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Presence and importance of organochlorine solvents and other compounds in Germany's groundwater and drinking water

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Summary. - Organochlorine compounds are widely used in Germany although the inland production of chlorinated solvents has greatly decreased since 1985. Data on groundwater contamination are incomplete, but there are some regional data sets from the States (Länder). Approximately 25% of the groundwater samples contain more than 1 µg/l of a single solvent, the most prominent ones being tri- and tetrachloroethene, 1,1,1-trichloroethane and dichloromethane, but also chloroform. The most important causes for contaminations of the groundwater are unprotected storage and leaking sewage systems. Abandoned waste sites are, besides chlorinated compounds, also a source of many other contaminants. A ranking procedure according to their exposure potential (concentration, incidence, toxicology) is proposed. The compound of greatest concern is vinyl chloride, which is formed from tri- and tetrachloroethene under reducing conditions in the subsoil. The most important contaminant in drinking water is tetrachloroethene followed by 1,1,1-trichloroethane and trichloroethane. Chlorobenzene may also be present on occasion, while only about 20% of the finished drinking waters contain more chloroform after treatment than before. Only about 10% of all analyses of drinking water derived from groundwater shows the presence of organochlorine sovents and most of these show total concentrations less than 2 µg/l. The degradation product, vinyl chloride, was found up to now only in different groundwaters. To stabilize and to improve the situation, which still is much more favorable for drinking than for groundwater, precautions are going to be taken which should assure that these and other problematic substances which endanger water are used only in closed systems and rigid safety measures be imposed on their disposal and transport.

Key words: drinking water pollutants, organochlorine solvents.

Riassunto *(Presenza e importanza dei solventi organoclorurati e altri composti nelle acque sotterranee e potabili in Germania).* - I composti organoclorurati sono ampiamente impiegati in Germania, sebbene la produzione interna di solventi organoclorurati sia in forte riduzione dal 1985. I dati sulla contaminazione delle acque sotterranee sono incompleti, ma sono disponibili quelli di alcune regioni (Länder). Circa il 25% dei campioni d'acqua contiene più di 1 µg/l di uno dei composti organoclorurati. Tra questi, tri- e tetracloroetilene, 1,1,1-tricloroetano, diclorometano e cloroformio sono i più rilevanti. Le principali cause di contaminazione delle acque di falda sono dovute a infiltrazioni dalle reti fognarie. Le discariche abbandonate sono una fonte di altri tipi di contaminazione oltre a quella da composti organoclorurati. In questo lavoro viene proposta una procedura di classificazione in relazione al potenziale di esposizione di questi composti (concentrazione, frequenza, tossicologia). Il prodotto di maggior interesse nel sottosuolo è il cloruro di vinile, che si forma in condizioni riducenti dal tri- e tetracloroetilene. Il composto più importante nelle acque potabili è il tetracloroetilene, seguito dal 1,1,1-tricloroetano e dal tricloroetilene. Occasionalmente possono essere presenti clorobenzeni, mentre soltanto circa il 20% delle acque trattate contengono concentrazioni di cloroformio più alte delle acque grezze prima del trattamento. Circa il 10% di tutte le analisi dell'acqua potabile derivata da acqua di falda mostra la presenza di solventi organoclorurati e nella gran parte dei casi le concentrazioni sono inferiori a 2 µg/l. Il cloruro di vinile è stato rilevato finora soltanto nelle acque sotteranee. E' necessario tuttavia promuovere le misure per assicurare che il cloruro di vinile e altri prodotti di particolare tossicità siano usati soltanto a ciclo chiuso e che siano imposte norme rigide per il loro trasporto e smaltimento.

Parole chiave: contaminanti delle acque potabili, solventi organoclorurati.

Introduction

Organochlorine compounds are widely used in Germany. They are produced as solvents, extracting and cleaning agents, and oil removers for industrial and household use, amounting to approximately 260,000 (metric) tons per year. The majority of this reaches the environment sooner or later due to their high volatility. This is particularly true with respect to the atmosphere, where they disperse widely. The components that cannot be degraded photochemically dissolve in rain water [1] or adsorb on suspended particles to reach the Earth's surface from where they either directly or in the form of various metabolites enter groundwater. There they are quite stable as well as mobile unless anaerobic conditions prevail. Should this be the case, then normally multiphasic metabolism occurs [2].

The committee on storage and transportation of substances dangerous to water convened by the Bundesminister des Innern (Federal Minister of the Interior) [3] has deemed chlorinated hydrocarbons to be generally "dangerous to water" according to the evaluation scheme established in August of 1980. Presently, trichloroethene, tetrachloroethene and 1,1,1-trichloroethane have been assigned to dangerous substances' class 3 [4].

Oils for fats, wax, resins, tar and bitumens are highly soluble in organochlorine solvents which also dissolve the usual sealing materials used for sewage pipes. The high density of these solvents, compared to water, promotes their potential for groundwater contamination. Since they have good wetting properties, they penetrate relatively quickly into wet soil and also diffuse into clay layers and even concrete [5]. Chlorinated hydrocarbons can migrate through the groundwater aquifer in solution or as a separate phase resulting in very extreme pollution. Restoration measures are extremely difficult, because the solvents penetrate deep into the aquifer.

Schwille [6] conducted model experiments to obtain a better understanding of the conditions surrounding the subterranean migration of chlorinated hydrocarbons, and the knowledge gained has been included in the "Guidelines for chlorinated hydrocarbons" produced by Baden-Württemberg [7].

Groundwater

Regional contamination

Data gathered on groundwater contamination in Germany are incomplete. However, there are data from the individual Länder on regional contamination that can be quite detailed.

There has been an increasing number of incidents of chlorinated hydrocarbons causing groundwater pollution in Baden-Württemberg since 1978. A distinctive research and experimental project, conducted to assess the extent of this pollution disclosed about 80 incidents of chlorinated hydrocarbons as groundwater contaminants as early as the end of 1981 [8]. By mid 1983, over 150 incidents of pollution had been discovered [7]. A monitoring network was being set up by early 1985 which was aimed at continually describing groundwater quality. Completion of this data set was expected in 1991.

North Rhine-Westphalia published a report on groundwater [9] at the beginning of 1986. A total of 1637 samples was taken between October 1983 and April 1985 (Table 1). Approximately a quarter of all samples revealed concentrations exceeding 1 µg/l, due mainly to 1,1,1-trichloroethane, trichloroethene and tetrachloroethene. Trichloromethane, commonly accompanied by the chlorinated solvents trichloroethene and tetrachloroethene, was about as widely spread as the latter two. Dichloromethane, the only substance biologically readily degradable, was detected in only 3 of the 100 samples.

There was no recognizable regional pattern relating to use or type of urbanization.

In Duesseldorf County (Regierungsbezirk) of North Rhine-Westphalia, 49 (31%) of the 159 water catchment areas with 80 wells were found to be contamined with organochlorine solvents (single substance > 0.5 µg/l). Trichloroethene was detected in about 30%, tetrachloroethene in 35% and 1,1,1-trichloroethane in 25% of the samples. The maximum concentration of trichloroethene and tetrachloroethene extended into the mg/l range at the seepage sites. Trichloromethane was present in 646 (39.4%) of the 1637 samples and was about as widely spread as trichloroethene.

From the 71 cases that were registered and published [10] in Hesse up to the end of 1985, 77.5% were in South Hesse.

Table 1. - Occurrence of chloroorganic solvents in the groundwater of North Rhine-Westfalia 1983-1985 [9]. Total number of samples: 1637 (= 100%)

	Concentration range (µg/l)				
Contaminant	< 1.0	> 1-25	> 25-100	> 100-1000	> 1000
Sum of trichloroethene tetrachloroethene 1,1,1-trichloroethene dichloromethane	1254 (76.6%)	266 (16.3%)	61 (3.7%)	41 (2.5%)	15 (0.9%)
trichloromethane	1524 (93.1%)	109 (6.6%)	1 (0.1%)	3 (0.2%)	0

Inappropriate storage was the major cause of groundwater contamination in 57.1% of the cases. The second most important cause was leakage from the sewage systems with 18.4% of cases. Position number three with 12.2% of cases was occupied by the "abandoned sites," the present significance of which was not foreseeable. Further circumstances triggering groundwater pollution and amounting to about 10% each were a lack of protective measures and handling these substances carelessly. The metallurgical industry is not only the major user of organochlorine solvents but was also the major polluter of groundwater with 49.0% of cases. The dry cleaning industry was the second most important with 15.7% of cases. Used oil reprocessing plants, solvent distilleries, tobacconists, leather goods manufacturers, plants using chemicals and the manufacturers of chemical or pharmaceutical products caused between 5.9 and 7.8% of pollution cases.

Recently collected data showed some differences from this i.e., the metallurgical industry in its broadest sense 48.8%, the chemical industry 19.8%, companies marketing chemicals and dry cleaners 9.1% each, used oil and solvent reprocessing plants 5.09%. The leather goods industry with 4.1% and the optics industry share the lowest positions with other branches of industry.

As of the 31st of December 1988, it was assumed that in Hesse there were 183 incidents of pollution resulting from organochlorine solvents, known to the pertinent authorities. Of these, there were 125 in south Hesse, i.e., almost threefold that of three years previously. These figures do not include abandoned waste disposal sites. Table 2 lists all 125 incidents according to the extent of groundwater contamination. There appear to be some 100 additional incidents above and beyond those known to the Hessian water authority which were not reported by the companies involved, despite their legal obligation to do so. Incidents of pollution by organochlorines have caused long-standing massive contributions along the lower Main river between Hanau and Mainz with the highest concentration in Frankfurt.

A number of good examples of incidents have been described in detail including sampling strategy, findings, and initial restoration measures [10].

Contamination by and transport from point sources

The increased concentration of organochlorine compounds in groundwater and the resulting influence on the groundwater quality are also caused by varying "point sources." These are mostly due to infiltration from urban and industrial (abandoned) landfills and abandoned disposal sites. Small-volume contamination with high source concentration and frequently, with a huge of diverse organochlorines, can be generated in this way (Table 3).

The Institute for Water, Soil and Air Hygiene of the Federal Health Office (Bundesgesundheitsamt, BGA) of Germany has been conducting a research project since 1982 that is sponsored by the Federal Minister of Research and Technology (Bundesminister für Forschung und Technologie, BMFT). Its purpose is the development of standardized methods or procedures for the detection, characterization and evaluation of anthropogenic influences on groundwater. It was able to prove on the basis of representative statistics, which substances occur most frequently and/or at the highest concentrations (the main contaminants) in contaminated groundwater, and which of them also exhibit a high toxicological and geological risk potential (the priority contaminants).

Data from investigations at about 100 landfill sites in the original area of the FRG and West Berlin prior to unification are described below. In addition results from about 150 landfill sites that were provided by various authorities of the Federal Lander are also included.

The results were verified by comparing them to an even more extensive set of information from the United States. These data stem from investigations of groundwater contamination downstream of approximately 500 landfill sites. Plumb *et al.* detected in the USA approximately 1200 groundwater contaminants in concentrations >l µg/l downgradient from waste landfill sites of each type and of every age. The results showed however, that only a few of these contaminants occur frequently in the USA, the majority being found only very seldom [11-13]. This is essentially due to the fact that only a comparatively low number of the organic contaminants transported in seepage from the waste site are mobile and persistent.

Table 2. - Number and concentration ranges of groundwater incidents with chloroorganic solvents *(*)* in South Hesse as per December 31, 1988 (modified from [10])

Number of registered incidents	Range of concentration in groundwater
24	< 100 (µg/l)
29	≤ 500 (µg/l)
12	≤ 1,000 (µg/l)
26	≤ 5,000 (µg/l)
5	≤ 10,000 (µg/l)
16	≤ 100,000 (µg/l)
10	> 100,000 (µg/l)
3	no data reported

(*) Tri- and tetrachloroethene, 1,1,1-trichloroethane, dichloromethane.

Table 3. - Chlorinated organic compounds in groundwater from loose-sediment aquifers of the Federal Republic of Germany (West) contaminated by abandoned and other waste disposal sites

Parameter	**no. of analyses (n)** *(a)*	**dl** *(b)* µg/l	**n >dl** *(b)*	**df** *(c)* (%)	**Concentration µg/l**		**Percent./conc.**	
					mean	**max**	**50%**	**75%**
tetrachloroethene	227	0.1	195	70.40	56.1	6504.0	1.4	3.7
trichloroethene	277	0.1	154	55.60	1013.1	128,000.0	2.3	11.0
cis-1,2-dichoroethane	153	4.0	46	30.07	22,095.1	411,000.0	165.5	1150.0
1,1,1-trichloroethane	206	0.1	47	22.82	16.5	270.0	1.0	7.4
trichloromethane	236	0.1	52	22.03	76.2	2800.0	1.4	10.1
1,2-dichloroethane	16	5.0	3	18.75	107.3	210.0	-	-
vinylchloride	136	1.0	24	17.65	1693.2	12,000.0	99.5	1950.0
dichloromethane	114	10.0	17	14.91	38,066.5	499,000.0	437.5	16,835.0
tetrachloromethane	201	0.1	29	14.43	1.2	23.0	0.2	0.3
chlorobenzene	93	0.1	12	12.90	52.9	388.0	2.3	6.5
1,2-dichlorobenzene	90	0.1	11	12.22	1.4	6.6	0.9	2.1
1,4-dichlorobenzene	90	0.1	11	12.22	31.9	265.0	2.2	37.5
2,4,6-trichlorophenol	124	0.1	11	8.87	3.2	24.1	0.6	1.5
1,3-dichlorobenzene	90	0.1	7	7.78	11.5	74.0	1.1	38.2
trans-1,2-dichloroethene	134	5.0	10	7.46	57.1	135.0	50.0	95.0
1,1-dichloroethane	130	10.0	7	5.38	52.7	110.0	53.0	90.0
2,4-dichlorophenol	124	0.1	6	4.84	3.5	17.2	0.9	9.6
3-chlorophenol	124	0.1	6	4.84	12.7	22.8	12.3	20.8
2,4,5-trichlorophenol	127	0.1	5	3.94	7.1	31.9	1.3	16.6

(a) investigated down-gradient wells of approximately 100 different waste disposal sites.
(b) detection limit; *(c)* detection frequency.

If one defines a detection frequency of >0.1% as relevant, which as a statistical statement means that any certain compound will only be detected once in every 1000 contaminated groundwater samples, and if one only takes concentrations of >1 µg/l into consideration, which appears tolerable under toxicological-hygienic aspects for the vast majority of the contaminants, we arrive at the distribution of detection frequency of organic groundwater contaminants from waste landfill sites for the FRG prior to unification as represented in Fig. 1. From the ten most frequently detected contaminants, eight are compounds containing chlorine. Eighteen or 56% of the compounds listed among the contaminants shown in Fig. 1 (>0.1%) contain halogen [14].

The comparison [15] of these findings correlates well with the pertinent results from the United States (Fig. 2). This clearly demonstrates the predominance of organic compounds containing halogen as groundwater contaminants from landfill sites. Worthy of special mention are the halogenated alkanes, alkenes and aromatic substances (Fig. 3 and Table 4). On the other hand, other environmentally relevant groups of substances are missing, e.g. polychlorinated biphenyls (PCBs), chlorinated dioxins/furans or pesticides containing halogen. This is essentially a result of the inferior hydrogeochemical mobility in this group of substances, although they are very persistent.

Table 3 lists the substances according to the number of the respective positive findings (%), along with the statistical parameters of the individual concentrations. As was to be expected, the detection frequency also depends upon the detection limit. For example, tetrachlorethane's low detection limit produces a detection frequency of 70.4%, however, with a median concentration of only 1.4 µg/l. This is different from dichloromethane, that due to its high detection limit of 10 µg/l in this study has a detection frequency of only 14.9%.

From among the 19 detected contaminants containing chlorine, there are five chlorinated alkenes, six chlorinated alkanes, four chlorinated benzenes and four chlorinated phenols. Methylene chloride, cis-1,2-dichloroethene and vinyl chloride are of particular interest, because of their high concentration at the 50 percentile.

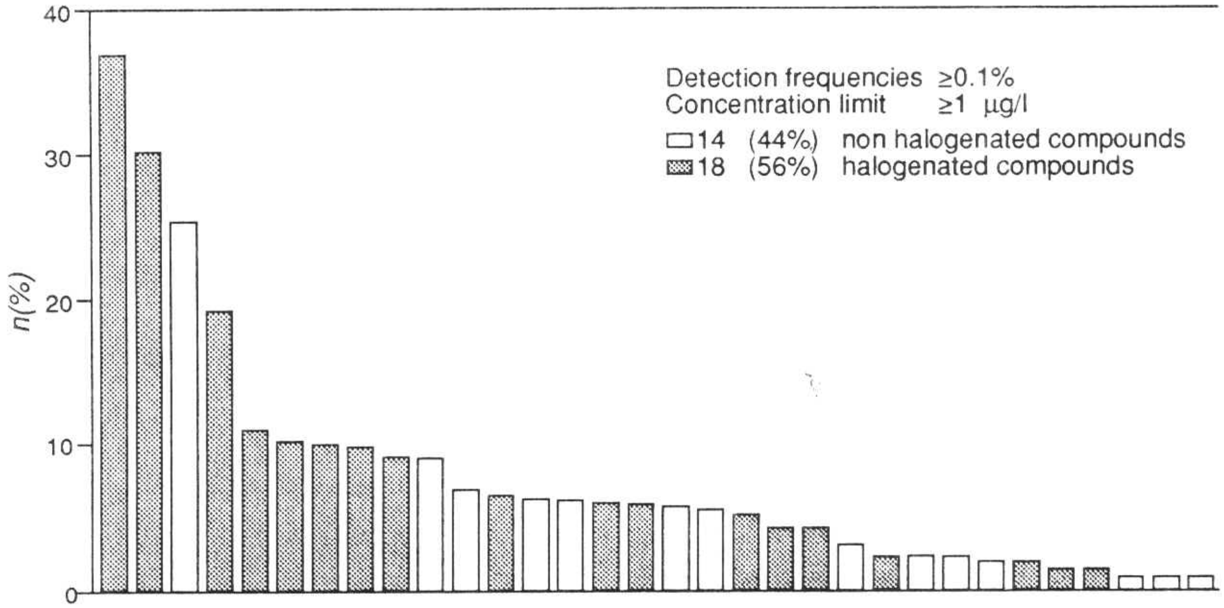

Fig. 1. - Distribution of detection frequencies (%) of organic groundwater contaminants from down-gradient wells of 250 waste disposal sites in the Western part of the FRG.

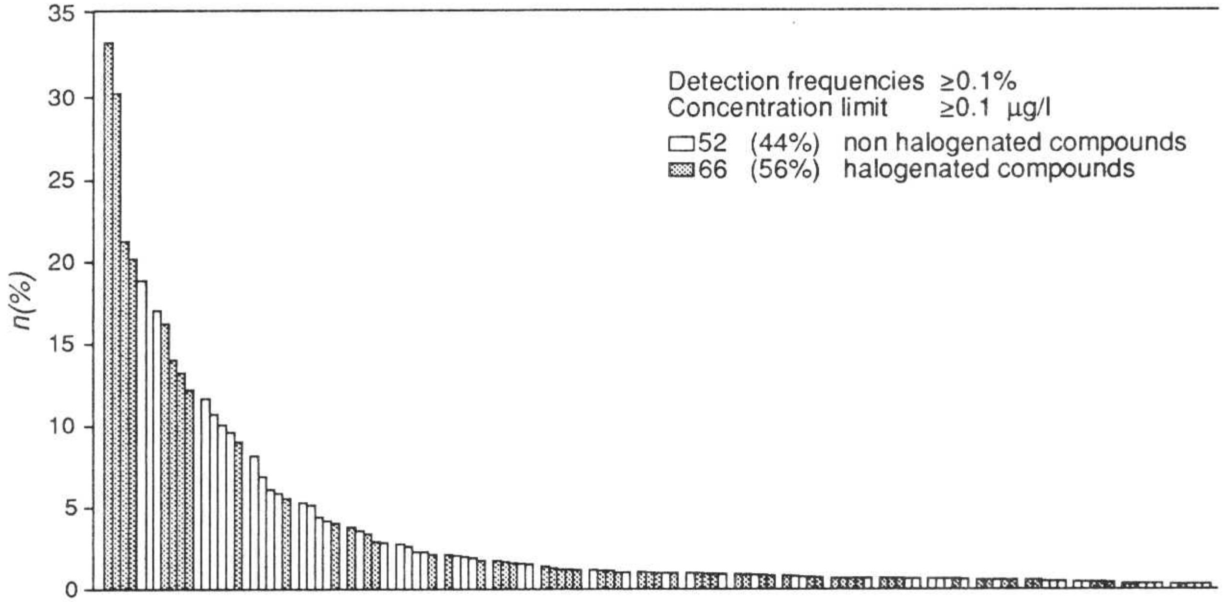

Fig. 2. - Distribution of detection frequencies (%) of organic groundwater contaminants from down-gradient wells of 500 waste disposal sites in the USA [11, 12]. Data compiled by the authors.

Metabolism

Until not long ago, most of the listed chlorinated solvents (except dichloromethane) were regarded as persistent and hardly ever degradable in the subsoil and it is a fact that they can be detected at large distances from the source of pollution. However, since the mid-1980's there have been indications from model studies that trichloroethene and tetrachloroethene are microbiologically dehydrochlorinated under reducing conditions. An important intermediate product of the total mineralization is vinyl chloride [16, 17], a substance of particular relevance for drinking water since it is a known human carcinogen. Vinyl chloride has been observed in groundwater in an area of Berlin [18, 19] as a sequential dehydrochlorination product of tetrachloroethylene via trichloroethene and cis-1,2-dichloroethene. The characteristic hazardous-substance

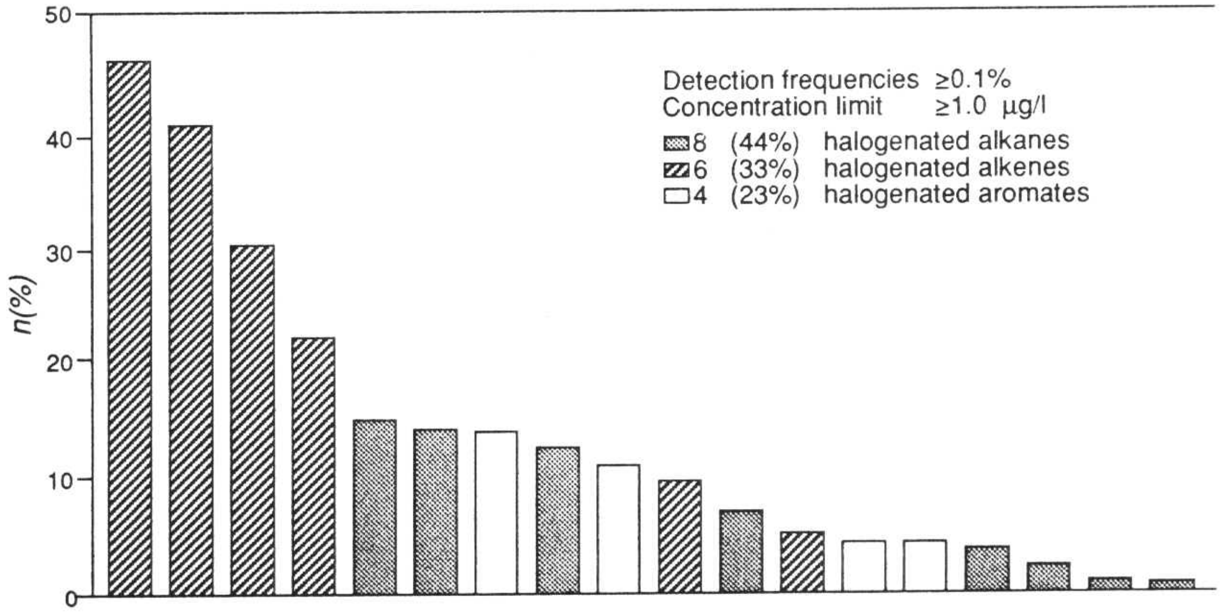

Fig. 3. - Distribution of detection frequencies (%) of halogenated organic groundwater contaminants from down-gradient wells of 250 waste disposal sites in the Western part of FRG.

Table 4. - Proportions of different groups of halogenated contaminants from the total groundwater contamination by organic compounds in down-gradient wells of 500 waste disposal sites in the USA; data from Plumb *et al.* [11, 12] as compiled by the authors

Groups of halogenated contaminants	**Typical compounds**	**no.**	**total no.**	**%**	**total %**
Halogenated hydrocarbons one /several/ mixed substitution (s)	Alkanes	17		41	
	Aliphates				
	Alkenes	7	33	38	89
	Alicycles	3		3	
	Aromates	6		7	
Halogenated derivates of group 1 (mostly O- and N-containing)	Phenols	6		3	3.75
	Ethers	5	11		0.75
Polychlorinated biphenyls and derivates	Di-,tri-tetra penta- and hexa subst substituted cpds		7		2.1
Pesticides containing halogen	**Alicycles** and O-derivates; **DDT** and similar compounds		14		5.1
Halogenated PAHs	2-chloronaphtalene	1	1		0.05
Total no. of compounds with detection frequencies of more than 0.1%			66		100

tail from the pollution source, with the position of the groundwater measuring sites and the concentrations of the various chloroethenes is shown in Fig. 4. Up to 1600 μg/l of cis-1,2-dichloroethene and 120 μg/l of vinyl chloride were detected under anaerobic conditions on a stretch of 500 m, although none of these substances occurred directly at the sources A or B of contamination.

The investigations conducted by Brauch *et al.* [20] have also shown that vinyl chloride can be formed in the subsoil under anaerobic (reducing) conditions.

Table 5 lists the typical concentrations of the most important highly volatile halogenated hydrocarbons found in contaminated groundwaters. Trichloethene and tetrachloroethene have been found in quite different concentrations. Other chlorinated hydrocarbons have been found also, e.g. the dichloroethene isomers, but in usually smaller concentrations. Cis-1,2-dichloroethene sometimes even appears as the most important contaminant. The vinyl chloride concentration that has been entered in the right column of the Table 5 varies in these examples between <5 mg/m^3 and several hundred mg/m^3. It is evident that vinyl chloride could not always be detected in groundwater contaminated with halogenated hydrocarbons even in the presence of higher concentrations of cis-1,2-dichloroethene.

The results of several comprehensive studies conducted on contaminated groundwaters are presented in Table 6, using a large area contamination as an example [20]. The mean values are listed for the individual chlorinated hydrocarbons from at least five test series at various wells. The standard deviation is approximately 3% for the halogenated hydrocarbons and between 5 and 10% for vinyl chloride. The results show that the individual wells have different burdens, according to the spread of contamination. In all cases, there was a higher concentration of cis-1,2-dichloroethene than of vinyl chloride. The concentrations for cis-1,2-dichloroethene are between 550 and 2300 mg/m^3 and for vinyl chloride between 15 and 1000 mg/m^3. Trichloroethene and tetrachloroethene levels are relatively low although it was proven that virtually only these two compounds had reached the subsurface regions from the topsoil.

When we compare the concentration in the individual wells, it becomes evident that the level of cis-1,2-dichloroethene can be very high even when relatively low amounts of trichloroethene and tetrachloroethene are present. There is also a correlation between the amount of cis-1,2-dichloroethene found and the concentration of vinyl chloride.

Groundwater used for drinking water production

At the end of 1985 approximately 1000 water supply plants in the old Federal Lander, i.e., the area of the FRG prior to unification, were requested to complete a questionnaire concerning the content of various organochlorine compound in their untreated raw water and their drinking water [21]. Answers concerning groundwater were obtained from 395 plants, which represents 79.3% of the groundwater used for the production of drinking water, i.e., 2089 x 10^6 m^3/a from a total of 2634 x 10^6 m^3/a. The percentage distribution of the analyses and/or findings for dichloromethane, trichloromethane, 1,1,1-trichloroethane, trichloroethene and tetrachloroethene within the amounts of water sampled are listed in Table 7.

Contamination by dichloromethane of groundwater used for drinking water production can be ignored. However, about 2.5% of that groundwater contains 1.0 μg/l of 1,1,1-trichloroethane, and 9% contains more than 1.0 μg/l trichloroethene. With regard to tetrachloroethene, 10% of the groundwater contains more than 1.0 μg/l and 4% contains more than 10 μg/l.

The appearance of trichloromethane in groundwater used for drinking water production (Table 7) is surprising, despite the position and designation of these less endangered regions as protected areas. A close

Table 5. - Concentrations (mg/m^3) of chlorinated ethenes in contaminated groundwaters [20]

	PCE	TCE	1,1-DCE	cis-1,2-DCE	trans-1,2-DCE	Vinyl chloride
groundwater A	8.1	415	22	247	<5	<5
groundwater B	36	12	<2	45	<5	15
groundwater C	98	355	27	1500	<5	460
groundwater D	112	147	37	330	<5	23
groundwater E	8300	1300	5.3	405	<5	100

PCE: tetrachloroethene; DCE: dichloroethene; TCE: trichloroethene.

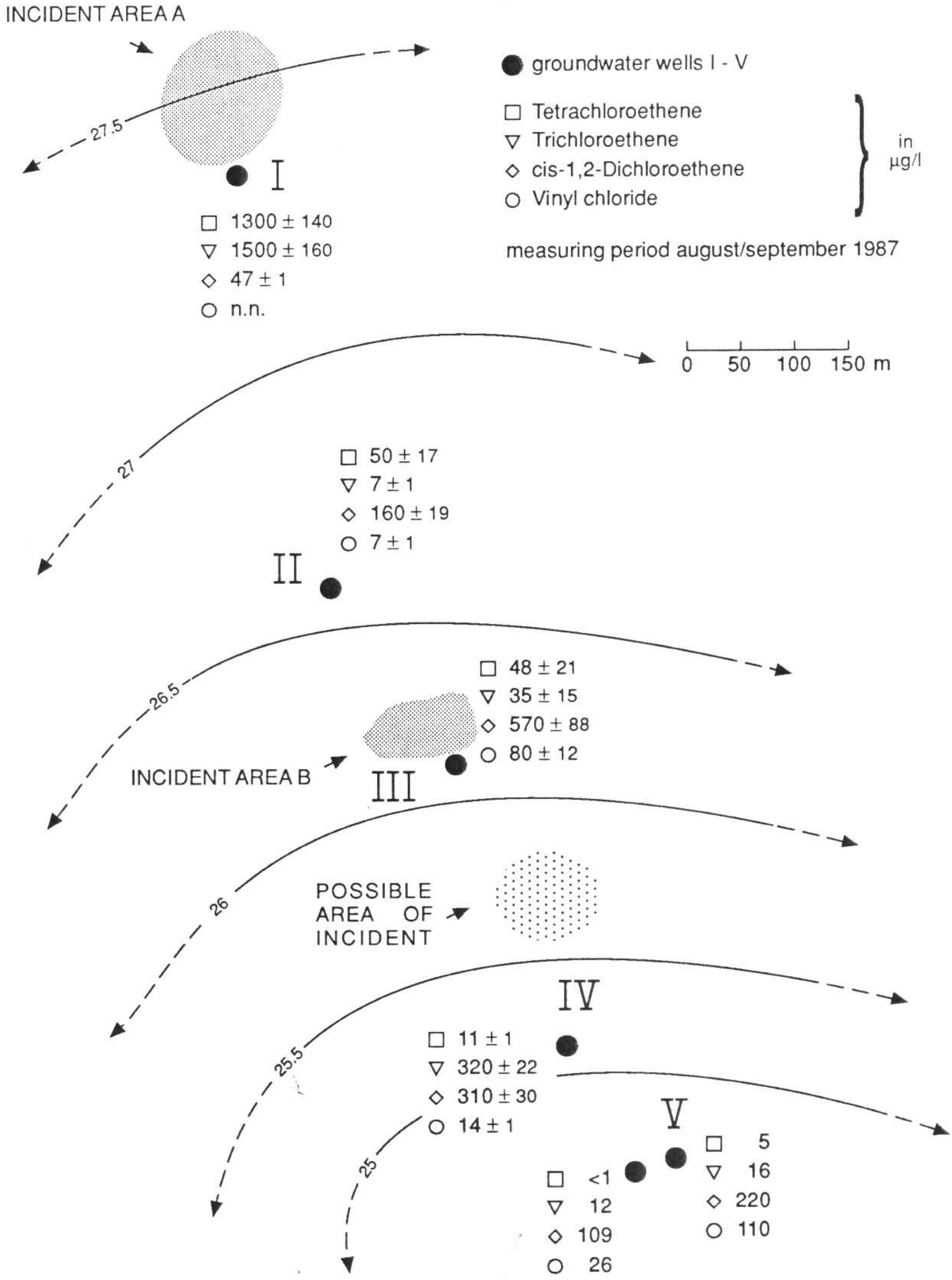

Fig. 4. - Tail of chloroorganic solvents and their degradation products vinyl chloride and cis-1,2-dichlorooethene in a damaged drinking water catching area.

Table 6. - Concentrations (mg/m^3) of chlorinated ethenes in different wells of a large surface contamination [20]

	PCE	TCE	1,1-DCE	cis-1,2-DCE	trans-1,2-DCE	Vinyl chloride
well 1	0.7	200	9.0	550	<5	15
well 2	84	145	16	1430	7.5	322
well 3	178	169	15	1050	6.5	406
well 4	135	348	49	2310	13	1040

PCE: tetrachloroethene; DCE: dichloroethene; TCE: trichloroethene.

Table 7. - Occurrence of chloroorganic compounds in 79.2% of those groundwaters which were used for drinking water production in Germany 1985/86 (Modified from [21])

	Occurrence in % of that amount of groundwater, which was analysed on the respective contaminant questionnaire [21]				
Concentration range (µg/l)	**dichloromethane**	**1,1,1-trichloroethane**	**trichloroethene**	**tetrachloroethene**	**trichloromethane (chloroform)**
≤ 0.001	96.3	72	65.3	66.6	77.6
> 0.001 up to 0.5	2.4	23.6	21.2	20.5	13.4
> 0.5 up to 1.0	0.6	2.0	4.7	3.0	6.4
> 1.0 up to 5.0	0.1	1.7	4.3	4.9	2.2
> 5.0 up to 10	0.6 *(a)*	0.5	1.6	1.3	0.4 *(b)*
> 10.0 up to 50	-	0.2	2.7	4.5	-
> 50 up to 500	-	-	0.2	0.5	-
Amount of water with no data reported	$1214 \cdot 10^6\ \mathrm{m^3/a}$	$1013 \cdot 10^6\ \mathrm{m^3/a}$	$840 \cdot 10^6\ \mathrm{m^3/a}$	$836 \cdot 10^6\ \mathrm{m^3/a}$	$898 \cdot 10^6\ \mathrm{m^3/a}$

(a) upper level: 11 µg/l.
(b) lower level: 8.0 µg/l.

examination of the questionnaires revealed that the results did indeed refer to non-chlorinated groundwater. The explanation may be that the solvents stemming from recycling processes contain a significant amount of trichloromethane, so that contamination of groundwater with these widely used solvents also results in trichloromethane reaching the groundwater [21].

As to the dichlorbenzenes, there were analysis available only for 2% (132 x 10^6 m^3/a) of the distributed drinking water. Their concentrations were between 0,001 and 0,5 µg/l. This result is not representative because of the small fraction of drinking water examined on these substances [21]. For vinyl chloride, there is no information at all on its occurrence in drinking water.

The detection frequency of a number of organochlorine compounds was determined at our institute up to 1989. These data are presented in Table 8. They differ somewhat from the information on detection frequency in Table 7, but this is probably because of the different detection limits. Even so the chloroform was detected in (non-chlorinated) groundwater quite frequently. There were no data collected on vinyl chloride during this test programme.

Summary of the findings on groundwater and conclusions

Volatile organic substances containing halogen are the most prominent groundwater contaminants, both in terms of the frequency with which they are detected, as well as the concentration found. The majority of the contaminants detected belong to the group of halogenated alkanes, alkenes and aromatic substances in which the chlorine-substituted, highly volatile substances clearly dominate.

Table 8. - Chlorinated organic compounds in groundwater from loose-sediment aquifers of the Federal Republic of Germany (West) used for drinking water production

Parameter	No of analyses *(a)*	dl *(b)* µg/l	> dl *(b)* no.	df *(c)* (%)	Concentration mean	Concentration max
AOX (µg/l)	**202**	**5.0**	**75**	**37.1**	**< 5**	**9.1**
1,1,1-trichloroethane	345	0.1	51	14.8	< 0.1	< 0.1
trichloroethene	346	0.1	62	17.9	< 0.1	0.22
tetrachloroethene	345	0.1	72	20.9	< 0.1	0.1
dichloromethane	302	10.0	0	0	< 10	< 10
trichloromethane	280	0.1	59	21.1	< 0.1	0.1
tetrachloromethane	222	0.1	15	6.8	< 0.1	< 0.1
bromodichloromethane	69	1.0	14	20.3	< 1	< 1
dibromochlomethane	126	1.0	13	10.3	< 1	< 1

no.: number of analyses.
(a) Groundwater samples of 153 water works.
(b) Detection limit.
(c) Detection frequency.

Table 9. - Priority of contaminants from old waste sites as it results from the incidence and concentration of their occurrence and their toxic potential in drinking water

vinyl chloride
trichloromethane
trichloroethene
trans-1,2-dichloroethene
1,4-dichlorobenzene
chlorobenzene, dichloromethane
tetrachloroethene
1,1,1-trichloroethene

↓ Decreasing priority

The most important groundwater contaminants downstream from waste landfill sites are tetrachloroethene, trichloroethene, cis-1,2-dichloroethene, chloroform, vinyl chloride and dichloromethane. PCBs, dioxins/furans or halogenated pesticides are not important because of their inferior hydrogeochemical mobility.

A further aim of the investigation was to determine which halogenated organic contaminants would be most appropriate to examine the contamination of groundwater by abandoned sites. A scaling of the toxicological potential of the main contaminants is necessary to establish such "priority contaminants." A comprehensive evaluation concept was developed [22] for this purpose. Table 9 lists the priority contaminants detected, taking into consideration their scaled toxicological potential.

Since depositing waste in landfill sites is still the most common means of waste disposal, further contamination of groundwater from existing or future landfills should be avoided by neither disposing of any of the substances listed in Table 3 nor any mixtures containing them in this way. Vinyl chloride is unlikely to be disposed of as such in landfills since it is a gas at normal temperatures, but is most likely to be present as a degradation product of tetrachloroethene and trichloroethene, as well as cis- and trans-1,2-dichloroethene. Prohibiting the disposal of the starting compounds tetrachloroethene and trichloroethene would prevent vinyl chloride contamination.

In practical terms it should be assumed that complete "avoidance" of these substances in landfills is not possible. This means that other prerequisites must be fulfilled for future landfills. For example, the landfill base should be sealed, taking into consideration these and other even more mobile substances [23].

There is still very little known about the behaviour of natural and synthetic sealings of waste landfills in the long term. It does not seem feasible to achieve total retention for more than 100 years, since many groundwater contaminants have escaped even from sealed landfill sites. Thus, future landfill sites have to be selected very carefully and chosen only on the basis of scientifically evaluated criteria.

Drinking water

Drinking water in the Federal Republic of Germany is made up of 72.8% groundwater and 27.2% surface water, the latter also including bank filtrate and enriched groundwater [24]. Both types of water can prove to have an organochlorine burden. The German Drinking Water

Table 10. - Occurrence of chloroorganic compounds in 78.8% (= 3242 · 10^6 m^3/a) of the drinking water in Germany 1985-86 (Modified from [21])

	Occurrence in % of that amount of groundwater, which was analysed on the respective contaminant and was reported on the questionnaire						
Concentration range (μg/l)	**dichloromethane**	**1,1,1-trichloroethane**	**trichloroethene**	**tetrachloroethene**	**trichloromethane (chloroform)**		**dichlorobenzenes**
					raw water	**drinking water**	
≤ 0.001	98.6	68.7	60.8	51.1	62.0	41.8	97 *(a)*
> 0.001 up to 0.50	1.2	28.3	28.5	39.7	15.8	25.6	3 *(a)*
> 0.5 up to 1.0	0	0.9	5.2	5.4	9.5	7.9	
>1.0 up to 5.0	0	2.0	4.4	3.0	12.4	22.8	
> 5.0 up to 10.0	0.2 *(b)*	0.1	0.7	0.5	0.2	1.9	
> 10.0 up to 50	-	-	0.4 *(c)*	0.3 *(d)*			
> 50 up to 500	-	-					
Amount of water with no data reported	1086 · 10^6 m^3/a	385 · 10^6 m^3/a	241 · 10^6 m^3/a	256 · 10^6 m^3/a	293 · 10^6 m^3/a		2337 · 10^6 m^3/a

(a) These data are not representative for the amount of water examined is too low.
(b) Upper limit: 8 μg/l.
(c) Upper limit: 21 μg/l.
(d) Upper limit: 16.5 μg/l.

Regulations (Trinkwasserverordnung, [25]) provides for a limit calculated for the sum total of five organochlorine compounds, i.e., trichloroethene, tetrachloroethene, dichloromethane, 1,1,l-trichloroethane, carbon tetrachloride, amounting to 10 μg/l and containing at most 3 μg/l of carbon tetrachloride. The Federal Health Office (BGA) considers deviations amounting to 50 μg/l, containing at most 6 μg/l of carbon tetrachloride and limited to a one-year period to be toxicologically tolerable [26].

Findings

Data on 78.8% (= 3242 x 10^6 m^3/a) of the drinking water supply in the area of the FRG, i.e., prior to unification, were obtained from the answers to the questionnaire that was sent to approximately 1000 water supply plants and mentioned above in context with Table 7. Since the information concerning the actual number of consumers supplied was incomplete and could not be evaluated, this number was calculated from the amount of water supplied to domestic premises and small enterprises, which is about 145 l per capita per day. According to this calculation, the number of inhabitants supplied with the water covered by the questionnaire was about 47 million. That is 77% of the entire population of the Federal Republic at that time. Thus, the results given below are considered sufficiently representative. It is not expected that supplies not sampled would be significantly different, since these contaminants have been observed in small-scale catchment areas and individual wells [21]. Therefore, the percentages cited in Table 10 may be considered to be representative, with the exception of dichlorobenzenes.

Dichloromethane levels in drinking water are insignificant. There is a low background concentration of 1,1,1-trichloroethane, but there are also clearly elevated concentrations in many cases. Trichloroethene was detected in more than one third of the samples and drinking water with more than 1.0 μg/l of trichloroethene is being supplied to 5.5% of the entire population. In the case of tetrachloroethene, the detection frequency was almost 50% with the concentrations being approximately the same as for trichloroethene.

The information gathered on dichlorobenzenes is not representative, unlike the other substances, since the samples reflect only 6.2% of the total drinking water supplied in 1986 (100% = 2493 x 10^6 m^3/a).

Table 10 shows that approximately 25% of the population is being supplied with drinking water that contains more than 1 μg/l of trichloromethane. Comparison with the corresponding untreated waters, as shown in Table 7, reflects the fact that there is a contamination present prior to chlorination in many cases. Only in approximately 20% of the drinking water supplied is the concentration of trichloromethane higher than in the corresponding untreated water. We therefore conclude that much less than half of the drinking water supplied in the Federal Republic of Germany is being disinfected with chlorine. In fact, about 60% of the drinking water is supplied to the consumer without any chemical disinfection [27]. The German Drinking Water Regulations restricts the content of trihalomethanes to 10 µg/l as of the first of January 1992; or in exceptional cases, i.e. when larger amounts of chlorine are needed, to 25 µg/l [25]. The residual free chlorine in supplied drinking water is limited to a maximum of 0.6 mg/l.

Two further studies on the organochlorine-compound burden of drinking water in the Federal Republic of Germany have been published [28, 29]. Although they are not as representative as the study discussed above, their results do not essentially differ.

There are also 7689 more recent entries on drinking water analyses "at the works" stored in the data bank, BIBIDAT [30], at the Institute for Water, Soil and Air Hygiene of the Federal Health Office (BGA). In the German Drinking Water Regulations, 5 chloroorganic solvents, i.e. tetrachloroethene, trichloroethene, dichloromethane, 1,1,1-trichloroethane and carbon tetrachloride are regulated. Of the 4901 entries concerning the first 4 of these organochlorine compounds, they were not detected in 4459 while CCl_4 was not detected in 4735 out of 4935 analyses (Tables 11 and 12).

From the 442 positive analyses on these organochlorine compounds excluding CCl_4, 368 revealed less than 2 µg/l, and of the 160 positive analyses on CCl_4, 148 showed less than 0.6 µg/l. The limit prescribed by the Drinking Water Regulations (since 1 January 1992: 10 µg/l, until then 25 µg/l; CCl_4 unchanged since 1986: 3.0 µg/l) was exceeded in 14 of the former and only 1 of the latter analyses. These data from 1989 do not essentially vary from those obtained from questioning the water works in 1985/86, mentioned above.

Baden-Württemberg reported somewhat less satisfactory regional data. In 1987/88 more than 10% (BIBIDAT 1988/89: 1.5%, see above) of the water supply plants exceeded organochlorine concentrations of 2 µg/l [31].

In the former GDR (prior to 3 October 1990), organochlorine compounds were the most frequently occurring anthropogenic drinking water contaminants detected in 1990/91. However, none of the concentrations observed were high enough to directly damage health. Water supply plants with more than 50 µg/l of organochlorine compounds contained in the drinking water were shut off from the supply network immediately after the concentration became known as part of the "immediate measures' programme" enacted by the Federal Minister of the Environment. The alternative was to initiate appropriate measures to reduce the organochlorine burden down to the valid limit of 25 µg/l before the end of 1992. An analagous procedure was used for trichloromethane the by-product of drinking water chlorination [32, 33].

Experience in water management has shown that point-site contamination occurs primarily in highly urbanized areas and that these can mostly be identified. Consequently, high-priority tasks are seen in continually monitoring industry and developing replacement substances or methods [34-36].

In cases where no alternative supply is available, for example remote household wells, otherwise unavoidable burdens [37] might be avoided by boiling the water used in the household in order to reduce its content of volatile, chlorinated hydrocarbons [38].

Table 11. - Occurrence of trichloroethene, tetrachloroethene (total concentrations) in the drinking water of the Federal Republic of Germany 1988/89 [30]

Concentration range (µg/l)	Analyses	
	Number	%
n.d.	4459	91
> n.d. ≤ 2	368	7.5
> 2 ≤ 5	41	0.8
> 5 ≤ 8	11	0.2
> 8 ≤ 10	2	0.4
> 10 ≤ 15	7	0.14
15	7 *(a)*	0.14
Analyses with no data reported	2794	36.3

(a) Maximal value: 50 µg/l.
n.d.: not detectable.

Table 12. - Occurrence of carbon tetrachloride in the drinking water of the Federal Republic of Germany 1988/89 [30]

Concentration range (µg/l)	Analyses	
	Number	%
n.d.	4775	97
> n.d. ≤ 0.6	148	3
> 0.6 ≤ 1.5	5	0.1
> 1.5 ≤ 2.4	4	0.1
> 2.4 ≤ 3.0	2	0.04
> 3.0 ≤ 4.5	-	-
> 4.5	1 *(a)*	0.02
Analyses with no data reported	2754	35.8

(a) Maximal value: 50 µg/l.
n.d.: not detectable.

The Federal Health Office (BGA) has published recommendations in 1992 for circumnstances when groundwater contaminated with vinyl chloride is needed for drinking water abstraction [39]. These recommendations are aimed at the responsible authorities and water supply plants with the goal of reducing the vinyl chloride concentration in drinking water to the lowest possible level and to maintain, or reattain a groundwater quality free from anthropogenic influences. In cases where groundwater with an high-level of vinyl chloride contamination is used by water supply plants, the Federal Health Office recommends to continuously test for vinyl chloride and to proceed with rehabilitation measures until the concentration in untreated water has fallen below 0.002 mg/l.

The methods of analysis presently available have to be further developed, to determine and to monitor rehabilitation and purification measures.

Recently, the detection limit for vinyl chloride is being cited as 0.40 ng/l by the Dortmund laboratory of the "Institut Fresenius" [40].

Avoidance and removal of volatile organochlorine compounds from drinking water

Avoiding by-products from disinfection processes. - According to data gathered by the Deutscher Verein des Gas- und Wasserfaches (DVGW), more than 60% of the drinking water supplied in the Federal Republic in 1983 has not been chemically disinfected. In most cases, this refers to supply plants that used microbiologically flawless groundwater. However, there are also several cases of metropolitan supply plants which do not need disinfection, such as Köln or the western parts of Berlin [27].

Should disinfection using chlorine become necessary, the water works have to ensure that only technically unavoidable amounts reach the consumer [41]. They are required to remove haloforms which are formed and to reduce the potential for haloforms generation by removing dissolved organic carbon (DOC) before disinfection. The same applies to the formation of chloramines when chlorinating drinking water that contains ammonium. This, however, is associated primarily with taste-related acceptance problems rather than aspects of health [24].

In the cases of leaks in the distribution system, which allows microorganisms to penetrate the system, the necessity of "preventive chlorination" is often stressed. This measure is generally indicated for as long as it takes to properly repair the damage, which can also result in water losses. Systematic "preventive chlorination" is not practised by state of the art water supply plants [24, 42, 43].

Purification measures. - Soil passage and river-bank filtration extract substances from water only to a very limited extent or not at all if these substances are difficult or impossible to be degraded chemically or biologically. Therefore, the purification of the contaminated raw water has to be completed by filtering the water through activated charcoal after ozonization or, more recently, a combined treatment with UV and hydrogen peroxide. This then extracts a total of approximately 80%. 1,1,1-Trichloroethane and tetrachloroethylene are volatile compounds that are the most resistent to degradation [44]. The standing times of the activated charcoal filters until the organohalogen compounds break through are now only three to six months, due to the organic burden of river-bank filtrates [24].

Aeration is particularly good at removing vinyl chloride from water. The treatment plants require an effective gas exchange to raise the pH by 1.5 or more due to elimination of CO_2. Therefore, it proves to be frequently necessary to absorb the organic pollutants once they are in the gas phase on activated charcoal but to retain the CO_2 in the circulating air, so that the pH value described by the calcium-carbonate saturation is not exceeded too far [45]. The rest of the above-named organochlorine compounds can be stripped as well under these conditions. But when the starting concentration is low, removal can be unsatisfactory and is often less than 30%. Apart from vinyl chloride, 1,1,1-trichloroethane is well removed by aeration but this method is not effective for removal of trichloromethane [21].

The effectiveness is usually far greater in water works and experimental setups that were perfected for extracting individual organochlorine compounds, than it is at water works that extract other classes of substances as well with the same purification steps.

The following figures were obtained by attempting to estimate the amount of organochlorine solvents eliminated by the water works, based on the information gained from the above-mentioned questionnaire: approximately 5000 kg of trichloroethylene contained in the untreated water reaches the water works in the old Federal Lander each year, of which 1100 kg are retained in the purified drinking water. The water works therefore extract 3900 kg per annum from the water cycle. Similarly 5500 kg of tetrachloroethylene reaches the plants, of which 1000 kg remain in the water, resulting in a total of 4500 kg extracted in 1985/86 [21].

Evaluation of the overall situation and conclusions

This survey has shown that both large-area contamination and frequent point-source pollution of groundwater by volatile organochlorine compounds occurs in Germany. The substances which occur in the greatest amount are trichloroethene and tetrachloroethene. The degradation product, vinyl chloride, is toxicologically highly relevant and appeared up to now in significant concentrations in unprotected groundwaters. It is comforting that these and the other chemically related substances still play an insignificant part in the contamination of drinking water. This is probably the result of groundwater protection by enforcing protective zones and the long term use of extensive purification processes in those areas that rely on river-bank filtrate for drinking water. In addition aeration and oxidation which remove iron may in many cases also purge vinyl chloride from contaminated raw waters.

It is the goal of the German water management to not require chemical purification in as many plants supplying drinking water as possible. This already applies to at least 60% of the groundwater used for drinking water. The regulative basis for this are the Federal Act on Epidemics and Contagious Diseases (Bundesseuchengesetz), the Drinking Water Regulations and DIN 2000 [46]. To both stabilize and improve the position, it will be necessary to ensure that these and other problematic substances that may contaminate water are only used in closed systems, and that the most rigid of safety measures are imposed on their disposal and transport [47]. Such measures already appear to have taken effect in Germany on a voluntary basis, since the production of organochlorine solvents for the German inland market has declined from 180,000 t per year in 1985 to 95,000 t per year in 1990 [48].

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