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BEHAVIOUR OF ORGANIC SOLVENTS IN THE ENVIRONMENT

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1. INTRODUCTION

Chlorinated organic solvents-such as perchloroethylene, trichloroethylene and 1.1.1-trichloroethane - easily dissolve unpolar substances; they therefore came into widespread use for degreasing processes in all branches of metal-industry and for dry cleaning of textiles. Minor amounts are nedded for fat extraction (animal carcass processing, cacao refining etc.). Only in the case of perchloroethylene a considerable quantity, i.e. 5-20 %, is subjected to chemical change (Teflon production).

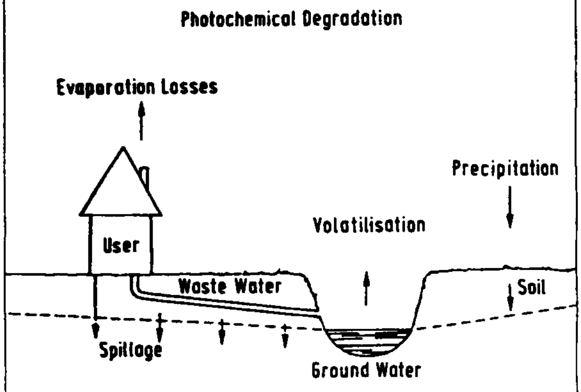
Since relevant P-C parameters of solvents (i.e. boiling point, specific heat, evaporation energy) are comparably low, their recycling at a low energy demand is performed easily (desorption of charcoal filters and/ or destillation). Thus, theoretically a recycling rate of nearly 100 % could be achieved. With the exception of minor quantities for chemical synthesis and stock enlargement, nowadays nearly all purchases of the solvents balance losses during application.

Thus table 1 indicates rough values of the approximate quantity of contaminating input into the environment. A scheme of solvent's pathways into and through environmental compartments is given in figure 1. Control of emission is extremely difficult because of the high number of potential sources;

TABLE 1: Consumption and production of solvents (LÖCHNER 1980) and estimated percentage entering the environment

Solvent	consumption FRG 1979 producer's statement	world production 1973 estimated	percentage entering environment
Perchloroethylene	95.200 t	1.050.000 t	80 - 95
Trichloroethylene	56.400 t	1.010.000 t	80 - 100
1.1.1-Trichloroethane	30 - 35.000 t	———	80 - 100

SÜMMERMANN and KORTE determined numbers of applicants in Bavaria (10.3 mio. inhabitants) in 1978: 22,574 metal working and 1,653 dry cleaning shops.



Pathways of Highly Volatile Chlorinated Solvents in the Environment

Fig. 1

2. PATHWAYS INTO GROUNDWATER

Groundwater - the most important drinking water source in Germany - may be inflicted in two ways - either by accidental spillage including all kinds of leakage or from primarily volatilized solvent via atmosphere - soil; the resulting distribution patterns are different.

Direct Contamination

Larger quantities of liquid solvent poured onto the soil (accident of a tank lorry) will move vertically through soil and - because of its higher density - through groundwater, polluting but not mixing. On the base of the aquifer it will collect in its own phase becoming a long lasting source of future contamination of the groundwater above (SCHWILLE 1981).

Considerable spillage leading to heavy groundwater contamination can be caused by improper storage; especially for used solvent cases are reported, where rotten steel barrels were stored away in the open without or with leaky concrete containments, unsheltered against temperature rise, leading to cracking pressure increases.

Improper disposal of solvent-containing residues at waste deposits or uncontrolled dumping sites as well as immission of solvents or solvent-containing liquids into sewage systems have caused peak values of groundwater contamination due to leakage of a sewage pipe.

Figure 2 shows a patters of groundwater contaminations in the Heidelberg area (DIETZEL 1980). At least five sources may be assumed, among them a yard where used solvents are stored before recycling, a waste deposit where in the past solvents were burnt, and a small chemical plant.

As the plumes of contamination - dependent on the hydrogeological conditions controlling the flow pattern of groundwater - in some cases

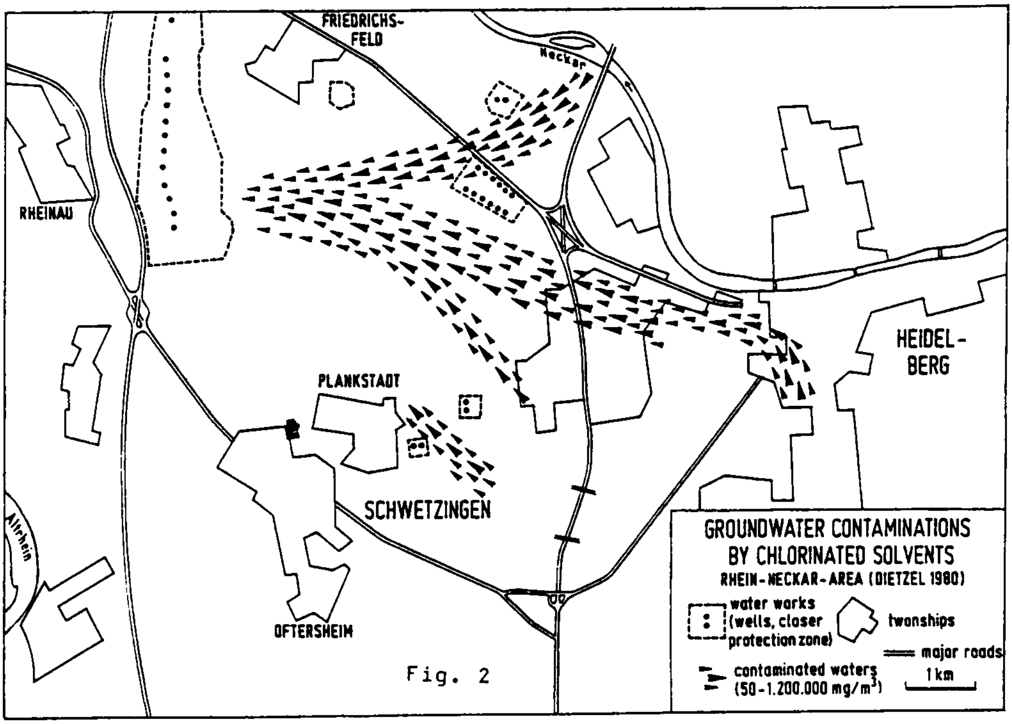


Fig. 2

contact the draw-down areas of water plant's wells, there is an urgent need for sanitation of the groundwater contamination. This is done by drilling of catching wells by means of which groundwater is pumped off at considerable costs into the neighbouring sewage systems after charcoal treatment.

Whereever to any larger extent these substances are handled, improper handling will cause similar situations because once chlorinated organic solvents have entered subsoil, there is little degradation to be expected (see table 2).

TABLE 2: **Half life times of hydrolytic degradation reaction (c.f. SCHERB 1978)**

Solvent	$t_{1/2}$ **years**
Perchloroethylene	**6**
Trichloroethylene	**2,5**
1.1.1-Trichloroethan	**0,75**

3. ATMOSPHERIC CONTENTS

However severe the hazard - as mentioned above - may be only a very small part of the solvents entering the environment directly goes to the compartment "groundwater". By far the larger quantities volatilize into the atmosphere either during application of the solvents or from their residues in treated products and wastes or out of sewage or open receiving systems.

SCHERB (1978) studied the half life times of evaporation out of a model flow system (table 3). His results indicate that within hours solvents emitted by sewage systems into rivers will evaporate into the atmosphere. Recent research of our institute in the Rhein-Main area, controlling solvent concentrations along the Main river directly at and downstreams of point source emissions, proved his results.

TABLE 3: Half life times of evaporation out of a model flow system (SCHERB 1978)

Solvent	$t_{1/2}$ hours
Perchloroethylene	3,64
Trichloroethylene	3,14
1.1.1-Trichloroethane	4,31

Resulting atmospheric concentrations of perchloroethylene (table 4) range from 1 $\mu g/m^3$ in the countryside to an average of about 5 $\mu g/m^3$ in major towns up to extreme values of 174 $\mu g/m^3$ in the neighbourhood of a dry cleaner (LÖCHNER 1978) . A possible sink of solvent contamination is photochemical degradation in the atmosphere, a process for which half-life times between 6 and 10 weeks have been reported (McCONNELL e.a. 1975). However - mean duration in atmosphere is unknown and an estimation of the degraded quantities not possible. Atmospheric concentrations seem to have reached an equilibrium constant over the last years (ROHLEDER; personal communication). As already mentioned above an unknown subquantity of the atmospherical contents contacts soil and infiltrates, therefore current research of the institute within the frame work of ecotoxicology deals with distribution studies of the three solvents in saturated and unsaturated soils, with investigations of mechanisms during subsoil-passage and transport into groundwater with special respect to the possibility of negative secondary-effects.

TABLE 4: Perchloroethylen concentrations in air ($\mu g m^{-3}$) *at several distances from the center of Munich* (Karlsplatz) (LÖCHNER 1978)

distance	series I			series II		
	min	mean	max	min	mean	max
0 km	2	3	6	3	5	6
1 km	1	6	25	3	7	14
5 km	1	4	11	2	5,5	15
10 km	0	4	17	1	4	15

4. SOLVENT CONCENTRATIONS IN SOILS

Table 5 shows the distribution pattern of concentrations in soil air in the Black Forest. (The observed contents cannot be traced down to specific sources of emission but are taken to represent ubiquitary background values in Middle Europe). There is a remarkable correlation between altitude and concentration on both the western and eastern slopes of the mountain range, differing significantly in absolute values due to exposition. A connection between degree of contamination and altitude-correlated parameters such as precipitation and temperature can be assumed. Soil air concentrations exceed observed concentrations above the soil surface up to two orders of magnitude. Concentrations rise along the soil profile from a surface minimum to maxima considerably far below, even in a depth of 80 cm, where drillings in these mountain soils usually touch the parent rock, high contamination values are found (NEUMAYR 1981).

TABLE 5: **Distribution pattern of solvents in soil air in a W – E sequence across the Black Forest Mountains ($\mu g \cdot m^{-3}$) (NEUMAYR 1980)**

soil depth. cm	West. SLOPE			East. SLOPE			altitude above sea level (m)
	PER.	TRI.	1.1.1 T	PER.	TRI.	1.1.1 T	
15	96	38	7	17.9	11.8	1.3	500
30	112	57	15	21.5	13.4	1.3	
80	98	41	12	18.2	12.0	1.2	
15	38	16	3	13.9	7.6	<1	300
30	42	19	5	15.2	7.9	<1	
80	39	17	3	14.2	7.5	<1	
15	8.6	3.7	<1	5.2	1.9	<1	200
30	12.8	4.9	<1	7.1	2.3	<1	
80	9.1	4.3	<1	5.6	1.9	<1	

In three natural test soils - all sites located in South Hessia - the solvents distributions in a three-phase-system (solid - gaseous - liquid) has been studied (table 6). As it is to be seen clearly, soil I is highly contaminated, probably due to lateral inflow from a nearby creek receiving the discharge of a municipal sewage plant. Soil II and III contain average concentrations of the ubiquitary compounds in question.

A very rough estimation for perchloroethylene, concerning its total burden in soils of the FR Germany, is tried to be achieved by consideration of the following values:
Regarding a section cube (a ◘ 100 cm) of soil III we gain an average of 6 $\mu g/m^3$ for the gaseous phase while the solid phase contains about 3000 $\mu g/m^3$, i.e. only about 0,2 percent of the solvent remain in the gaseous phase.

Assuming this type of soil to be representative and of average standard for our country, we calculated the total perchloroethylene content in the soils of FR Germany - by multiplying with the country's area - to be 750 t. This thumb value - though by no means exact - may give some idea of magnitude.

TABLE 6: Concentrations of solvents in three soils (NEUMAYR 1980)
(g = gaseous, $\mu g \cdot m^{-3}$; d = dissolved, $\mu g \cdot l^{-1}$; s = solid, $\mu g \cdot kg^{-1}$)

Soil	Hor.	Depth. cm	Perchloroethylene			Trichloroethylene			1.1.1-Trichloroethane		
			g	d	s	g	d	s	g	d	s
I	O_f	3	435	–	51.7	98	–	5.2	5.6	–	< .1
peaty	T	11	950	–	88	117	–	5.8	7.2	–	< .1
gley	A_a	22	1250	–	96	152	–	6.1	10.1	–	< .1
(saprist)	A_a	36	–	9.7	12.1	–	1.7	1.1	–	1.0	< .1
	G_r	50	–	11.3	6.2	–	2.1	1.3	–	1.1	< .1
	G_r	80	–	14.2	2.2	–	2.8	1.5	–	1.3	< .1
	G_r	100	–	14.7	2.2	–	2.9	1.7	–	1.3	< .1
II	$A_{h,Ca}$	8	23	–	3.7	14	–	< .1	0.8	–	0.1
Czer-	$A_{h,Ca}$	17	24	–	3.9	17	–	< .1	0.9	–	0.1
nitsa	$A_{h,Ca}$	32	38	–	4.1	28	–	< .1	3.0	–	0.2
(aquoll)	G_{OCa}	50	–	0.5	1.2	–	0.1	< .1	–	< .1	< .1
	C_{Ca}	70	–	0.6	0.9	–	0.2	< .1	–	< .1	< .1
	C	90	–	0.6	0.8	–	0.2	< .1	–	< .1	< .1
III	A_h	5	16.9	–	2.1	5.8	–	0.2	0.9	–	< .1
brown	B_{V1}	10	15.2	–	1.9	5.1	–	0.2	0.8	–	< .1
earth	B_{V2}	30	11.3	–	1.2	2.1	–	< .1	< .2	–	< .1
(ochrept	C_{V1}	50	10.2	–	1.1	1.9	–	< .1	< .2	–	< .1
	C_{V2}	70	14.2	–	1.5	3.4	–	< .1	< .2	–	< .1
	C_{V3}	90	13.1	–	0.9	2.9	–	< .1	< .2	–	< .1

A comparison with quantities used in the country during one year only (table 1) points out that it seems unlikely for soils to possess an adsorption-capacity of sufficient efficiency for highly volatile chlorinated organic solvents. Therefore, filtering effects preventing solvent from percolating into groundwater may be quite low.

5. SOLVENT CONCENTRATIONS IN GROUND- AND DRINKING WATERS

Consequently KUSSMAUL e.a. (1980) surveying drinking waters in the Rhein-Main area (table 7) found trichlorethylene concentrations of more than 1 µg/l with average maxima up to 3,7 µg/l in five out of ten regional groups of analyzed waters. Corresponding contents of perchloroethylene were slightly lower. The five less contaminated groups, too, showed measurable concentrations of perchloroethylene and trichloroethylene in most of the analyzed waters.

Comparable results are reported from the New Jersey Groundwater Survey (c.f. KUSSMAUL e.a. 1980) where trichloroethylene and trichloroethane were detected in most of the water samples, perchloroethylene

TABLE 7: **Solvent concentrations in drinking waters in the Rhein–Main area ($\mu g \cdot l^{-1}$) mean values, minimum and maximum in brackets (KUSSMAUL e.a. 1980)**

	TRI	PER	1.1.1–T
Wiesbaden (4)	0.1 (n.d./0.2)	0.7 (n.d. / 1.8)	n.d. (n.d. / n.d.)
Ried (38)	0.4 (n.d. / 5.5)	0.3 (n.d. / 2.7)	0.05 (n.d. / 1.5)
private utilities (Odenwald / Ried, 7)	0.7 (0.4 / 1.1)	0.2 (0.1 / 0.3)	n.d. (n.d. / n.d.)
surface wells (Ried, 8)	0.6 (0.2 / 2.6)	0.4 (n.d. / 2.7)	0.1 (n.d. / 1.0)
Odenwald (6)	0.6 (0.2 / 1.1)	0.1 (n.d. / 0.3)	n.d. (n.d. / n.d.)
Frankfurt (21)	1.1 (n.d. / 3.8)	1.1 (0.1 / 7.1)	n.d. (n.d. / n.d.)
Mannheim (6)	1.6 (0.3 / 7.1)	0.5 (n.d. / 2.5)	0.4 (n.d. / 2.5)
Taunus (16)	2.5 (n.d. / 9.5)	2.5 (n.d. / 10.5)	n.d. (n.d. / n.d.)
Rödermark (9)	3.7 (n.d. / 14.2)	2.3 (0.1 / 9.8)	0.1 (n.d. / 0.8)
drinking water from surface water (7)	2.5 (0.2 / 8.0)	0.9 (0.2 / 2.5)	0.2 (n.d. / 0.6)

still in 23 % of the analysis. While the contents of each, perchloroethylene and trichlorethylene, in about 10 % of the samples exceeded 1 μg/l, 50 % of the 1.1.1-trichlorethane concentrations were above 1 μg/l, 10 % even exceeding the 10 μg/l level.

Another estimation - like above - of the total perchloroethylene content of all groundwaters of the FR Germany, basing on a mean concentration of 1 μg/l, yields a thumb value 2500 t. Though this does not take into consideration the more contaminated groundwaters it still may allow doubts whether groundwater is a major sink of the volatile chlorinated solvents (compare table 1).

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