BIOLOGICAL DEGRADATION OF VOLATILE CHLORINATED HYDROCARBONS IN GROUNDWATER

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ABSTRACT

Chlorinated organic solvents - such as tetrachloroethene, trichloroethene and 1,1,1-trichloroethane - are the most frequently used compounds e.g. for degreasing in all branches of industries.

Due to their widespread use, their large consumption quantities (Fed. Rep. of Germ. 180 x 10^3 t/a) and their physical properties, these organic solvents are the most important point-source of groundwater contamination.

A serious case of soil, soil air and groundwater contaminating by these organic solvents (maximum concentrations detected were 500 mg/kg, 7g/m³, 50 mg/l respectively) is reported, caused by the metal industry, rendering plant and paper production.

A special effect is the comparatively rapid degradation sequence of tetrachloroethene to trichloroethene to cis-1,2-dichloroethene and to vinyl chloride. Concentrations of cis-1,2-dichloroethene observed in groundwater were up to 1600 µg/l and of vinyl chloride up to 120 µg/l, respectively, although none of these substances were primary pollutants in the investigated area.

Results of laboratory tests give rise to the suggestion that degradation of chlorinated hydrocarbons in contaminated areas is mainly by microbiological means.

This effect is of special hygienic relevance, due to the fact that one of the metabolites, vinyl chloride, is known to be a human carcinogen and the polluted area (approx. 4 km²) is located in a catchment area of a waterworks.

KEYWORDS

Groundwater, volatile chlorinated hydrocarbons, biological transformation.

INTRODUCTION

Chlorinated organic solvents - such as tetrachlorethene (PCE), trichloroethene (TCE), and 1,1,1-trichloroethane - easily dissolve nonpolar substances; that is why they are widely used in degreasing processes in all branches of the metal industry and in the dry cleaning of textiles. Minor quantities are needed for fat extraction (animal carcass processing, waste paper processing, etc.) and for the production of chemicals. The annual consumption (1979) of the three solvents in the Federal Republic of Germany was approx. 190,000 t of which...
approx. 80 to 100% is entering the environment (170,000 t) (Löchner, 1981). The largest proportion of these contaminants will be volatilized and released into the atmosphere. A possible decomposition of the solvent is caused by photochemical degradation, a process for which half life periods between 6 and 10 weeks have been reported (McConnel, 1975).

Groundwater, the most important drinking water source in Germany and other countries, may be affected in two ways, either by accidental spillage including all kinds of leakage, or by contamination by primarily volatilized solvents via the atmosphere and the soil.

Many cases of serious groundwater pollution mainly caused by spillages have been reported.

For example, a ground water survey in New Jersey showed positive results for trichloroethene in 73% of the samples. Out of the 378 samples with a content of 10 μg/l, 15 samples had concentrations of 10 to 100 μg/l, and 4 of more than 100 μg/l.

If a spillage caused by volatile chlorinated hydrocarbons (CHC) occurs, their solubility in water, their density, and other factors create a typical migration pattern (Schwille, 1981). Investigations show that the spillage region itself is characterized by an area with CHC in phase surrounded by an area of residual saturation. If a large spillage surplus exists, a saturated CHC cone will develop on the impermeable bottom layer. In the groundwater downstream area, the saturated pollution cone releases a pollution plume consisting of dissolved chlorinated hydrocarbons only.

These dissolved chlorinated hydrocarbons are the cause of the above-mentioned contamination of ground and drinking water. The first studies in this field were made in the late nineteen seventies. During these years and later, field studies showed the persistence of these chlorinated hydrocarbons. Travel distances of the unaltered pollutants up to 8 km and more in unconsolidated sand and gravel aquifers have been observed (Dietzel, 1981).

In recent years, new pollution cases have been reported, where biodegradation of the halogenated solvents took place and where the contamination has been limited in space and time.

**BASIC CONDITIONS OF NATURAL BIOTRANSFORMATION**

According to the existing observations the halogenated solvents are persistent in oxygenated groundwater. Under anaerobic conditions they can undergo a sequential reductive dehalogenation from tetrachloroethene to trichloroethene, then to cis-1,2-dichloroethene and finally to vinyl chloride (Kühn, 1986; Vogel & McCarty, 1985). Laboratory investigations with a maximum duration of 60 days showed that the biological half-life was 34 days for tetrachloroethene under such ideal conditions and 43 days for trichloroethene. For cis-1,2-dichloroethene and vinyl chloride, the biological half-life was long, which means that during the observation period of 60 days no reduction of the compound was detected (Wood, 1985).

The following bacteria participated in the biodegradation of tetrachloroethene: *Clostridium cadaveris*, *Clostridium limosum*, Gram positive cocci, large Gram positive rods, filaments (2 x 10 Trichome), *Pseudomonas maltophilia*, *Pseudomonas fluorescens*, Gram negative short wide rods, *Proteus vulgaris*, *Enterobacter cloacae*, *Escherichia coli*, *Pseudomonas aeruginosa*. In the laboratory tests also biodegradation of either tri- or tetrachloroethene was found to result in the production of cis over trans-1,2-dichloroethene by a factor of approx. 25 to 1 or more (Wood, 1985).

The process of reductive dehalogenation is similar to respiration. The chlorinated compound accepts electrons and is reduced to the hydrogenated compound, while chlorine is released as chloride ion. The electron donor can be the co-occurring contaminants or organic carbon in the geological matrix (peat, lignite) (Wilson, 1986). According to Bouwer & McCarty (1983) it could not be demonstrated up to now that nitrate- or sulfate-respiring microorganisms can degrade chlorinated ethenes or ethanes. Recent research indicates that bacteria that grow on aliphatic hydrocarbons like methane contribute to
Degradation of volatile chlorinated hydrocarbons

the biological decomposition of tetrachloroethene, trichloroethene etc. Methanogens are only active in highly reducing environments (Wilson, 1986).

**Fig. 1. Reductive dehalogenation of tetrachloroethene**

**INVESTIGATION RESULTS**

The investigation results are described in order to present data from a case of such natural biotransformation.

**General situation**

The investigation was carried out in the catchment area of Pleistocene outwash, sand and gravel aquifers with a saturated thickness of approx. 25 - 35m. In the mostly unsaturated cover very often Holocene fine sand occurs with intercalations of peat, silt and sapropel having a maximum thickness of 10m. The permeability of the saturated aquifer is approx. 1x10⁻⁶ m/s (1x10⁻⁹ to 5x10⁻⁷ m/s). Below the main aquifer there is often organic matter containing interglacial clayish sediments. Therefore, enough sources of organic material are present in the top and bottom sediments as well as in the aquifer itself. In some areas, the interglacial bottom aquiclude does not exist. There is a connection between the Pleistocene and the underlying Miocene sands with intercalations of very thin lignite seams which occur in a saturated zone with a thickness of about 100m containing an additional organic carbon source.

After the first appearance of chlorinated hydrocarbon contamination in the groundwater (25 μg/l), a survey was initiated to investigate its sources in the catchment area.

The survey of the handling of chlorinated hydrocarbons in the close catchment area showed that nearly 300,000 kg/y of these solvents were used. Only one fifth of this quantity was eliminated by waste disposal. 83 places of handling were recorded. In some areas the solvent used was tetrachloroethene only; in other areas approx. 75% tetrachloroethene and approx. 25% trichloroethene were used. No use of dichloroethene and vinyl chloride was observed.

The investigation of ground and waste water showed a different distribution of chlorinated hydrocarbons. When analyzing groundwater in the general catchment area, only 1 μg/l could be detected, but in a few sections, up to 50,000 μg/l
were found. The latter could be delineated in most cases by means of soil air analysis.

Investigation of the waste water was also important. An examination of sewers which drain polluted waste water containing high concentrations of chlorinated hydrocarbons (sometimes up to 120 mg/l) for possible leakages often proved to be successful.

In the investigation area, a total of 1,400 soil air samples was taken and analyzed. Thus it was possible to subdivide the area into sections with comparable soil air concentration: up to 200 μg/m³ (as background level in the respective area); up to 100,000 μg/m³ (handling areas); and up to 7,000,000 μg/m³ (centres of contamination).

The soil investigation, carried out in the areas of maximum concentration, gave information on the distribution of chlorinated hydrocarbons in the soil. Concentrations between a few μg/kg as background level and 1,000,000 μg/kg in the centres were found.

Findings on natural biotransformation

Previously the analytical methods were oriented towards the primary pollutants tetrachloroethene and trichloroethene only. Substantial losses of primary pollutants along the ground water pathway between sources and wells directed the attention towards the microbiological transformation of the primary parent pollutants to daughter compounds like cis-1,2-dichloroethene and vinyl chloride. The investigation results showed that gaps could be closed in this way.

The first preliminary results are presented here, i.e. results from investigations using samples of vertically mixed groundwater pumped out of the individual sampling well. To recognize differences in the geochemical microfacies, a vertically differentiated sampling is in preparation. Additional hydrogeochemical parameters will be investigated. The recent results are presented for three different sections of the whole investigation area (sections I, II, III).

Section I represents an area where the mother contaminants were tetrachloroethene (75%) and trichloroethene (25%). Two main point sources of contamination were found, one at monitoring well 1 and the other between wells 4 and 5. Downstream of these point sources the highest concentration of the mother contaminants could be measured (Fig. 2). The time passed since the first con-

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**Fig. 2.** Investigation results at section I
Degradation of volatile chlorinated hydrocarbons

Tamina$t seepage was long enough to allow the formation of daughter contaminants, but the concentration of daughter contaminants at monitoring wells 1 and 5 was lower than that of primary parent contaminants. With the slow groundwater downstream movement, the content of parent contaminants decreases simultaneously with the relative increase of daughter contaminants. Maximum contents of parent contaminants (PCE 1600 µg/l; TCE 2000 µg/l) in the catchment area decrease to minimum contents downstream (PCE 34...0,1 µg/l; TCE 79...1µg/l). Conversely, daughter contaminants reach maximum concentrations of 1000 µg/l cis 1,2-dichloroethene and 62 µg/l vinyl chloride in the catchment area. In the well-area cis-1,2-dichloroethene with levels between 1 and 360µg/l and vinyl chloride between 1 and 57 µg/l were found.

Very low dissolved oxygen concentrations (0,1...0,7 - point 5 there is an outlier caused by a recently drilled well) were also observed. Taking into consideration that these levels were found in mixed groundwater samples, it may be concluded that in many microfacial areas there are environments where groundwater-reducing conditions exist (reduced groundwater has 1,4mg/l O₂; whereas the general O₂ content is between 6 and 12mg/l). The temperature occasionally exceeds the background levels (10,1 °C), (Fig.2) by more than 3 °C. Also the background value for conductivity (360 µS/m) is drastically exceeded reflecting, presumably, the general influence of industrial activity in the catchment area.

The distribution of contaminants in section II, (Fig. 3) shows a very similar pattern. The parent pollutant was tetrachloroethene only. In the course of the groundwater flow, a considerable change from parent to daughter components could be observed.

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Fig. 3. Investigation results at section II

Section III (Fig. 4) reflects a high decrease in the concentration of the pri-

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Fig. 4. Investigation results at section III
mary contaminant tetrachloroethene, which in this case is also due to natural biotransformation. Contents of vinyl chloride between 9 and 38 μg/l are especially critical. The geochemical environment is generally characterized by the known low oxygen content. Also elevated temperatures and conductivities are observed.

**Laboratory investigations**

In the laboratory, decomposition tests were carried out. In one section a rendering plant is located. Its waste water may contribute to the intensive groundwater contamination by solvents as well as by other organic pollutants. The laboratory test performed with this waste water containing high amounts of organic substances shows ideal conditions for the transformation of solvents. In the non-sterile sample, all primary parent pollutants are transformed into daughter pollutants after only 6 days. The biological nature of this transformation was proved by a sterilized parallel test in which no transformation took place (Fig.5).

![Diagram of laboratory decomposition tests]

**CONCLUSION**

A serious case of soil, soil air, and groundwater contamination (maximum concentrations detected were 500mg/kg, 7g/m³ and 50 mg/l, respectively) by the primary pollutants, tetrachloroethene and trichloroethene, is described, caused by the metal industry, rendering plant and paper production.

Special attention is paid to the comparatively rapid degradation sequence of tetrachloroethene to trichloroethene, cis-1,2-dichloroethene and to vinyl chloride. The latter two substances were not primary pollutants in the investigated area. The examination of the geochemical environment and results of laboratory tests indicate that the degradation of chlorinated hydrocarbons in this case is of microbiological nature.

**REFERENCES**


Degradation of volatile chlorinated hydrocarbons

KUHN, W. (1986). Aufbereitung von Wasser, das durch leichtflüchtige Chlor-

LÖCHNER, F. (1981). Lösungsmittel aus leichtflüchtigen Halogenkohlen-
wasserstoffen (HKW). Produktion, Einsatzbereiche und Verwendungs-
technologien. in: AURAND, K. & FISCHER H. (eds.). Gefährdung von
Grund- und Trinkwasser durch leichtflüchtige Chlorkohlenwasserstoffe.

Kohlenwasserstoffe in der Umwelt. Endeavour, 34, 13-18

SCHWILLE, F.(1981). Schadensermittlung, Verursachersuche und Sanierungs-

to Trichloroethylene, Dichloroethylene, Vinyl Chloride, and Carbon
Dioxide under Methanogenic Conditions. Applied and environmental
Microbiology, 49, 5, 1080-1083.

WILSON, J.T., LEACH L.E., HENSON M. & JONES J.N. (1986). In Situ Bioresto-
ration as a Ground Water Remediation Technique. Ground Water
Monitoring Review, Fall 1986, 56-64.

WOOD, P.R., LANG P.F. & PAYAN J.L. (1985). Anaerobic Transformation, Trans-
port, and Removal of Volatile Chlorinated Organics in Ground Water. in: