dubendorf	1978	0.65 μmol/l (100 μg/l)				78
CH	Northern Switzerland	1984	0.92*	0.8	0.27		79
D	Frankfurt	1979	0.4-159	0.7->1,000			80
D	Mannheim	1981	≤0.16 & 2-120	≤0.30 & 2-120			81
D	Mannheim German/Swiss border Hamburg	1981	Tri, Per & 111-Tri together: from 0.5 to 1452; several figures in between: 0.9, 3.2 12.7, 175, 367, 850				82
D	Mannheim Karlsruhe	1983	30-130	30-130	30-130		83
D	Near border River Rhine	1985	<0.01	0.01		0.8	84
I	Novate Milanese		7.0	2.8	0.6	4.5	85
I	Milan		12-80	4-20			86
I	Sesto San Giovanni	1980-81	34-138	9-29			87
I	Cities of northern Italy	1981-82	0.1-1.1 (max 81-158)	0.1-0.3 (max 15-32)			88
A	South of Vienna	1983	<1->10	<1->10	<1->10		89
GB	Marlow, Bucks	1981	Generally ≤2	Generally (max 4 & 70) ≤2			90
NL	(Max. level detected)		1,100	< 22	0.1		91
NL			1 (*)	< 1(*)			92
NL		1982	<0.01-1				93

(*) In 50% of ground water sources

results may be relevant to clean up process options. Steam stripping is a useful technique for recovering solvent from an effluent or at least ensuring that the residual concentration is acceptable (levels of 1mg/litre can be achieved).

Aeration. When water containing a dissolved volatile or semi-volatile compound is in contact with air, an equilibrium of molecules migrating from the water to the air (evaporating) and from the air to water (dissolving) is established. Henry's Law describes the relationship of the concentration of a substance in the liquid phase, (dissolved in water) to the partial pressure of the compound in the vapour phase (concentration in air). There is a direct relationship between these two parameters. The coefficient of proportionality is known as Henry's Law coefficient. By providing an environment where the concentration in air is low – i.e. by continuously replacing semi-saturated air with fresh air – the system will tend toward an equilibrium condition of low concentration in water.

Because of their relatively low solubility and high vapour pressure, these solvents have a natural tendency to migrate from water to the air, giving them relatively high Henry's Law coefficients. This tendency can be put to use in aeration treatment systems which enhance the migration, or transfer, by providing large water/air interfacial areas, large volumes of air relative to the volume of water treated and sufficient contact time for the transfer to occur.

Granular activated carbon. Activated carbon removes organic contaminants from water by the mechanism of adsorption. Contaminant molecules migrate to the external surface of the carbon and into the extensive pore structure in the interior of the carbon particle, where they are effectively removed from the solution.

The capacity of activated carbon is a function of:

- the type of carbon
- the molecular structure of the compound
- the concentration of the compound in water
- the presence of competing organic substances and a number of other factors.

Because the effect of all the many factors on the adsorption capacity cannot be well defined, capacity is determined empirically, usually by laboratory equilibrium tests known as adsorption isotherms.

Adsorption isotherms and other equilibrium tests permit the development of an equilibrium equation which relates the concentration of adsorbate (solvent) in the liquid phase to the concentration of adsorbate on the solid phase (concentration of solvent absorbed per unit weight of activated carbon). This allows an estimate to be given of the amount of activated carbon necessary to treat water with a given concentration of solvent. Adsorption of solvent from contaminated water is achieved practically by passing the water through a bed of granular activated carbon. Contaminant molecules penetrate deeper into the bed, and the appearance of detectable concentrations of solvent in the treated water is known as break through. When the concentration of volatile organic solvent (VOC) in the treated water reaches an unacceptable level, the activated carbon in the bed is removed and replaced with either virgin carbon or reactivated carbon.

Resins. Adsorption of chlorinated solvents can also be achieved using columns packed with certain resins[94]. Another technique is to use a molecular sieve. These options are expected to attract increasing interest in the next few years. They are particularly suitable for achieving low contaminant levels after initial stripping by aeration.

Bacterial degradation. Another method which is beginning to attract interest, is the possibility of biodegradation[95]. Good results have been reported with methylene chloride[96,97,98]. Mechanisms have been proposed by Parsons *et al* and the subject reviewed by Kästner *et al*[99,100].

Table 10 **Location of packed towers aeration in USA (Federal Register/40 CFR Parts 141/142)[101,102]**

Location		Major contaminant	Raw water concentration range (μg/l)	Air: water ratio	Percent removal	Treated in water concentration (μg/l)
Worthsmith AFB	(Mi)	Tri	(50-8000)	25:1	99.9	4-8
Liberty	(Mo)	Tri	(36-69)	–	80	7.4
Fairfield	(NJ)	Tri	(26-400)			TCE 1-16
		111-Tri	(17-29)	–	96	111-Tri 1-12
						Total < 10
		Per	(2-172)	–		PCE 1-7
Rockaway	(NJ)	Tri	(50-220)	144:1	99	< 1-2
Rock Hill	(NJ)	Tri	(45-96)	83:1	99	< 1
Brewster	(NY)	Per	(420-470)	33.1	90	4-6
Upper Merion	(PA)	Tri	(3-20)	11:1	94	< 1-1.2
Warrington	(PA)	Tri	(3-20)	40:1	97	4
Tacoma	(WA)	Tri	(54-130)	62.1	95	7
Hartland	(WL)	Tri	(175)	50:1	99	< 2

Table 11 **Purification of ground water**

Biesterfield – Cologne[103] West Germany

Product: Trichloroethylene
Perchloroethylene
111-Trichloroethane
Methylene chloride
3000 μg/l
Depth 9m

Water flow (output) – 48 m^3/h

Concentration discharge of chlorinated solvent < 25 μg/litre

111-Tri Per

Energy – 25,000 DM
Analysis – 20/25,000 DM
Maintenance – 5/10,000 DM

Investments: 75,000 DM x 2 = 150,000 DM

Price per m^3 of processed water: 7 Pfg

Clean-up process evaluation

Packed tower aeration and granular active carbon (adsorption) are considered to offer the most efficient technology.

The advantages of these systems include: high level (99% or more) of VOC removal; no limit to climatic conditons such as temperature or geographic conditions; compatibility with other water treatment processes; installation can either be at the well head or in central treatment plant; relatively economic equipment necessary for the work is commercially available; no pre-existing structure is required.

Considerable experience has been obtained with both technologies over a number of years. For example: packed tower aeration has been successfully applied to the removal of VOC's in at least 24 full scale plants in the USA. Granular active carbon has been applied in at least five plants in USA to the removal of VOC's.

References

1 World Inteorological Organization Global Ozone Research Monitoring Project – Report No. 16. Volumes 1, 2 & 3. 'Atmospheric Ozone 1985 – Assessment of our understanding of the processes controlling its present distribution and change.'
2 Singh, H.B., Salas, L.J., & Stiles R.E., *J. Geophys. Res.*, 1983, **88** (C6), 3675-83T
3 Rasmussen, R.A., & Khalil, M.A.K., PAGEOPH, 1981, **119**, 990-7
4 Rasmussen, R.A., & Khalil, M.A.K., Geophysical monitoring for climatic change annual report, 10, NAA/ERL, Boulder: US Department of Commerce, 1983
5 Rasmussen, R.A., Khalil M.A.K., Crawford, A.J., & Fraser, P.J., *Geophys. Res. Lett*, 1982, 9 (6), 704-7
6 Rasmussen, R.A., & Khalil, M.A.K., *Chemosphere*, 1982, **11** (3), 227-35
7 Prinn, R.G., Rasmussen, R.A., Simmonds, P.G., Alyea, F.N., Cunnold, D.M., Lane, B.C., Cardelino, C.A. and Crawford, A.J., *J. Geophys. Res.*, 1983, 88, 8415-8426
8 Rasmussen, R.A., & Khalil, M.A.K., *Chemosphere*, 1983, **12**, 371-5
9 Khalil, M.A.K., & Rasmussen, R.A., Geophysical monitoring for climatic change, Summary report, 13, 1984, NOAA/ERL Boulder· US Department of Commerce 1985
10 'Trichloroethylene in metal cleaning and other industrial applications', *Brussels· CEFIC*, 1984
11 'Perchloroethylene in dry cleaning and other industrial applications,' *Brussels: CEFIC*, 1984
12 '1,1,1-Trichloroethane in metal cleaning and other industrial applications', *Brussels: CEFIC*, 1984
13 Edwards, P.R., Campbell, I., & Milne, G.S., Chem. Ind. (London), 1982, 574-8; 619-22
14 Rasmussen, R.A., & Khalil, M.A.K., *Antarctic Journal of the United States* 1983, **17**, (5), 203-5
15 Kontamination der Umwelt durch leichtflüchtige aliphatische chlorierte Kohlenwasserstoffe (Tri, Per, 1,1,1-Tri teilweise Dichlormethan) im Auftrag des Bund-Länder-Arbeitskreises Umweltchemikalien (BLAU) – 1985
16 Derwent, R.G., & Eggleton, A.E.J. *Quart., J. Met. Soc.* 1981, **107**, 231-42
17 McConnell, J.C., Schiff, H.I., *Science* 1978, **199**, 174
18 Chang, J.S. & Penner, J.E., Preprint entitled 'Analysis of global budgets of halocarbons' submitted to *Atmos, Environ*
19 Prinn *et al, J. Geophys. Res.* Oct 1983, **88**, 8415-26
20 Khalil, M.A.K., & Rasmussen, R.A. *Chemosphere* 1984, **13**, 7, 789-800
21 Lightowlers, P.J., & Cape, J.N., 'Hydrochloric acid emissions, attributable to incineration of PVC wastes', Institute of Terrestial Ecology, (Natural Environment Research Council), ICI/NERC Contract F6/92/39, ITE Project 960
22 Valach, R., *Tellus*, 1967, **19**, 509, 516
23 Hoeter, F.G., 'Chlorine and hydrogen chloride,' EPA, 600/1-76-020 April 1976
24 Eriksson, E. *Tellus*, 1960, **12**, 63-109
25 Terry Dana, M., Lee, R.N. & Hales, J.M., Pacific Northwest Laboratory, Richland, WA 99 352
Cupitt, T., Atmospheric Chemistry and Physics Division Environmental Sciences Research Laboratory, Research Triangle Park, NC 27711
'Hazardous air pollutants: wet removal, rates & mechanisms' PB85 – 138626, EPA-600/3-84-113, December 1984, Atmospheric Sciences Research Laboratory, Office of Research & Development, US Environmental Protection Agency, Research Triangle Park, NC 27711
26 Liss, D.S., & Slater, P.G., *Nature* 1974, **247**, 181
27 Khalil, M.A.K., Rasmussen, R.A., & Hoyt 1974, *Tellus*, 1983, 35B, 266-74
28 McConnell, J.G., *Journal of Water Engineers & Scientists*, 1976, **30**, 431-445.
29 Russell, A.D., & Thompson, G.M., *Water Resources Research*, Feb 1983, **19**, (1), 57-60
30 Hazardous air pollutants, wet removal rates and mechanisms. Battelle Pacific Northwest Labs, Richland, WA. Environmental Protection Agency Research Triangle Park, NC
31 Lapp, T., Proceedings of the conference on methyl chloroform and other halocarbon pollutants, Washington DC, 27-28 February 1979. EPA-600/9-80-003. PB80-142433
32 Dilling, W.L., Tefertiller, N.B. & Kallos, J., *Environmental Science & Technology*, 1975, **9**, (9) 833
33 Bauer, U., *Zbl. Bakt. Hyg.*, 1981, 15-56
34 Bauer, U., *Wa Bo Lu-Berichte*, 1978, **III**, 64-74
35 Dietz, F., & Traud, J. *Vom Wasser*, 1973, **41**, 137-55
36 Boh, B., *et al., Wa Bo Lu-Berichte*, 1978, **III**, 43-51
37 *Wa Bo Lu-Berichte*, 1981 **III**
38 Hellmann, H. *Haustechnik Bauphysik Umwelttechnik Gesundheits Ingenieur*, 1984 **105**, 269-278
39 Kühn, W, & Sander, R. *Wa Bo Lu-Berichte*, 1978, **III**, 30 & 39
40 Zoeteman, B.C.J. *et al, Chemosphere*, 1981, **9**, 231-49
41 VCI: Chemie und Umwelt: Wasser, 36
42 Karrenbrock, F. & Haberer, K., Report EUR (Eur 8518), 1984, 179-88
43 Zürcher, F., & Giger, W., *Vom Wasser 47*, 1976, 37-55
44 Grob, K., & Grob, G., *Journal of Chromatography*, 1974, 90, 303-13
45 Schwarzenbach, R.P., *Env. Sci. and Technol.*, 1979, 13, 1367-73
46 Fahrni, H.P., *Gas-Wasser-Abwasser*, 1984, **64**, (11), 689-95
47 McConnell, G., *J. of the Institute of Water Eng. and Scientists*, 1977, 31, 431-45
48 McConnell, G., *Journal of Institution of Water Engineers and Scientists*, 1976, **30**, No. 8. 431-445
49 Löchner, F., *Wasser Luft und Betrieb*, 1975, **19**, (11), 661-2
50 Eklund, G., *et al, J. of High Resolution Chrom. and Chrom. Comm.*, July 1978, 34-40
51 Gilli, G., *et al., Igiena Moderna*, 1979, 1195-205
52 Bolzer, W.E., *Österreichische Wasserwirtschaft*, 1982, **34**, (9/10), 198-204
53 Fytianos, K., *et al., Bull. Env Contam. Toxicol.*, 1985, **34**, (3), 390-5
54 Netherlands: 'Indicatief Meerjarenplan Milieubeheer' 1986-1990 with Annex; Vergaderjaar 1985/1986 Tweede Kamer; 19204, nrs. 1, 2 and 3
55 Baden-Württemberg: 'Kontamination der Umwelt durch Per, Tri, 1, 1, 1-Tri, teilweise MC', im Auftrage des BLAU, 1985
56 BarrioLage, G., Parsons, F.Z., Nassar, R S., & Lorenzo, P.A., *Env. Sc. Tech.*, 1984, **20**, 96-9
57 EEC Directive 76/464, 1976
58 Fahrni, H-P., *Gas-Wasser-Abwasser 64*, 1984, 11, 689-95; 691

59 Dutch Law 13 Nov 1969 on pollution of surface water
60 Decree 28 Nov. 1974 on pollution of surface water
61 Dutch Law 5 June 1975 on pollution of seawater
62 Informationsblatt zum innerbetrieblichen Umgang mit leichtfluchtigen chlorierten Kohlenwasserstoffen; Oktober 1985; page 26 and "Anhang" IV, page 47 and 48 (Ausarbeitung VCI, Verband Chemiehandel)
63 Italian Law 319 (1976) and 650 (1979)
64 Bauer, U., *Zbl. Bakt Hyg.*, 1981, **1**, 18
65 Netherlands: "Indicatief Meerjarenplan Mileurbeheer" 1986-1990 with Annex, Vergaderjaar 1985/1986 Tweede Kamer; 19204, nrs. 1, 2 and 3
66 *Wa Bo Lu-Berichte*, 1981, **III**, 21-94
67 International Conference on Ground Water Contamination with organochlorine compounds of Industrial Origin – Milan, January 1983
68 'International Symposium on quality of Ground Water' Noordwijkerhout, Netherlands, March 1981
69 'Guidelines for drinking water quality' vol 1, Recommendations, *Geneva: World Health Organization*, 1984
70 'European standards for drinking water' 2nd ed *Geneva: WHO*, 1970
71 'International standards for drinking-water' 3rd ed. *Geneva: WHO*, 1971
72 EEC Directive 80/778, 1980
73 DCP-8/2/85 'Caratteristiche di qualita delle acque destinate al consumo umano' (published in. Italian official Gazzetta 9/5/85)
74 Giger, W., Molnar-Kubica, E., & Wakeham, S. in: Aquatic Pollutants – Ed Hutzinger, Pergamon Press, 1978, 101
75 Molnar-Kubica, E. & Giger, W.: *Nouvelles de l'EAWAG: News*, Oct 1977
76 Grob, K., *et al*, *J. of Chrom*, 1974, **90**, 303-13
77 Giger, W., *et al.*, *Bull. Env. Contam. and Toxic.*, 1978, **19**, 475-80
78 Kummert, R., *et al.*, *Anal. Chem.*, 1978, **50**, 1,637-9
79 Fahrni, H. P., *Gas-Wasser-Abwasser*, 1984, **67**, 689-95
80 Fritschi, G., *et al.*, *Wa Bo Lu-Berichte*, 1979, **I**, 1-35
81 Aurand,. K., *Wa Bo Lu-Berichte*, 1981, **III**, 9-99
82 *DVGW-Schriftenreihe Wasser*, (29), Eschborn: 1981, 41-89
83 Kühn, W., *Wiener Mitteilungen*, 1983, **51**, 1-28
84 Hellman, H., *Haustechnik, Bauphysik, Umwelttechnik, Gesundheitsingenieur*, 1984, **105**, (5), 269-78
85 Cocheo, V., Gaffuri, Benzom, A., 'Ground water contamination with organochlorine compounds of industrial origin', International conference, Milan, January 1983, Ed Monguzzi – Bologna 1983, 643
86 Ziglio, G., Fara, G.M., Beltramelli, G., & Preghiasco, E., *Arch Environ Contam. Toxicol.*, 1983, **12**, 57-64
87 Ziglio, G., *et al, L'Igiene Moderna*, 1984, **82**, 133-61
88 Ziglio, G., Beltramelli, G., & Giovanardi, A., *L'Igiene Moderna*, 1984, **82**, 419-35
89 Kasper, W., *et al*, *Oesterreische Wassenwirtschaft*, 1983, 35, 7-8, 153-8
90 Fielding, M., *et al.*, *Env. Technol. Letters*, 1981, **2**, 545-50
91 Zoeteman, B.C.J., Harmsen, K., Linders, J.B.H.J., Morra, C.F.H., & Slooff, W., *Chemosphere*, 1980, **9**, 231-49
92 Trouwborst, T., *The Science of Total Environment*, 1981, **21**, 41-6
93 van Beek, C.S.E.M., *H_2O*, 1982, **15**, 400-403
94 Dummer, G., & Schmidhammer, L., *VDI*, 1986, 885-901
95 Ground water decontamination systems
I – Bio-reclamation of ground and ground water by in-situ biodegradation.
II – Bio-reclamation of ground and ground water – Vidyut Jhaveri – PhD – Alfred J. Hazzaca, Ch, E – Suite 210-140 Route North – Paramus NJO7652
96 Brunner, W., Straub, D., & Leisinger, T, *Applied Environ Microbiology*, 1980, **40**, (5), 950-8
97 Verband Chemiehandel – Verband des deutschen Chemikalien-Gross- und Aussenhandels EV – Kundeninformation NR 7 – Stand. 15 August 1985. EPA/600 – 9-85/025 September 1985
98 Proceedings international conference on new frontiers for hazardous wastes management, Cincinnati, M., O H M 45268, EPA/600-9-85/025 September 1985
99 Parsons, F., Lage, G.B. & Rice, R., *Env. Tox. and Chem.*, 1985, 4, 739-42
100 Kaestner, M., Harborth, P., & Hanert, H.H., *Biologische Endoxidation leichtflüchtiger Halogenkohlenwasserstoffen Seminar Nr S-71-104-091-6*, Haus de Technik, 4300 Essen 1986
101 Federal Register/40 CFR Part 141, 1985, 46, 880-46, 901
102 Federal Register/40 CFR Parts 141-142, 1985, 46, 902-46, 936
103 Ministerium für Ernährung, Landwirtschaft, Umwelt und Forsten Baden-Württemberg. Leitfaden fur die Beurteilung and Behandlung von Grundwasser-Verunreinigungen durch leichtflüchtige Chlorkohlenwasserstoffe – Stand August 1983.