

Vinyl chloride in the aquatic environment

Jürgen Wittsiepe, Fidelis Selenka

RUHR-UNIVERSITÄT BOCHUM, Institut für Hygiene,
Universitätsstraße 150, D-4630 Bochum,
Federal Republic of Germany

Summary. Vinyl chloride (VC) is formed under anaerobic conditions and in the presence of nutrients, by the microbial decomposition of volatile halogenated hydrocarbons such as tri- and tetrachloroethene. The main intermediate of the reaction is *cis*-1,2-dichloroethene. This reaction has up to now only been observed in cases of very high concentrations of the volatile halogenated hydrocarbons such as occurs after an industrial accident, in problem landfills and in waste water emissions etc.. It has however now been also shown to be present in ground water, which is only slightly polluted with tri- and tetrachloroethene caused by their ubiquitously spread. This discovery of trace VC is due to a recently developed highly sensitive method with a detection limit of 0.4 ng/l. The other place that VC can be seen to go directly into the aquatic environment is in the direct vicinity of industrial plants producing or working with vinyl chloride or polyvinylchloride (PVC). Through technical deficiencies in the plants the concentration of VC in surface waters can reach high levels and VC can be also be detected a long way downstream. A further contamination path into humans can result from the transfer of VC residue monomers from finished PVC products.

1. Introduction

About 15-20 million tonnes of VC are produced yearly world-wide of which 1.5 million tonnes is produced in the Federal Republic of Germany (FRG). Of this 99% is converted into PVC or other mixed polymers with the remainder used as an intermediate in the synthesis of other halogenated hydrocarbons, mostly 1,1,2-trichloroethane and 1,1-dichloroethene [Verband der Chemischen Industrie (1986), Platzer, LeBlanc (1985), Albright (1986), Frey, Freeman (1984)]. VC is a purely synthetic substance and is not found in nature. Even though VC has been first synthesized for more than 150 years [Regnault (1835)] and produced in large quantities in many countries since the beginning of the 1930's, its carcinogenic properties have only been known since the beginning of the 1970's and its toxic relevance has only been of significant interest since 1974.

The United States Environmental Protection Agency (USEPA) evaluated VC as a carcinogen and estimated that for a life long adult consumption of 2 litres of water daily with a concentration 1.5 µg/l VC, 0.15 µg/l, or 0.015 µg/l the risk of getting cancer is 10^{-4} , 10^{-5} , 10^{-6} respectively [USEPA (1985), Freon et al. (1981)]. The German Health Authority (Bundesgesundheitsamt) therefore proposes that the value to be achieved in Germany should be below 0.1 µg/l. However, due to the detection limits of current analytical methods, a threshold value of 2 (µg/l) for drinking and ground water has been discussed.

2. Direct entry of VC into the aquatic environment

The uses of mass produced synthetic VC described above mean that it appears and spreads in the environment generally in a different manner to other industrial volatile halogenated hydrocarbon solvents such as tri- and tetrachloroethene. The direct entry of VC into the aquatic environment can be expected to occur during its synthesis, transport, processing, or by the transfer of residue monomers from PVC products.

2.1 VC entry through synthesis and processing

The first way that VC can enter the environment is during its synthesis. Depending on the type of synthesis process used different amounts of VC can be found in the process' waste water. The second route is attributable to the fact that VC polymerization to PVC is normally carried out in aqueous solution and the VC contaminated waste water should be treated before being disposed of. We tested some waste water from the synthesis of VC in the FRG and found it to contain between 0.012 and 0.38 mg/l VC. We also tested the waste water from the VC polymerisation to PVC in a PVC production plant and found that to contain between 0.97 and 13.8 mg/l of VC. This water had also flowed through a water treatment plant where it had been aerated which removed a large percentage of the VC by evaporation into the atmosphere. Vinyl chloride can also usually be traced a long way downstream from a VC/PVC plant. In random sample experiments on water from the river Lippe in the FRG the concentration of vinyl chloride was shown to increase from 11 ng/l to 400 ng/l after it had flowed past a VC/PVC production plant. For a further 40 km down to the river mouth in the Rhein, the concentration of VC in the Lippe steadily decreased to 110 ng/l. In the same stretch of water the concentrations of tri- and tetrachloroethene fell by only a half. An unequivocal concentration increase of VC traceable back to the mouth of the river Lippe can also be seen in the Rhein. However, due to the high dilution factor from the water of the Rhein the increase observed was lower, from 6.3 ng/l to 23 ng/l. Apart from increasing dilution, evaporation also plays an important role in lowering the concentration of VC in the river. The half-life for the evaporation of VC in flowing water was estimated by Scherb (1978) to be 0.9 - 1.3 hours.

A concentration increase from 46 to 69,000 ng/l VC in the river Saale between Leuna and Korbetha (German Democratic Republic) was also shown to be due to chemical plant emissions.

2.2 Residue monomer concentrations in PVC finished products

The concentration of residual VC monomers in raw PVC using current technology depends on the method of polymerisation adopted, but usually lies between 2 and 5 mg/kg. The raw PVC is then further refined and the monomer concentration generally reduced through emissions to around 0.1 mg/kg [Beratergremium für umweltrelevante Altstoffe (1989)]. The main products which can cause VC contamination in humans are in particular PVC food packaging, utensils and water pipes. In the FRG the legal limit of VC residue monomers in these types of PVC utensils is 1 mg/kg and the limit for migration onto food is less than 0.01 mg/kg [Vinylchlorid-Bedarfsgegenstände-Verordnung (1979)]

3. Microbiological degradation of volatile halogenated hydrocarbons

It had long been thought that aerobic or anaerobic microbial decomposition of the C-Cl bond in the volatile C₁- and C₂-chlorohydrocarbons such as 1,1,1-trichloroethane, tri- and tetrachloroethene did not take place [McConnell et al. (1975), Pearson, McConnell (1975)]. The fact that in many different accidents involving these chemicals they could also still be detected unchanged in the ground water supported this view [Hartmetz et al. (1985), Kinzelbach (1985)]. However, very recently, advances in organic trace analysis have helped in the detection of cis 1,2-dichloroethene in highly polluted ground water in the FRG, even

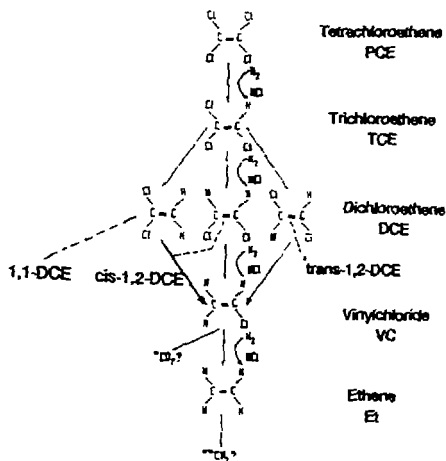
though it can be proved that they were not directly placed in the water [Baldauf, Zimmer (1986)]. The first experiments to confirm the presence of microbial decomposition of volatile halogenated hydrocarbons were carried out since the middle of the 1970's [Bouwer et al. (1981), Haider (1980), Tabak et al. (1981), Wilson, Wilson (1985), Nelson et al. (1986), Little et al. (1988), Bouwer, McCarthy (1983), Bouwer, McCarthy (1983a), Fathepure, Boyd (1988)] (see figure 1).

A sequential dechlorination from trichloroethene through cis-1,2-dichloroethene to vinyl chloride was observed in the groundwater from a highly trichloroethene polluted area, under anaerobic conditions, in 500 m seepage by Nerger and co-workers [Nerger, Mergier-Völkl (1988), Milde et al. (1988)]. The concentrations of the cis-1,2-dichloroethene metabolite reached up to 1600 µg/l and of VC 120 µg/l. The pathway of the microbial decomposition was then later proven in the laboratory.

Brauch and co-workers (1987) showed in a laboratory experiment the decomposition of VC under methanogenic conditions. They also tested water from a tri- and tetrachloroethene polluted area and found the level of cis-1,2-dichloroethene to be between 550 and 2300 µg/l and for VC to be between 15 and 1000 µg/l.

The investigations detailed above that have been carried out to date show that subterranean decomposition of chlorinated methane, ethane and ethene in the strongly dependent on the surroundings. The microbial decomposition to VC occurs preferably under anaerobic conditions. Branch et al. (1987) stated that VC can only be expected where there is also a high concentration of ammonia, iron and manganese present. Apart from that it appears that a high concentration of cis-1,2-dichloroethene is also necessary even though this compound is not believed to be the only intermediate in the formation of VC. The bacteria in question also seem to have a long adaption time before they start to form VC. Favorable conditions are to be found in the largely anaerobic environments under waste disposal landfill sites. VC can often be identified in the gaseous emission and the water seepage from such sites [Angrick (1987), Lipsky, Jacot (1977), USEPA (1982), Markle (1976), Bruckmann, Müller (1982), Werner (1988), Janson (1989), Häfler et al. (1986)].

Fig. 1: Decomposition scheme for volatile halogenated hydrocarbons (after Vogel, McCarthy (1985), Kühn (1986); figure from Nerger, Mergier-Völkl (1988))



3.1 Occurrence of VC following industrial accidents and from problem land fills

In our investigations the microbiological degradation of tetra- and trichloroethene to VC in several cases of industrial accidents has been proven and cis-1,2-dichloroethene was observed to be the predominant intermediate. Concentrations of vinyl chloride in soil air reached up to 170 mg/m³ and in the ground water up to 1600 µg/l.

3.2 Formation of VC in the subterranean passages

The same decomposition mechanisms as described above occurring at the high concentrations found in industrial accidents and problem land fill sites can be observed, even in the low concentrations generally found in surface water. Surface water, after seepage to a sufficient depth is then reclaimed as ground water. In the last few years a well equipped network for testing the ground water has been set up which runs on the principle described above. The decomposition of the sub µg/l concentrations of tri- and tetrachloroethene present in the surface water could be traced in an anaerobic seepage of 250 m length, where the VC concentration increases to 130 ng/l.

4. Discussion

VC belongs to the group of chemicals which are proven potential carcinogens. In contrast to the other volatile halogenated hydrocarbons it appears relatively seldom in the natural aquatic environment. This is because it is practically only used for polymerisation to PVC. A direct freeing of VC into the aquatic environment is partly due to the synthesis process but is mainly due to the production conditions in its polymerisation to PVC. VC reaches rivers, seas and lakes through industrial waste water emission even after being treated. The river contamination, from technically deficient production plants, can reach levels of 50 µg/l or more. The worst pollution points can be expected in the vicinity of industrial plants handling or producing VC/PVC. Even 40 km downstream from a VC/PVC plant the VC pollution can still be traced, even though it evaporates twice as fast as tri- and tetrachloroethene. In the FRG the legal limit for VC residue monomers in PVC products is set at 1 mg/kg and the migration limit on to food is 0.01 mg/kg. Problems can occur where food is consumed following long term storage in PVC containers. Along with the direct entry of VC into the environment it also appears as a metabolite from the microbial anaerobic decomposition of tri- and tetrachloroethene in soil or ground water. Apart from the high concentrations of tri- and tetrachloroethene found in problem land fill sites and after industrial accidents VC can also be found in water where low concentrations of volatile halogenated hydrocarbons were present and which is, as ground water, intended as a source for drinking water. Here, there is a high risk that VC will also be carried into the water mains. As long as the water treatment includes intensive aeration this health risk is however practically removed from the water.

Since VC is a microbial metabolite under anaerobic conditions and can be formed from the decomposition of tetra- and trichloroethene through the intermediate cis-1,2-dichloroethene, we can count on the appearance of VC wherever these specific conditions are to be found.

Notice: The quantification of VC was carried out using gas chromatography after derivatization to 1,2-dibromochloroethane with a detection limit of 0.4 ng/l. The analysis of the volatile halogenated hydrocarbons was also carried out using gas chromatography after a pentane extraction following DIN 38 407 [(Deutsches Institut für Normung (1988))]

5. References

- Albright, L. F., Vinyl Chloride Production, in: Nass, L. I.; Heidelberger, C. A. (Ed.), *Encyclopedia of PVC*, 2nd Ed., Marcel Dekker Inc., New York, Basel, p. 27, 28 (1986)
- Angrick, M., Gaszusammensetzung, Emissionen und Reinigungstechniken bei ausgewählten Anlagen zur Deponiegasnutzung, *Müll und Abfall* 4, 142-150 (1987)
- Baldauf, G.; Zimmer, G., Adsorptive Entfernung leichtflüchtiger Halogenkohlenwasserstoffe bei der Wasseraufbereitung, *Vom Wasser*, 66, 21-31 (1986)
- Beratergremium für umweltrelevante Altstoffe (BUA) der Gesellschaft Deutscher Chemiker, Vinylchlorid (Chlorethen), BUA-Stoffbericht 35, Verlag Chemie, Weinheim (1989)
- Bouwer, E. J.; McCarty, P. L., Transformation of halogenated organic compounds under denitrification conditions, *Appl. Environ. Microbiol.*, 45 (4), 1295-1299 (1983)
- Bouwer, E. J.; McCarty, P. L., Transformation of 1- and 2-carbon halogenated aliphatic organic compounds under methanogenic conditions, *Appl. Environ. Microbiol.*, 45 (4), 1286-1294 (1983-A)
- Bouwer, E. J.; Rittmann, B. E.; McCarty, P. L., Anaerobic degradation of halogenated 1- and 2-carbon organic compounds, *Environ. Sci. Technol.*, 15, 596-599 (1981)
- Brauch, H. J.; Kühn, W.; Werner, P., Vinylchlorid in kontaminierten Grundwässern, *Vom Wasser*, 68, 23-32 (1987)
- Bruckmann, P.; Mülder, W., Der Gehalt an organischen Spurenstoffen in Deponiegasen, *Müll und Abfall*, 12, 339-346 (1982)
- Deutsches Institut für Normung, Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, Gemeinsam erfaßbare Stoffgruppen (Gruppe F), Bestimmung von leichtflüchtigen Halogenkohlenwasserstoffen (LHKW) (F 4), DIN 38 407 (Teil 4) (1988)
- Ferou, V. J.; Hendrickson, C. F. M.; Speck, A. J.; Til, H. P.; Spät, B. J., Lifespan oral toxicity study of vinyl chloride in rats, *Food Cosmetic Toxicol.* 19, 317-331 (1981)
- Frey, H. E.; Freemann, I., Polyvinyl Chloride Resins, *Chemical Economics Handbook* (CEH) (1984)
- Haider, K., Degradation of chlorinated aliphatic and aromatic compounds by aerobic and anaerobic soil microorganism, *Comm. Eur. Communities, (Report)*, EUR-6388, 200-204 (1980)
- Hartmetz, G.; Bornhoff, J.; Bornhoff, M., Vorkommen leichtflüchtiger Chlorkohlenwasserstoffe in Trinkwässern von Rheinland-Pfalz, *Forum Städte-Hygiene*, 56, 316-319 (1985)
- Höfler, F.; Schneider, J.; Möckel, H. J., Analytical investigations on the composition of gaseous effluents from a garbage dump, *Fresenius Z. Anal. Chem.*, 325 (4), 365-368 (1986)
- Janson, O., Charakterisierung von Deponiegasen anhand ausgewählter Spurenstoffe unter besonderer Berücksichtigung der Schwefelverbindungen, *Müll und Abfall* 4, 198-208 (1989)
- Kinzelbach, W. K. H., Modelling of the transport of chlorinated hydrocarbon solvents in groundwater: a case study, *Water Science and Technology*, 17 (9), 13-21 (1985)
- Kühn, W., Aufbereitung von Wasser, das durch leichtflüchtige Chlorkohlenwasserstoffe verunreinigt ist, in: Boehlen, B. (Ed.), *Fachtagung Pro Aqua - Pro Vita*, Vol. 10 C, Kap. 12, Basel (1986)
- Lipsky, D.; Jacot, B., Hazardous emissions from sanitary landfills, *Proc APCA Ann. Meet.* 5, Program Number 85-69.4, 1-13 (1985)
- Maride, R. A.; Iden, R. B.; Sliemers, F. A., A preliminary examination of vinyl chloride emission from polymerization sludges, during handling and land disposal, EPA - 600/9-76-015 (1976)
- McConnell, G.; Ferguson, D. M.; Pearson, C. R., Chlorierte Kohlenwasserstoffe in der Umwelt, *Endavour*, 34, 13-18 (1975)

- Milde, G.; Nerger, M.; Mergler, R., Biological degradation of volatile chlorinated hydrocarbons in groundwater, *Water Sci. Technol.*, 20 (3), 67-73 (1988)
- Nelson, M. J. K.; Montgomery, S. O.; O'Neill, E. J.; Pritchard, P. H., Aerobic metabolism of trichloroethylene by a bacterial isolate, *Appl. Environ. Microbiol.*, 52 (2), 383-384 (1986)
- Nerger, M.; Mergler-Völk, R., Biologischer Abbau von leichtflüchtigen Chlorkohlenwasserstoffen in Grund- und Abwasser, *Z. Wasser Abwasser Forsch.*, 21 (1), 16-19 (1988)
- Pearson, C. R.; McConnel, G., Chlorinated C₁ and C₂ hydrocarbons in the marine environment, *Proc. R. Soc. Lond. B.* 189, 305-332 (1975)
- Platzer, N.; LeBlanc, J., Polyvinyl Chloride, In: *Digest of Polymer Developments*, Springborn Lab., Series II, No. 37, 2 (1985)
- Regnault, W., Ueber die Zusammensetzung des Chlorkohlenwasserstoffs (Oel des ölbildenden Gases), *Ann. d. Chem.*, 14, 22-38 (1835)
- Scherb, K., Untersuchungen zur Ausdampfung einiger niedermolekularer Chlorkohlenwasserstoffe aus einem Fließgerinne, In: *Schadstoffe im Oberflächenwasser und im Abwasser*, Oldenbourg Verlag, München, Wien, 235-248 (1978)
- Tabak, H. T.; Quave, S. A.; Mashni, C. I.; Barth, E. F., Biodegradability studies with organic priority pollutant compounds, *Journal - Water Poll. Control Fed.*, 53, 1503-1518 (1981)
- USEPA, Vinyl chloride - A Review of National Emission Standard, EPA - 450/3-82-003 (1982)
- USEPA, Final draft for the drinking water criteria document on vinyl chloride. TR-540-162. USEPA Office of Drinking Water, Washington DC (1985)
- Verband der Chemischen Industrie e.V., *Chemiewirtschaft in Zahlen*, 28. Auflage, Frankfurt (1986)
- Verordnung zur Begrenzung des Gehaltes an monomeren Vinylchlorid in Bedarfsgegenständen, (Vinylchlorid-Bedarfsgegenstände Verordnung) vom 26.10.1979, Änderung vom 09.02.1983, BGBl I, 80 (1979)
- Werner, M., Entfernung halogener Kohlenwasserstoffe aus Deponiegas, Müll und Abfall 11, 520-524 (1988)
- Wilson, J. T.; Wilson, B. H., Biotransformation of trichloroethylene in soil, *Appl. Environ. Microbiol.*, 49, 242-243 (1985)
- Wittsiepe, J.; Selenka, F.; Jackwerth, E., Gas-chromatographic determination of trace amounts of vinyl chloride in water and air after derivatization to 1,2-dibromochloroethane, *Fresenius J. Anal. Chem.* 336, 322-327 (1990)