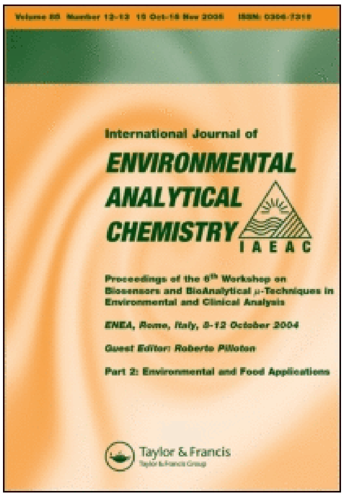

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Leschber, Reimar , Mergler-voelkl, Rolf and Nerger, Manfred(1990) 'Soil and Groundwater Contamination by Low Boiling Chlorinated Hydrocarbons in Berlin. Formation of Metabolites and their Analytical Determination', International Journal of Environmental Analytical Chemistry, 39: 2, 159 — 164

To link to this Article: DOI: 10.1080/03067319008027692

URL: http://dx.doi.org/10.1080/03067319008027692

Intern. J. Environ. Anal. Chem., Vol. 39, pp. 159–164
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SOIL AND GROUNDWATER CONTAMINATION BY LOW BOILING CHLORINATED HYDROCARBONS IN BERLIN

Formation of Metabolites and their Analytical Determination

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(*Received 9 January 1989; in final form 27 July 1989*)

INTRODUCTION

Some years ago, drinking water analysis in Berlin showed a remarkable but not critical concentration of low-boiling chlorinated hydrocarbons in the μg-range which led to investigations of the wells of one of the Berlin water works and of the respective catchment area.

A certain number among a total of 51 wells which were located within a pleistocene sand and gravel aquifer were found to be contaminated with trichloroethene and to a lesser degree with tetrachloroethene.

Following these findings, an intensive investigation programme was undertaken which comprised an extended grid of sampling points for soil-air analyses in the respective catchment area, groundwater analyses in existing observation wells, and soil analyses in profile pits, exploratory drillings, and newly drilled investigation wells.

During these examinations which were reported to the customer in two internal reports,[1] different sources of pollution could be identified. In some cases they could be attributed to former industrial activities or to handling of chlorinated solvents at present. When determining the extent of pollution and ways from the sources to the waterworks wells, a decrease of concentration of tetra- and trichloroethene along the groundwater pathways was found. This effect could be due to dilution with unpolluted groundwater, adsorption of contaminants to soil material, or biochemical reactions, e.g., dechlorination and biodegradation.

From these possibilities the third seemed to be the most probable one. Moreover, a third chlorinated hydrocarbon, *cis*-1,2-dichloroethene, could be identified in the water of polluted wells as a result of the improvement of the analytical technique, such as use of a suitable capillary column, FID detection,[2] and multiple headspace extraction.[3]

As *cis*-1,2-dichloroethene had never been used as solvent in the catchment area, its biochemical formation during underground flow under certain conditions seemed probable.

These calculations were in agreement with data reported by Bouwer and McCarty,[4,5] and Vogel[6] about possible pathways of degradation of halogenated organic compounds under methanogenic conditions. Moreover, this led to the conclusion that vinyl chloride must also be detectable in contaminated groundwater as another reaction product.

EXPERIMENTAL

Analytical Determinations

This led to further improvements of the analytical methodology, where another capillary column (CP Sil 8) with greater diameter and higher coating was used and a special temperature programme was worked out, comprising in special cases starting at 0 °C by nitrogen cooling of the column oven.

The following gas-chromatographic apparatus and analytical conditions were used:

Apparatus	Perkin-Elmer Sigma 2000/HS 100
Column	Fused silica, 50 m, 0.32 mm inner diameter, Coating CP Sil 8, 5.0 μm
Injection	Automatically splitless
Carrier gas	He, pressure 150 kPa
Temperature programme	2 min 40 °C, 5 °C/min to 120 °C, 3 min 120 °C
Detection	FID 250 °C, ECD 350 °C
Integrator	Shimadzu C-R2AX

The limit of detection for vinyl chloride was brought down to 1 μg/L which was necessary for investigation of unpolluted groundwater and drinking water. Now, the primary pollutants and their degradation products could be identified in a number of groundwater observation wells in the catchment area and in the raw water of the polluted wells of the waterworks. With increasing distance from the sources of pollution an increase of the concentrations of *cis*-1,2-dichloroethene and vinyl chloride was observed while the concentrations of tetra- and trichloroethene decreased as reported above (Figure 1).

Biodegradation Studies

The analytical findings led to considerations to study possible biodegradation/dechlorination reactions in laboratory incubation tests which were related to practical conditions in the catchment area.

Series A Waste water from an industrial user of chlorinated hydrocarbons which contained mainly tetrachloroethene and small amounts of other chlorinated substances was purged with inert gas to eliminate the pollutants. Then tetrachloro-

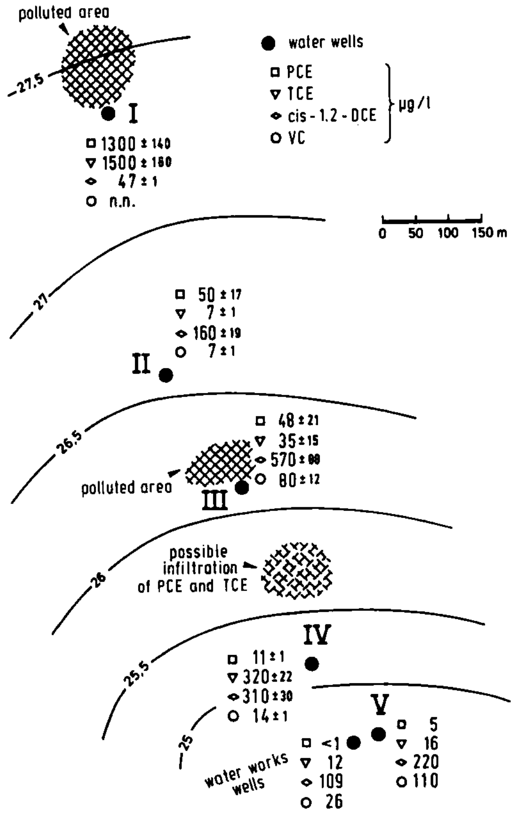

Figure 1 Part of catchment area of waterworks with sources of underground pollution by chlorinated hydrocarbons (CHC) and CHC changes during underground flow to waterworks wells. PCE: tetrachloroethene, TCE: trichloroethene, *cis*-1,2-DCE: *cis*-1,2-dichloroethene, VC: vinyl chloride, I-IV: Oberservation wells, V: water works drawing shafts.

ethene was added again up to 50 mg/L and the test solution was divided into 23 subsamples in completely filled gas-tight sealed vials which were stored in the dark at 8 °C. Results which are given in Figure 2 indicate that already, after one day of storage, nearly 25% of the tetrachloroethene present had been converted to trichloroethene and traces of *cis*-1,2-dichloroethene. After 5 days, more than 50% of the original amount had been transformed into *cis*-1,2-dichloroethene. After incubation for 12 or more days, the concentrations of tetrachloroethene and trichloroethene remaining were below 1 μg/L. *cis*-1,2-Dichloroethene was the main metabolite. In addition, very low concentrations of 1,1-dichloroethene and of *trans*-1,2-dichloroethene could be detected (Figure 2).

Series B In a parallel series, the waste water treated as described above was subjected to sterile filtration (0,2 μm) before adding tetrachloroethene. In these samples, no transformation of tetrachloroethene could be observed.

Series C In another experiment, non-sterile ground water polluted with chlori-

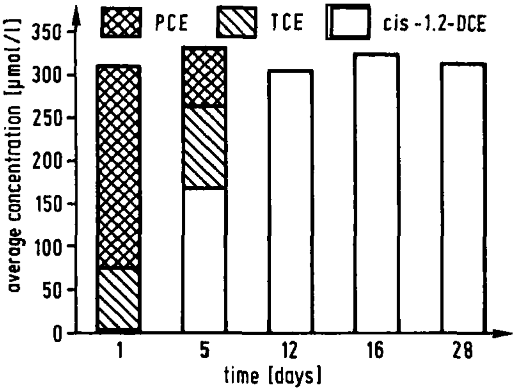

Figure 2 CHC degradation in waste water laboratory experiments under anaerobic conditions at 8 °C.

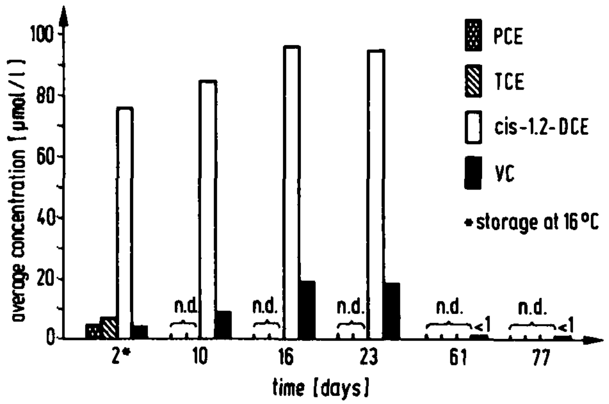

Figure 3 Changes in CHC composition of a groundwater/wastewater mixture (9:1) during storage at 21 °C.

nated hydrocarbons was mixed with waste water at a ratio of 9:1. The experimental procedure was as described above. However incubation took place at 21 °C. After 61 days under anaerobic conditions, a complete transformation of tetrachloroethene and trichloroethene into *cis*-1,2-dichloroethene and then to vinyl chloride could be observed. After 61 days, the concentration of vinyl chloride itself had decreased (Figure 3).

DISCUSSION AND CONCLUSIONS

Under the ideal conditions of series A, e.g. presence of nutrients and adapted microflora, the degradation periods of tetrachloroethene and of trichloroethene were in the range of several days. In series C, a transformation of the primary pollutants and their degradation products *cis*-1,2-dichloroethene and vinyl chloride into still unidentified metabolites was observed. In all the laboratory experiments,

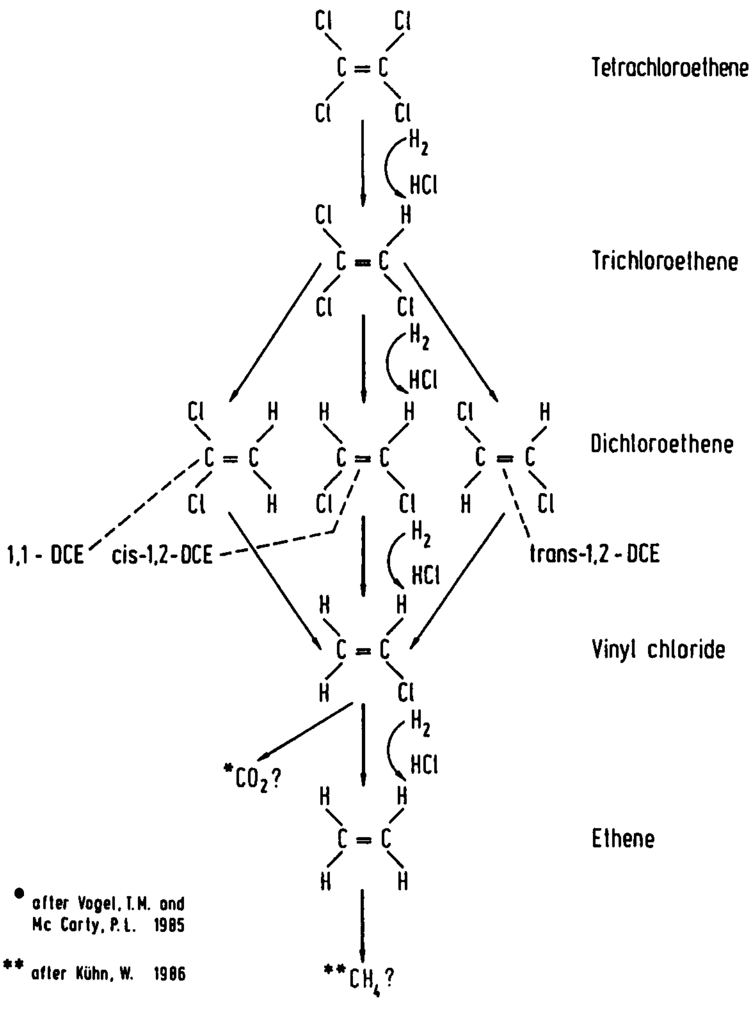

Figure 4 Pathways of reductive dechlorination of CHC.

there was a referential formation of the *cis*-isomer of 1,2-dichloroethene. This selective formation suggests reductive dechlorination reactions under participation of bacteria[7,8] leading to a sequence of reactions as postulated by Vogel and McCarty[6] and Kuehn[9] (Figure 4).

We conclude that the results of our preliminary laboratory experiments can be applied to the conditions in the aquifer of the catchment area because the results of our field investigations show a similar pattern of substances. In the aquifer a considerable potential of microorganisms may be present resulting from waste water pollution, and relatively high concentrations of chlorinated hydrocarbons may have promoted microbial adaptation to such environmental conditions. We think that there is a need for a more detailed study of the conditions for an *in situ* dechlorination in the aquifer.

The results demonstrate the necessity of determining not olnly the concentration of primary pollutants which in most cases may be tetra-and trichloroethene but the concentrations and mass flow of the metabolites formed in soil and ground water after an accident. Only then it will be possible to evaluate the relevance of pollution for drinking water supply by chlorinated hydrocarbons and the potential hazard involved.

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