

Natural attenuation of chlorinated organics in a shallow sand aquifer

Rosane C.M. Nobre, Manoel M.M. Nobre*

Departamento de Geociências, Universidade Federal de Alagoas, Maceió, AL, Brazil

Abstract

This work presents the second phase of a groundwater remediation program for the migration control of a 1,2-dichloroethane (1,2-DCA) contaminated plume which includes natural attenuation at a distance downgradient from the source area. The conceived system for the plume migration control, implemented just after a major accidental release of 1,2-DCA in the soil, included a 300 m long physical barrier (cement-bentonite diaphragm wall) and 12 extraction wells. Results of field investigations have provided evidence that 1,2-DCA was naturally biodegrading into vinyl chloride as well as ethene under the natural anaerobic-reducing conditions at the site. In that case, source control measures were implemented to accelerate the overall remediation process. Although the results are favorable, the natural degradation of the 1,2-DCA does not guarantee acceptable levels of concentrations. Therefore, a pilot test to evaluate the enhancement of these processes is being carried out through the use of a biosparging system. This test is being implemented near the source to achieve sequential aerobic–anaerobic treatment zones.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Natural attenuation; 1,2-Dichloroethane; Groundwater remediation

1. Introduction

An increasing interest in the implementation of non-structural solutions such as monitored natural attenuation (MNA) has been observed in recent years in many sites in North America and Europe. These solutions may be associated with engineered systems or applied as a sole remedial alternative to soil and groundwater contaminated sites. The motivation behind this fact is the complexities of subsurface systems and the costs associated with conventional engineered approaches. It has been concluded that there is not enough resources to clean up all contaminated sites to non-detect or background concentrations. In USA, for instance, regulators have adopted a risk-based corrective action (RBCA) for setting remedial goals and to promote the use of innovative treatment technologies such as natural attenuation [1]. The selection of natural attenuation as part of any site remedy, however, should be based on its ability to achieve remediation goals in a reasonable timeframe. Under favorable geochemical conditions, natural attenuation of groundwater contaminants can result in significant savings in cost over other remedial options. It is also

less intrusive and disruptive than conventional engineered methods.

“Natural Attenuation” is the term used to all natural processes that can be accounted for as part of a site remediation strategy. Some of these naturally occurring physical, chemical and biological processes can transform contaminants to less harmful forms or immobilize them in the subsurface, therefore reducing contaminant concentrations in water [2]. Aerobic and anaerobic biodegradation are considered the major processes for the reduction of contaminant mass in the subsurface [3]. Non-destructive attenuation processes, on the other hand, include dispersion, dilution, volatilization and sorption to soil particles. In addition to cost savings, the use of natural attenuation can lessen the problems of dealing with hazardous waste disposal. However, it may require more time to achieve cleanup goals and requires a commitment to long-term monitoring. In some cases, incomplete biodegradation can also create toxic by-products that are not easily degraded. Vinyl chloride is an example of a highly toxic chemical that results from incomplete biodegradation of chlorinated solvents.

Some natural attenuation mechanisms for chlorinated organics are described in this paper. Besides being among the most widespread contaminants in soil and groundwater, they have also significant impact on the subsurface, the environment and on human health. In addition, available

* Corresponding author.

E-mail address: maianobre@uol.com.br (M.M.M. Nobre).

technologies for remediating these compounds are usually costly and time consuming. Although chlorinated solvents tend to be more resistant to natural biodegradation processes due to their synthetic nature, significant evidence now exists that biochemical reactions can certainly break down these compounds into non-toxic or less toxic by-products.

In order to apply this *in situ* technology, it is necessary to demonstrate, through the design of an appropriate field monitoring program, that natural processes are taking place at a rate that is effective in reaching established goals, and that will continue for an acceptable period of time [4]. Several good indicators or “lines of evidence” can be useful to certify that natural processes are reducing contaminant concentrations. For example, historical trends indicating a stable or retreating plume; favorable geochemical conditions, such as depleted levels of oxygen, nitrate and sulfate and elevated levels of dissolved methane in groundwater; the breakdown of compounds and the advent of “daughter products” are among the best indicators. When these processes are detected in groundwater, they provide evidence that contaminant destruction is underway. Laboratory microcosm studies can also be used to simulate aquifer conditions to demonstrate the destruction of contaminants by native bacteria. The technical protocol developed by USEPA [3], among others, provides a logical method of conducting a specific monitoring program for intrinsic degradation.

It is also important to understand the processes affecting the transformation and fate of contaminants in the subsurface environment. Included are microbial physiology and the aerobic, co-metabolic and anaerobic contaminant degradation processes. In any environment with microbial activity, there is usually a progression from aerobic (oxygen-reducing) to anaerobic (methanogenic) conditions. As a consequence, a definite sequence of electron acceptors is used in this progression through distinctly different redox states. In wetland environments, for instance, sulfate concentrations are generally low and most organic carbon decomposition can be through methanogenesis [5]. In fact, in these environments, there is abundant supply of natural organic carbon that can provide enough electron donors for the reductive biodegradation of chlorinated solvents.

In this paper, a monitored natural attenuation investigation was carried out at a 1,2-dichloroethane (1,2-DCA) site located near an estuarine system where wetlands are a dominant part of the environment [6]. An appropriate field monitoring program was designed in addition to source control measures which were implemented to accelerate the overall remediation process.

2. Background on anaerobic degradation processes

Natural attenuation is well established as a remediation alternative for only a few contaminants, including BTEX. Only recently, however, natural attenuation for chlorinated organic compounds has been demonstrated in the litera-

ture. Researchers have first demonstrated the potential for anaerobic biotransformation of halogenated aliphatic hydrocarbons in 1981 [7]. Additional studies have shown that many of these compounds, including chlorinated ethanes and ethenes, can be biodegraded in a variety of conditions [8–12]. In 1994, Fiorenza et al. [13] showed evidence of reductive dechlorination of PCE, TCE, TCA and methylene chloride contamination in a field study in Ontario, Canada. The work of McCarty and Reinhard [14] presented evidence pointing to intrinsic bioremediation of chlorinated organics under methane fermentation conditions in municipal landfills. The degradation potential of 1,2-DCA under both aerobic and anaerobic conditions has also been well documented [6,15–18]. Complete dechlorination of 1,2-DCA into non-toxic end products such as ethane and ethene is believed to be faster and more likely to occur under methanogenic conditions. Most of the work present in the literature focused on mixed microbial cultures that use chlorinated solvents fortuitously as electron acceptors. Biodegradation, in these cases, is most likely to occur in the presence of excess organic material to serve as an electron donor.

3. Natural attenuation processes

The behavior of organic contaminant plumes in groundwater is determined by the interaction of physical, chemical and biological processes. These include the mechanisms of advection, dispersion, sorption and also volatilization at the water table. All of these processes except advection can cause lower aqueous concentrations and therefore contribute to natural attenuation, which is contaminant and site specific. Contaminants partition into four phases, including dissolved, vapor, sorbed to soil particles and a free phase, which displaces water from the spaces. As water moves through pores spaces, chemicals are desorbed from aquifer solids or dissolved from the free phase liquids. Their movement downgradient may be altered by further sorption to soil particles and also biodegradation. Partition of chemicals into aqueous phase may reach an equilibrium with the process of biological transformation at an acceptable time and distance from the source, which is the basis for plume natural attenuation. Contaminant nature and site hydrogeology are determinant factors in contaminant partition, which in turn affects plume movement in the subsurface.

In the biodegradation processes, three modes of contaminant degradation are possible, including aerobic, anaerobic and co-metabolic. Aerobic degradation involves oxygen as the electron acceptor, and dechlorination is usually faster and more complete. The contaminants, in this case, are utilized by bacteria as a sole source of carbon. Anaerobic degradation involves the passing of electrons to an acceptor other than oxygen, the primary ones being nitrate (denitrification), Mn (IV), Fe (III), sulfate (sulfate reduction) and ultimately carbon dioxide (methanogenesis). This latter is converted to organic acids to produce methane. Microorganisms

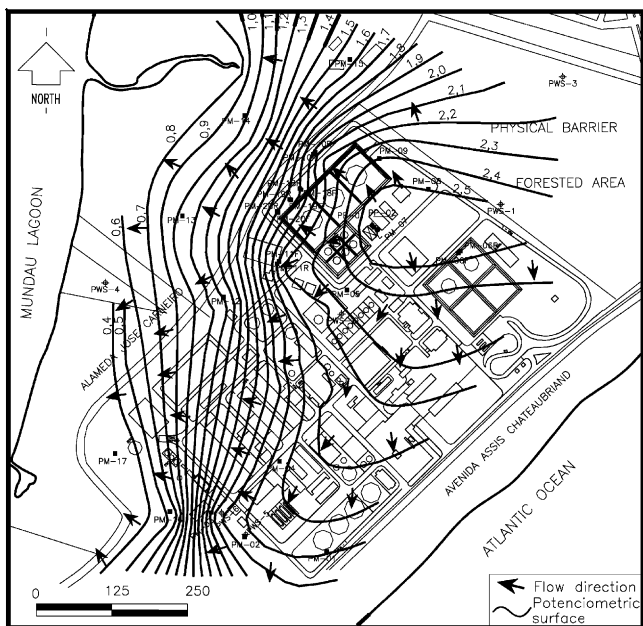


Fig. 3. Site and groundwater flow.

the system has already extracted over 110 metric tons of 1,2-DCA and controlled plume migration, the rate of mass removal has been reduced over the years which demanded the evaluation of alternative technologies to help accelerate the remediation process. Therefore, additional studies were carried out to investigate the potential for natural attenuation of the dissolved plume downgradient from the source, where sulfate-reducing conditions are predominant. In addition, the aerobic degradation potential of 1,2-DCA and vinyl chloride were also evaluated, through the use of an air sparging system near the source. The sequential aerobic-anaerobic biodegradation process was evaluated as a second-phase remedial program for the 1,2-DCA contaminated aquifer.

4.1. Hydrogeology setting

The schematic geology of the region is presented in Fig. 4. The site is located at a local recharge zone area, between the Atlantic Ocean and a lagoon channel that constitutes the

discharge zone of the contaminated aquifer. Recharge to the upper aquifer is directly through rainfall, with the potentiometric surface presented in Fig. 3. The area is underlain by about 30 m of surficial deposits above a silty clay layer, followed by a massive limestone and a confined sandstone aquifer. The surficial unit consists of a well graded sand of alluvial and marine origin from the Quaternary age. At about 11 m of depth, approximately, occurs a 4 m well cemented sandstone, with high organic fraction, that has constituted the vertical limit for the migration of the free-phase product. The investigation program at the site included CPTU tests in which the evaluation of pore pressure dissipation confirmed the behavior of this capillary barrier that limited the vertical extent of the DNAPL movement.

The hydraulic conductivity (K) of the surficial unit is estimated to range from 10^{-2} to 10^{-3} cm/s, with an anisotropy ratio (K_H/K_V) smaller than 10, except the organic sand layer with K values ranging from 10^{-5} to 10^{-7} cm/s. The hydraulic gradient is of small magnitude, about 0.5% at the rainy season. Water table at the site fluctuates from 3.5 m of depth (rainy season) to 4.5 m (dry season) below land surface. The dissolved concentrations of 1,2-DCA and vinyl chloride are significant on the upper portion of the aquifer, in the order of milligrams per liter closer to the free phase source.

The 1,2-DCA storage tanks, which are less than 500 m distant from the nearest open discharge zone, are surrounded by the 300 m physical barrier. Because of the confinement created by the diaphragm wall and the confining layer underneath, extraction wells located in the vicinity of this tank has been removing a significant amount of mass, with 1,2-DCA concentration in the order of hundreds to thousands of ppm. It is expected that the air sparging system accelerates mass removal at this location.

4.2. Aerobic and anaerobic biodegradation of 1,2-DCA

It is well known [6,15–18] that 1,2-DCA can be degradable under both aerobic and anaerobic conditions, as presented in Fig. 5. The aerobic transformations are usually biotic and occur through oxidation. The aerobic biodegradation of 1,2-DCA yields 2-chloro-ethanol and

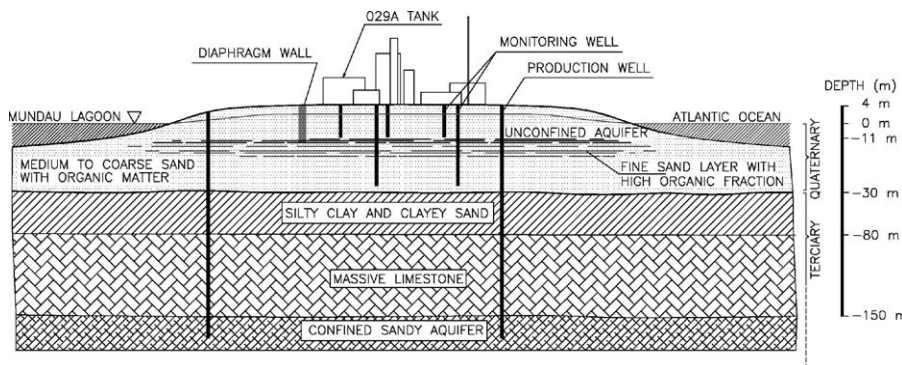


Fig. 4. Schematic geology of the site.

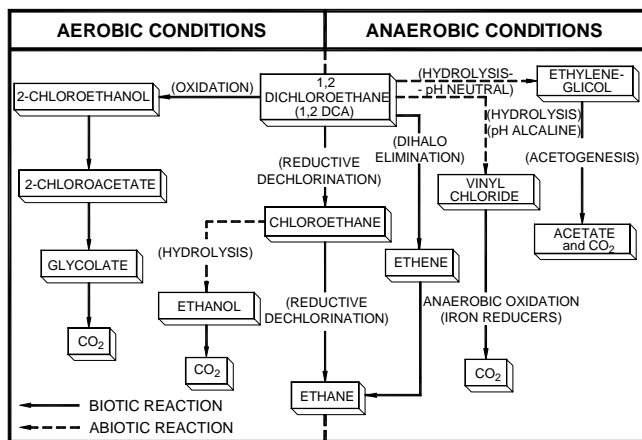


Fig. 5. Degradation paths for 1,2-DCA.

2-chloro-acetate, which are further mineralized. These oxidation products are not easily detectable in the field as they are degraded faster than 1,2-DCA [22]. Aerobic degradation processes with 1,2-DCA in the literature reveal that the indigenous microorganisms in the subsurface can easily biodegrade 1,2-DCA [15,23], with aerobic degradation half-lives of just a few days. This chlorinated compound may be used as a growth substrate by aerobic bacteria such as *Xanthobacter*, *Ancyllobacter* and *Pseudomonas* which are believed to completely oxidize 1,2-DCA to CO₂, H₂O and chloride [24]. Alternatively, methanotrophic bacteria can co-metabolize this contaminant as well [25]. 1,2-DCA may also be oxidized anaerobically under nitrate reducing conditions, with nitrate as the electron acceptor [16].

The anaerobic biotic processes generally are reductions that involve either hydrogenolysis—reductive dechlorination, the substitution of a chlorine atom from the molecule by

a hydrogen atom, or dihalo-elimination, where two adjacent chlorine atoms are removed, leaving a double bond between the respective carbon atoms [11]. The 1,2-DCA can also be degraded by the anaerobic abiotic process of hydrolysis. The formation of vinyl chloride from 1,2-DCA probably results from anaerobic abiotic hydrolysis under alkaline pH. Abiotic transformation of 1,2-DCA under anaerobic conditions also include hydrolytic substitution yielding ethylene glycol [26]. Anaerobic bacteria can also reductively dechlorinate 1,2-DCA to chloroethane which can either be further dechlorinated to ethane or undergo abiotic hydrolysis to ethanol. The half-life for the abiotic hydrolysis reaction is about 5.8 years [8]. These processes can be found in more detail in the specific literature [15,16,23].

4.3. Evidence of natural attenuation

A specific groundwater sampling program is being carried out to assess the potential for relying on natural degradation at the portion of the aquifer downgradient the physical barrier. The parameters associated with intrinsic biodegradation were monitored in accordance with USEPA protocols [3], including redox parameters (dissolved oxygen, redox potential), physical indicators (pH and water conductivity), biochemical and chemical oxygen demand, inorganic parameters (sulfate, nitrate, iron, alkalinity), dissolved hydrocarbon gases (ethane, ethene and methane).

Recent analytical results reveal that the process of abiotic hydrolysis, under alkaline pH, is possibly occurring in which part of the dissolved 1,2-DCA is being naturally transformed into vinyl chloride (VC). Furthermore, under the anaerobic-reducing conditions at the site, 1,2-DCA appears also to be degrading via dihalo-elimination to ethene. It is expected that 1,2-DCA and VC rapidly mineralize to CO₂,

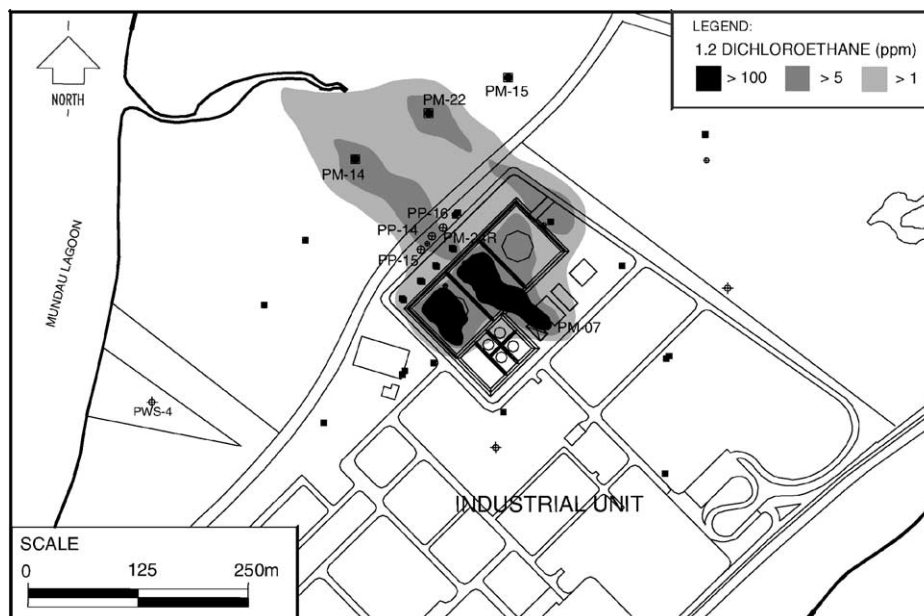


Fig. 6. Distribution of 1,2-DCA at the site.

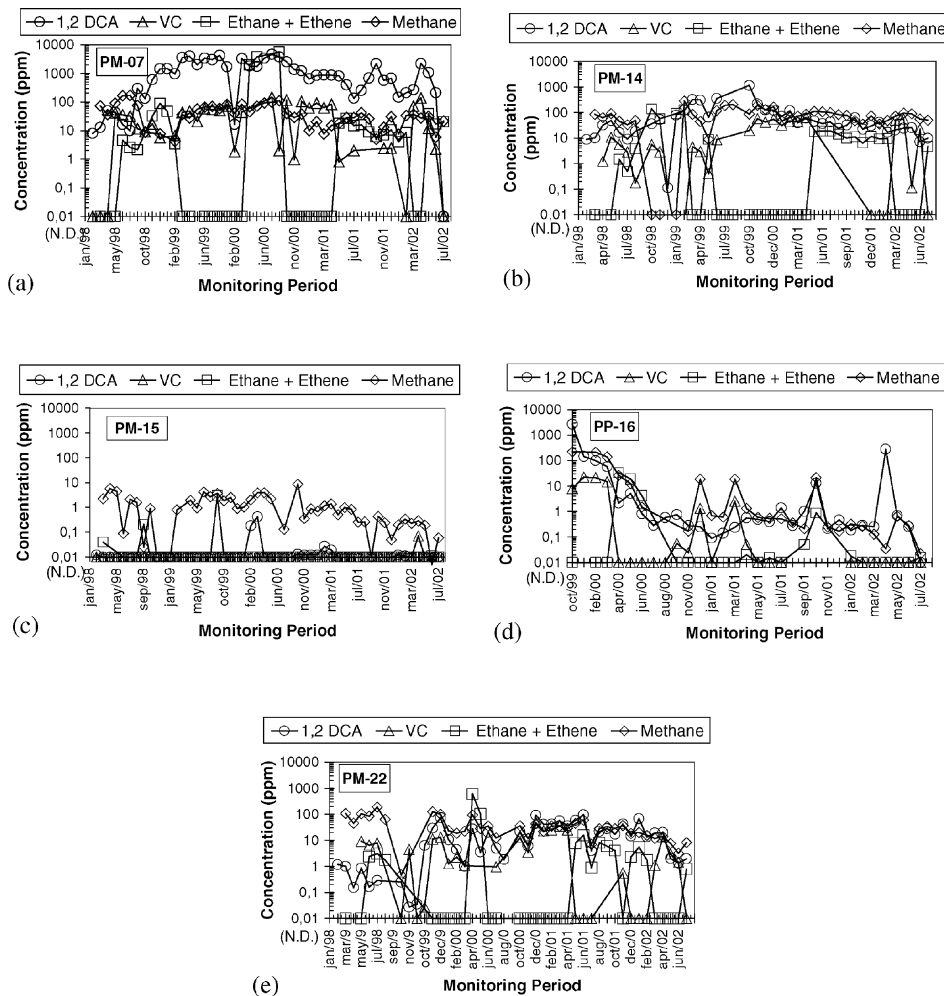


Fig. 7. Historical evolution of 1,2-DCA and its by-products at monitoring wells (a) PM-07, (b) PM-14, (c) PM-15, (d) PP-16 and (e) PM-22.

within the air sparging zone of influence, where groundwater redox conditions change to aerobic and oxidizing. Also, in the presence of oxygen and methane, methanotrophic bacteria appear to be using the methane produced within the anaerobic portion of the plume and be co-metabolically degrading the contaminants in the aerobic zone to produce CO_2 .

Figs. 6 and 7 show the current distribution of 1,2-DCA at the site and historical evolution of its by-products in some monitoring wells. High concentrations of ethene, VC and methane are always detected in association with high 1,2-DCA concentrations, with few exceptions. The dihalo-elimination of 1,2-DCA to ethene seems to be related to methanogenic microorganisms, where it has been verified that the distribution of methane and ethene had a strong correlation. The organic matter present at the 11m sand layer is probably behaving as a substrate source—electron donor—which is stimulating the reductive dechlorination process of 1,2-DCA to occur. Fig. 8 shows a schematic section beneath the storage tank and the various degradation zones that could exist hypothetically. In the real case, the iron

and nitrate reducing zones do not exist as the geochemical conditions of the site are not favorable for these particular stages of the degradation processes.

Fig. 9 presents the evolution with time of the normalized concentration of 1,2-DCA and its by-products showing a stable trend for a four year period at PM-07. Fig. 10 shows the spatial distribution of 1,2-DCA and its by-products in wells located downgradient the source with respect to groundwater flow. Fig. 11 presents the same data, with the y-axis indicating the normalized concentration of 1,2-DCA and its by-products. The relative concentration of the 1,2-DCA degradation products increases downgradient the source, confirming the occurrence of natural attenuation processes and reduction of the plume size.

The degradation process of 1,2-DCA at the site can be expressed as first-order reaction kinetics governed by the equation:

$$C = C_0 e^{-kt} \quad (1)$$

where C is the biodegraded concentration at time t ; C_0 the initial concentration, and k is the first-order decay

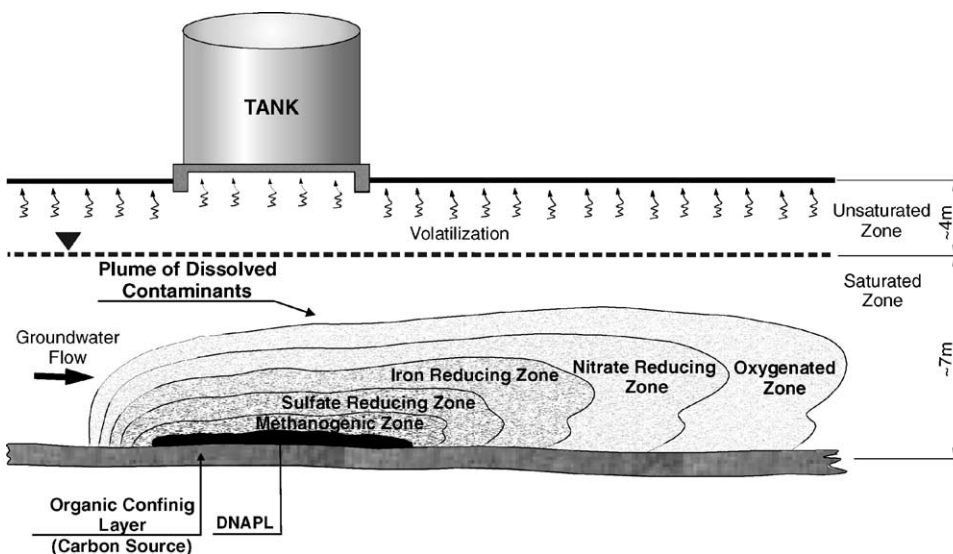


Fig. 8. Schematic section of a hypothetical plume and its various degradation zones.

coefficient. First-order constants are usually expressed in terms of half-life for the chemical

$$t_{1/2} = \frac{\ln 2}{k} \quad (2)$$

Regression methods were used to obtain first-order degradation rates to adjust field data. An average half-life equal to 225 days (~7,5 months) was obtained for the natural attenuation process of 1,2-DCA at the site. In that case, an average decay coefficient k equal to 0.003 per day was obtained. The results match with field results found in the literature. Suarez and Rifai [27], for example, analyzed data from approximately 280 studies to determine, statistically, ranges of biodegradation rates for various contaminants. In that work, DCA (including all

isomers) presented very high potential for biodegradation via aerobic cometabolism and reductive dechlorination with none of the studies reporting recalcitrance. Average half-lives equal to 1260 days and 15 days were found for reductive dechlorination and cometabolism, respectively [27].

Groundwater at the site is predominantly anaerobic with redox conditions ranging from -300 mV to $+487$ mV. Groundwater samples showing the highest 1,2-DCA concentrations presented pH slightly lower than the pH in non-contaminated groundwater, which was usually alkaline. The dissolved oxygen in those samples was depleted. The alkaline water pH was possibly responsible for the formation of vinyl chloride from 1,2-DCA.

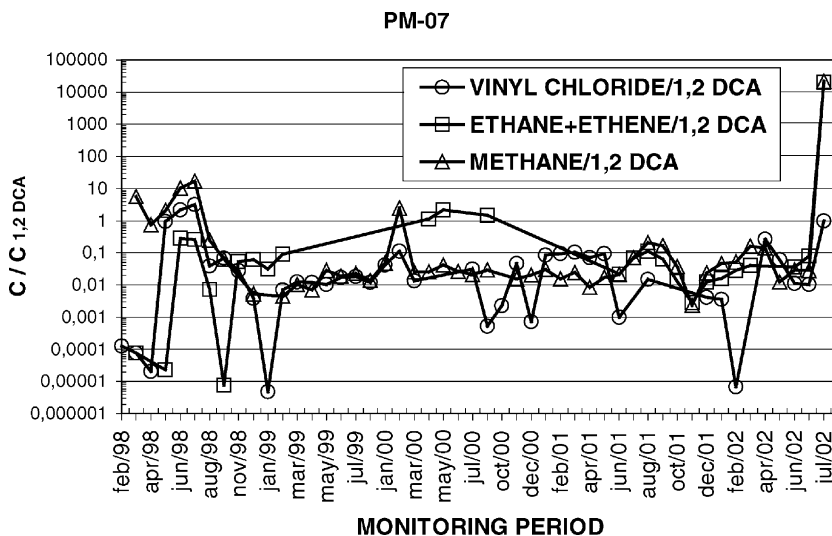


Fig. 9. Time evolution of the normalized concentration of 1,2-DCA and its by-products.

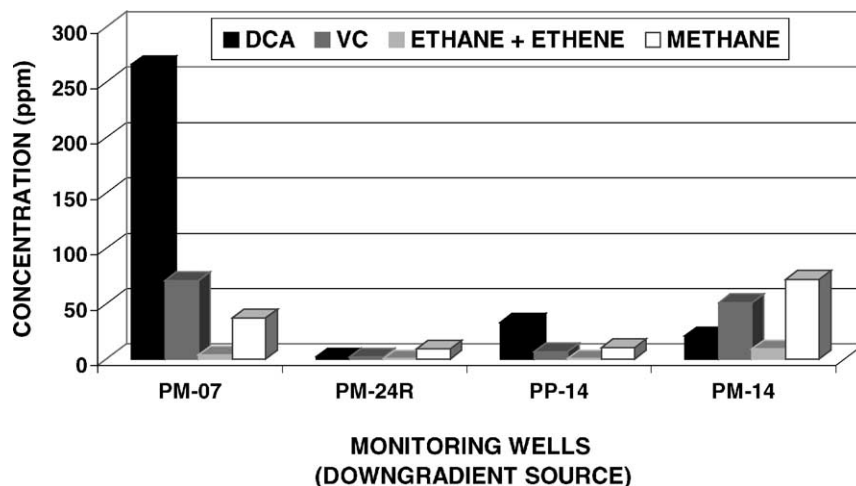


Fig. 10. Monitoring results for 1,2-DCA and its by-products for wells downgradient source.

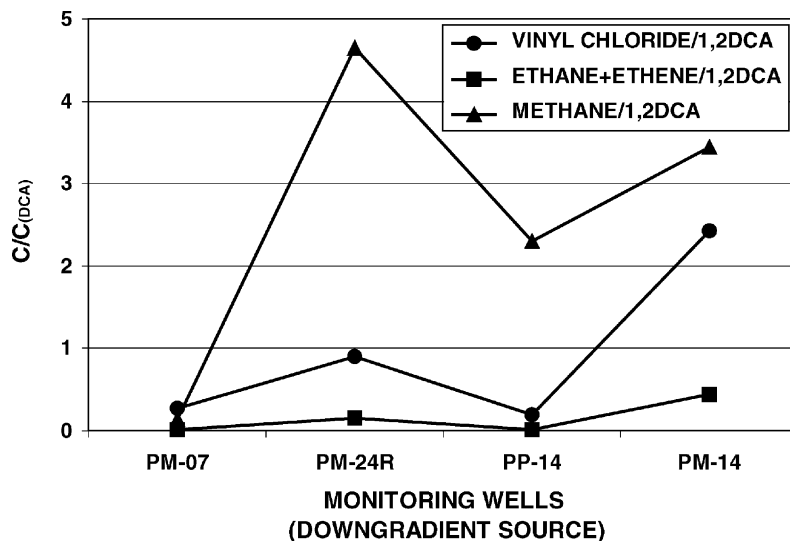


Fig. 11. Normalized concentration of 1,2-DCA and its by-products for wells downgradient source.

5. Summary

Much progress has been made recently in understanding the process of natural attenuation. In fact, this innovative remedial alternative has proved to be a cost-beneficial approach in many sites in North America and Europe. However, evaluating natural attenuation as a remedy requires extensive investigation and a commitment to long-term monitoring to achieve cleanup goals.

Natural attenuation is being evaluated as a component of the remediation strategy for a 1,2-DCA contaminated aquifer in northeastern Brazil. It has been observed several “footprints” for some loss of 1,2-DCA dissolved mass mainly by reductive dechlorination at the site. Data from monitoring wells at the site shows that the decrease in 1,2-DCA concentrations is associated with the formation of vinyl chloride, ethane and ethene. Also, the evidence of anaerobic processes is indicated by methane production

coinciding with the decrease of dissolved oxygen, nitrate and sulfate concentrations. The ratio between 1,2-DCA concentrations and its by-products has altered downgradient the source, indicating the occurrence of natural degradation processes. A first order decay model was applied to field data and an average half-life equal to 7.5 months was obtained for the 1,2-DCA natural degradation.

Although the results are favorable, the natural degradation of the 1,2-DCA does not guarantee acceptable levels of concentrations. Plume control is obtained as a result of combined efforts, which includes the operation of an integrated system of hydraulic and physical barrier. Hence, monitoring of natural degradation mechanisms is part of the overall remedial program. A pilot test to evaluate the enhancement of these processes is being carried out through the use of a biosparging system. This is being implemented near the source to achieve sequential aerobic–anaerobic treatment zones.

References

- [1] M.C. Small, Risk-based corrective action, natural attenuation, and changing regulatory paradigms, *Bioremed. J.* 2 (1998) 221–225.
- [2] National Research Council, *Natural Attenuation for Groundwater Remediation*, National Academy of Sciences, Washington, 2000, 274p.
- [3] T.H. Wiedemeier, M.A. Swanson, D.E. Moutoux, E.K. Gordon, J.T. Wilson, B.H. Wilson, D.H. Kampbell, P.E. Haas, R.N. Miller, J.E. Hansen, F.H. Chappelle, *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater*, EPA/600/R-98/128, 1998.
- [4] P.V. Brady, M.V. Brady, D. Borna, *Natural Attenuation*, Lewis Publishers, Boca Raton, FL, 1998, 245p.
- [5] M.M. Lorah, L.D. Olsen, Natural attenuation of chlorinated volatile organic compounds in a freshwater tidal wetland: field evidence of anaerobic biodegradation, *Water Res. Res.* 35 (1999) 3811–3827.
- [6] M.M.M. Nobre, R.C.M. Nobre, in: *Proceedings of the First Conference on Remediation of Chlorinated and Recalcitrant Compounds, Remediation of a Chlorinated Organic Contamination in a Coastal Lagoon Region of Brazil*, Battele Press, Monterey, CA, May 1998.
- [7] E.J. Bouwer, B.E. Rittmann, P.L. McCarty, Anaerobic degradation of halogenated 1- and 2-carbon organic compounds, *Environ. Sci. Technol.* 15 (1981) 596–599.
- [8] T.M. Vogel, C.S. Criddle, P.L. McCarty, Transformations of halogenated aliphatic compounds, *Environ. Sci. Technol.* 21 (1987) 722–735.
- [9] G.R. Chaudhry, S. Chapalamadugu, Biodegradation of halogenated organic compounds, *Microbiol. Rev.* 55 (1991) 59–79.
- [10] P.L. McCarty, In situ bioremediation of chlorinated solvents, *Curr. Opin. Biotechnol.* 4 (1993) 323–330.
- [11] P.L. McCarty, L. Semprini, Groundwater treatment for chlorinated solvents, in: *Norris R.D. Handbook of Bioremediation*, Lewis Publishers, Boca Raton, FL, 1994, pp. 87–116.
- [12] J.M. Gosset, S.H. Zinder, in: *Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Groundwater, Microbiological Aspects Relevant to Natural Attenuation of Chlorinated Ethenes*, Dallas, Texas, 1996, pp. 10–13.
- [13] S. Fiorenza, E.L. Hockman, S. Szojka, R.M. Woeller, J.W. Wigger, Natural anaerobic degradation of chlorinated solvents at a Canadian manufacturing plant, in: *Bioremediation of Chlorinated and Polycyclic Aromatic Hydrocarbon Compounds*, Lewis Publishers/CRC Press, Boca Raton, FL, 1994.
- [14] P.L. McCarty, M. Reinhard, Biological and chemical transformation of halogenated aliphatic compounds in aquatic and terrestrial environments, in: *The Biogeochemistry of Global Change: Radiative Trace Gases*, Chapman & Hall, New York, 1993.
- [15] G. Stucki, M. Thuer, Experiences of a large-scale application of 1,2-dichloroethane degrading microorganisms for groundwater treatment, *Environ. Sci. Technol.* 29 (1995) 2339–2345.
- [16] J. Gerritse, A. Borger, E. Heiningen, H.H.M. Rijnaarts, N.P. Bosma, in: *Proceedings of the Fifth Symposium on In situ and On-site Bioremediation, Assessment and Monitoring of 1,2-Dichloroethane Dechlorination*, San Diego, CA, April 1999.
- [17] M.D. Lee, L. Sehayek, B.E. Sleep, T.D. Vandell, Investigation and remediation of a 1,2-dichloroethane spill. Part II. Documentation of natural attenuation, *Ground Monit. Remed. Summer* (1999) 82–88.
- [18] R.C.M. Nobre, M.M. Nobre, in: *Proceedings of the Fourth Brazilian Conference of Environmental Geotechnics (4º Congresso Brasileiro de Geotecnia Ambiental—REGEO'99)*, Field Evidence of 1,2-Dichloroethane Degradation, São José dos Campos, SP, December 1999, pp. 400–408.
- [19] E.J. Bouwer, Bioremediation of chlorinated solvents using alternate electron acceptor, in: *R.D. Norris, Handbook of Bioremediation*, Lewis Publishers, Boca Raton, FL, 1994, pp. 87–116.
- [20] T.M. Vogel, P.L. McCarty, Biotransformation of PCE to TCE, DCE, vinyl chloride and carbon dioxide under methanogenic conditions, *Appl. Environ. Microbiol.* 49 (1985) 1080–1083.
- [21] M.M.M. Nobre, R.C.M. Nobre, Uma solução geotécnica para remediação de águas subterrâneas contaminadas por compostos organo-clorados (A geotechnical solution for the remediation of groundwater contaminated with chlorinated organics), *Revista Solos e Rochas (Solos e Rochas Journal)* 20 (1997) 121–134.
- [22] S.A. Zhang, J. Naus, M.J. O'Connor, D.R. Williams, in: *Proceedings of the First Conference on Remediation of Chlorinated and Recalcitrant Compounds, Remediation Life Cycle at an EDC Spill Site*, Battele Press, Monterey, CA, May 1998.
- [23] E.E. Cox, M. McMaster, D.W. Major, in: *Proceedings of the First Conference on Remediation of Chlorinated and Recalcitrant Compounds, Natural Attenuation of 1,2-Dichloroethane and Chloroform in Groundwater at a Superfund Site*, Battele Press, Monterey, CA, May 1998.
- [24] A.J. van der Wijngaard, K.W.H.J. van der Kamp, J. van der Ploeg, P. Pries, B. Kazemier, D.B. Janssen, Degradation of 1,2-dichloroethane by *Ancylbacter aquaticus* and other facultative methylotrophs, *Appl. Environ. Microbiol.* 58 (1992) 976–983.
- [25] N.A. Lazarone, P.L. McCarty, Column studies on methanotrophic degradation of trichloroethene and 1,2-dichloroethane, *Groundwater* 28 (1990) 910–919.
- [26] L. Lehmicke, N. Mukherjee, in: *Proceedings of the Fifth Symposium on In situ and On-site Bioremediation, Natural Attenuation of Chlorinated Methanes and 1,2-DCA at a Site in Southern California*, San Diego, CA, April 1999.
- [27] M.P. Suarez, H.S. Rifai, Biodegradation rates for fuel hydrocarbons and chlorinated solvents in groundwater, *Biodegradat. J.* 3 (1999) 337–362.