MACAOH R&D Project (2001-2006)
(Modeling, Attenuation and Characterization in Aquifers of Organo-Halogenated compounds)

NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN AQUIFERS

TECHNICAL GUIDE
Extended abstract
November 2008

IMPROVE YOUR KNOWLEDGE BEFORE ACTING
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About ADEME

The French Environment and Energy Management Agency (ADEME) is a public agency under the joint authority of the Ministry for Ecology, Energy, Sustainable Development and the Sea, and the Ministry of Higher Education and Research. The agency is active in the implementation of public policy in the areas of the environment, energy and sustainable development. ADEME provides expertise and advisory services to businesses, local authorities and communities, government bodies and the public at large, to enable them to establish and consolidate their environmental action. As part of this work the agency helps finance projects, from research to implementation, in the areas of waste management, soil conservation, energy efficiency and renewable energy, air quality and noise abatement.


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The three MACAOH technical guides in French and the abstracts in French and in English can be downloaded from the ADEME web site.

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This document is a summary of the MACAOH technical guide “Natural attenuation of chlorinated solvents in aquifers.” After introducing the objectives of the MACAOH R&D project, this guide summarizes key concepts of Natural Attenuation and presents the main differences compared to existing guides:

- definitions of Natural Attenuation (NA) and Monitored Natural Attenuation (MNA);
- NA processes;
- the MACAOH methodology for evaluating the feasibility of MNA;
- the qualitative evaluation of biodegradation;
- the quantitative evaluation of NA processes;
- the implementation of MNA: the groundwater long-term monitoring plan; and
- the acquisition of necessary data and their interpretation.

1. Objectives of the MACAOH R&D project

Since the 1950s, an increasing number of sites contaminated by halogenated solvents have been identified in industrialized countries. The most frequently encountered group of compounds is that of aliphatic chlorinated solvents (chloromethanes, chloroethanes, and chloroethenes). These compounds correspond to liquids that are immiscible in water and are denser than water (DNAPL, apart from vinyl chloride, chloromethane, and chloroethane). Consequently, the propagation mechanisms that occur during a chlorinated solvent spill event can be described according to two distinct, successive processes (Figure 1):

- a gravity-driven infiltration of the non-aqueous phase liquid, or NAPL, (liquid composed of one or more chlorinated solvents) in the soil, leaving behind a zone at the residual saturation. This process results in a source zone of limited size within the porous medium with respect to the characteristic dimensions of the aquifer;
- a dissolved plume spreading in the groundwater due to dissolution of the compounds present in the source zone and a gaseous plume spreading in the air of the unsaturated zone due to volatilization of the contaminants present in both the source zone and/or the groundwater. Due to slow dissolution and volatilization rates, disappearance of the contamination (i.e., NAPL) is a very long process (several years, possibly several decades) compared with the time frame required to reach a no-flow state (i.e., residual saturation) for NAPL in the source zone (several days to several weeks in a sandy porous medium).

Forecasting the behavior of chlorinated solvents in aquifers presents three difficulties: characterization of the source zone (locating the source zone, evaluating the NAPL volume and composition), qualitative and quantitative evaluation of the natural attenuation potential (both in the source zone and in the dissolved/gaseous plumes), and modeling (how to choose physical models, tools, and methodologies).

Based on these observations, ADEME initiated a Research & Development project focused on the behavior and fate of chlorinated solvents in aquifers. Known as MACAOH (Modeling, Attenuation, and Characterization in Aquifers of OrganoHalogenated compounds), this project involved the combined efforts of the consulting company BURGEAP, and three research organizations, IFP (Institut Français du Pétrole), IMFS/IFARE (Institut de Mécanique des Fluides et des Solides de Strasbourg / Institut Franco-Allemand de Recherche sur l'Environnement), and IMFT (Institut de Mécanique des Fluides de Toulouse). Spanning a period of 5 years (2001-2006), it was structured around the three above-mentioned themes and included experiments at the laboratory scale (batch, column) and pilot scale (SCERES basin) at two industrial sites, as well as modeling studies (such as performance tests of computational tools in the framework of an inter-comparison program associating MACAOH partners and 8 modeling teams).

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1 Site Contrôlé Expérimental de Recherche pour la réhabilitation des Eaux et des Sols, located at IFARE in Strasbourg (underground, instrumented basin measuring 25 m x 12 m x 3 m, and reconstituting an alluvial aquifer).
The target objectives were first, to help fill gaps in understanding and applied knowledge, and second, to produce three technical guides on the following themes: "Characterization of a source zone", "Natural attenuation", and "Modeling". These guides, available for download on the ADEME web site, are also referenced by the French Ministry of Ecology, Energy, Sustainable Development and Town and Country Planning as technical tools for the management of contaminated sites.

The MACAOH technical guides include a description of key concepts, methodologies, and protocols, as well as examples of applications. They are intended for both service providers (e.g., consulting companies, research organizations) and clients (industries, planners, communities, institutions).

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2 http://www.sites-pollues.ecologie.gouv.fr/DocumentsDiagnostics.asp

ADEME 5/22
2. Natural Attenuation and Monitored Natural Attenuation: two key concepts

The definitions of "Natural Attenuation" (NA) and "Monitored Natural Attenuation" (MNA) vary from country to country. France has not yet officially published a definition of these concepts. The main studies on the NA of organic compounds in aquifers have been conducted in the United States. The statutory reference document is the 1999 OSWER Directive 3 No. 9200.4-17P [5], which defines NA and MNA as:

**Natural Attenuation (NA)**

"Natural Attenuation" includes a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization, transformation, or destruction of contaminants.

**Monitored Natural Attenuation (MNA)**

"Monitored Natural Attenuation" refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods.

In this directive, the U.S. Environmental Protection Agency (USEPA) considered MNA to be a remediation technique that may be appropriate for some sites. It is a "passive" approach that requires comprehensive preliminary studies to evaluate the ability of NA processes to reach the remedial objectives within a given time frame. Upon completion of these studies, implementing MNA results in long-term monitoring of the site to ensure that the data measured is consistent with the predictions. One central criterion of MNA deals with the maximum time allowed for Natural Attenuation to reach the remedial objectives. This maximum time is not stipulated in the directive; rather it must be considered for each site while comparing MNA with "active" techniques. In practice, a period of about 30 years is generally accepted.

Considering the uncertainties related to the ability of MNA to reach the remedial objectives, the USEPA expects that source zone control and long-term monitoring will be two fundamental components of any MNA approach.

The NA processes mentioned in the OSWER Directive are generally present at any site. The first step of the approach is a qualitative analysis of the processes. However, this is insufficient for demonstrating that the NA processes will meet their objectives within the given time frame. In the directive, evaluating the effectiveness of the NA involves 6 steps:

1. a detailed 3D characterization of the site;
2. the development of a conceptual model;
3. an estimation of the attenuation rates of the pollution;
4. an evaluation of the health and environmental risks;
5. a prediction of the time required to attain the remediation objectives; and
6. a comparison of MNA to other solutions.

3 Office of Solid Waste and Emergency Response (the USEPA consists of about fifteen offices, including OSWER). The first version of the Directive was published in 1997.
Among the processes mentioned above, the OSWER Directive indicates that **processes that destroy or degrade contaminants are preferred**, which means that a distinction must be made between destructive and non-destructive processes.

In Europe, only a few of the available definitions of NA are similar to the definition given in the OSWER Directive (see the guides published by England and Wales (Environment Agency, 2000 [1]) and The Netherlands (NOBIS, 2001 [3])). However, translations of the concept of NMA sometimes differ from the USEPA definition.

The approach chosen for the MACAOH project is based on the OSWER definitions. There are certain differences, however, in the NA processes accounted for; in addition to the processes listed in the OSWER directive, NAPL/water (dissolution) and NAPL/gas (volatilization) mass transfers are also taken into account.

The industry standard document (also used by the MACAOH consortium) is the 1998 USEPA protocol entitled: "Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water, EPA/600/R-98/128" [4]. A considerable amount of technical documentation is associated with the American protocol; in particular, the 2004 report "Performance Monitoring of MNA Remedies for VOCs in Ground Water, EPA/600/R-04/027" gives the details of a long-term monitoring plan, whereas the 1998 protocol focuses more on studies to be conducted before implementing MNA.

For MNA feedback on sites contaminated by chlorinated solvents, the work by Newell et al. (2004), who summarized the application of MNA at some 200 sites, is a useful resource. The data from this extensive survey has also been reviewed in a report published by the WSRC (2004) [7]. The authors demonstrated that in 77% of the cases MNA was implemented alone or in combination with active techniques (Figure 2). MNA was applied alone in 30% of these sites. MNA was associated with treatment of the source zone in 42% of the cases, and with treatment of the plume in 13% of the cases.

![Figure 2 – MNA use as a remediation strategy (source: WSRC, 2004 [7])](image-url)
3. Natural Attenuation processes

NA processes may be classified as either non-destructive processes, which do not destroy the contaminant but transfer it to another compartment or attenuate its concentration within a compartment, or destructive processes, which destroy contaminants via chemical or biological processes. These processes can be divided into four categories:

- non-destructive processes that do not modify the mass of contaminants within a compartment (e.g., groundwater or the gaseous phase): advection, dispersion, and molecular diffusion. Advection, the "transport engine" of compounds in groundwater, does not reduce concentration levels on its own;
- non-destructive processes that modify the mass of contaminants within a compartment, which includes all phase transfer processes: dissolution, volatilization (NAPL/gas and water/gas transfers), and sorption;
- destructive processes: mainly biodegradation and, to a much lesser extent, chemical degradation (in particular for 1,1,1-TCA);
- non-destructive phenomena grouped under the word "dilution," which does not refer to any physical process such as the processes described above and involves mixing of polluted and non-polluted water due to the action of various phenomena (e.g., recharge by rain or pumping in a well).

These processes may also be classified by compartment (Figure 3):

- attenuation of the source zone: the main processes are NAPL/water (dissolution) and NAPL/gas (volatilization) mass transfers, as well as biodegradation in some cases. These processes generate two interacting plumes (of dissolved and gaseous compounds);
- attenuation of the plume of dissolved compounds by various processes: advection, dispersion (and possibly diffusion), sorption, volatilization, abiotic and biotic degradation, and "dilution";
- attenuation of the plume of gaseous compounds by various processes: diffusion (and possibly advection), dispersion, sorption, abiotic and biotic degradation (capillary water in the vadose zone), and "dilution" (e.g., vapor washout due to precipitation).

The MACAOH approach explicitly takes into account the source zone, i.e., the soil volume (in the unsaturated and/or saturated zones) that contains NAPL as well as its associated attenuation processes (dissolution and volatilization). This approach was chosen based on two observations:

- in terms of mass balance, NAPL represents most of the contaminant mass (Figure 4);
- the contaminant concentration level and its eventual evolution in the dissolved and gaseous plumes are largely determined by the composition of the NAPL and the mass transfer processes between the NAPL and water (dissolution, see Figure 4) and between NAPL and gas (volatilization).
A detailed description of these concepts is given in the extended abstract and the MACAOH guide, entitled: “Characterization of source zones.”

Biodegradation, considering its central role in Natural Attenuation and its double complexity, is described below. The biodegradation of chlorinated solvents is sequential (for example, PCE produces TCE) and the process mechanisms and kinetic rates vary with the redox conditions.

Biodegradation

In most cases, the biodegradation of chlorinated aliphatic hydrocarbons is an oxidation-reduction reaction catalyzed by microorganisms (especially bacteria) and involving electron donors and electron acceptors. Depending on the particular chlorinated aliphatic hydrocarbons, the bacterial population, and the geochemical environment, the active mechanism may be oxidation (for the least substituted solvents, the chlorinated hydrocarbon acts as an electron donor) or reductive dechlorination (for the most substituted chlorinated solvents, the chlorinated hydrocarbon acts as an electron acceptor). In addition, the bacterial metabolism can be either direct (metabolic) or indirect (cometabolic).

In an aquifer polluted with chlorinated hydrocarbons, the redox conditions change in the plume. In theory, the region located near the source zone is methanogenic, followed by a sulfate-reducing zone, an iron-reducing zone, a nitrate-reducing zone and, lastly, an aerobic zone. The kinetic degradation rates are generally quite different in each of these zones.

Typical electron donors (chemical species that undergo oxidation reactions, thus producing electrons and other by-products such as CO₂) are mainly petroleum hydrocarbons, acetate, methanol, humic acids, and the least substituted chlorinated hydrocarbons (e.g., DCE and VC for chloroethenes).

The dominant biodegradation mechanisms can be classified according to the redox zones (Figure 5):

- **reductive dechlorination**: the zones that are favorable for methanogenic and sulfate-reducing bacteria (efficient dechlorination of chloroethenes, production of chlorinated metabolic intermediates or completely dechlorinated daughter products such as ethene and ethane);
- **anaerobic oxidation**: conditions that allow the reduction of nitrates, iron, or even sulfates. This very minor mechanism concerns monochlorinated compounds and possibly dichlorinated compounds such as cis-1,2-DCE;
- **aerobic oxidation**: direct oxidation for VC, or even DCEs, and efficient direct oxidation for DCM and 1,2-DCA. In the presence of dissolved oxygen and substrates for microorganism growth (e.g., methane, toluene, phenol), cometabolic oxidation of VC, DCE, TCE, and other completely substituted chlorinated hydrocarbons (probably a minor process).
Figure 5 – The distribution of electron acceptors and the main biodegradation mechanisms for chlorinated hydrocarbons in groundwater contaminated by accessible organic matter.

Figure 6 shows the sequential dechlorination pathways for the three families of chlorinated solvents and the possible connections between chloroethenes, chloroethanes, and chloromethanes.

Figure 6 - Degradation of chlorinated aliphatic hydrocarbon via biotic and abiotic pathways
4. The MACAOH evaluation of the feasibility of Monitored Natural Attenuation

The MACAOH methodology was based on laboratory studies, as well as studies in the SCERES basin and two industrial sites. This methodology was also based on the 1998 USEPA guide [4]; however, four items are different in the MACAOH methodology:

- **the source zone, the dissolved plume, and the gaseous plume are taken into account**, which means that in terms of processes, dissolution and volatilization are accounted for;
- a "scoring" approach for the qualitative evaluation of biodegradation **is not implemented** since this method oversimplifies the complexity of a site (USEPA [4], NOBIS [3]);
- **a quantitative estimation of the processes at work**: for each of the three regions (source zone and plumes), an analytical approach, based on mass balances, has been developed to quantify the mass flux associated with the various processes;
- **a prediction of the NAPL saturations and aqueous and gaseous concentrations**: methodological insights are given for multiphase approaches that account for the NAPL. Accounting for the mass transfer processes involving NAPL is the only way to explain the reduction of concentration levels of dissolved or gaseous compounds over time for the immediate down-gradient plume.

The methodology for evaluating the feasibility of MNA includes four successive steps (Figure 7):

- **step 1**: preliminary data analysis to specify the spatial structure and temporal evolution of the pollution at the identified receptors;
- **step 2**: qualitative evaluation of the biodegradation mechanisms of dissolved and gaseous compounds in the plumes;
- **step 3**: quantitative evaluation, based on mass balances, of natural attenuation processes in the source zone and the plumes;
- **step 4**: prediction of the temporal evolution of NAPL saturations (source zone) and of concentrations in the groundwater and vadose plumes. The MACAOH "Modeling" guide proposes various recommendations concerning the choice of computational tools, the data required, the implementation of numerical codes, and the information that should be included in the study report.

After completing these steps, responsible parties (the consulting company, the industry and the public administration) must decide whether MNA is accepted as a remediation strategy, either implemented as a stand-alone technique or in combination with an "active" technique. For each scenario, there should be a consideration of the costs vs. the advantages, accounting for various constraints (e.g., technical, statutory, and health and environmental protection (risk evaluation)) as well as the social impact (e.g., to local residents). If MNA is accepted, the site should then be monitored until the remediation objectives are met (**step 5**).
Assessing Natural Attenuation processes

Step 1 – Preliminary data analysis
- Site geography, geology, hydrogeology and surface water bodies
- Receptors identification
- Nature, spatial distribution, and temporal evolution of contaminants
- Site conceptual model
- Complementary data acquisition plan

Step 2 – Qualitative evaluation of biodegradation
- Acquisition of biodegradation specific parameters (6 analytical packs)
- Biotic mechanisms identification
- Field data expertise (based on a comparison with concentration thresholds)

Step 3 - Quantitative evaluation of Natural Attenuation processes
- Mass balance in the source zone (groundwater and vadose zone)
- Mass balance in the groundwater plume
- Mass balance in the vadose plume (plume emitting from NAPL located in the vadose zone or from the groundwater plume)

Step 4 – Prediction of temporal evolution of contaminant distribution
- General methodology (refer to the MACAOH technical protocol on Modeling)
- Standard modeling scenarios (source area, groundwater and vadose plumes)

Feasibility and performance evaluation of MNA as a strategy to achieve site-specific remediation objectives within a given time frame
- Comparison with « active » clean-up approaches

Implementing Monitored Natural Attenuation

Step 5 - Long term groundwater monitoring
- Monitoring plan: monitoring points, parameters, frequency and interpretation methods
- Phase I: quarterly monitoring for at least 2 years (effects of non-permanent phenomena on NA effectiveness)
- Phase II: yearly (or less frequent) long term monitoring (pollution attenuation)
- Interpret new data, refresh monitoring plan (if needed)

Periodic re-evaluation of MNA performance and of its adequacy with respect to the attainment of the site-specific remediation objectives

Figure 7 - Methodological flowchart for evaluating NA and implementing MNA.
The blue boxes show the steps carried out by the contractor (e.g., consultants), and the green boxes show the steps performed by the client and the public administration.
5. Qualitative evaluation of biodegradation (step 2)

The objective of step 2 in the methodology is to determine whether or not biodegradation of the chlorinated solvents is active. This method consists of a list of parameters organized as analytical packages (Table 1) to be measured in at least 7 monitoring wells (1 up-gradient from the source zone, 2 in the source zone, and 4 down-gradient wells located along two different plume transects). The measurements characterize the chlorinated solvents and their degradation products, the dominant redox conditions in the groundwater, the carbon sources, and the geochemical conditions of the aquifer.

The evaluation, focused on the reductive dechlorination of chloroethenes, is conducted as a thorough data analysis that relies on the computation of a "dechlorination rate" and a comparison between the measured concentration and a proposed threshold value for each parameter (Table 2).

<table>
<thead>
<tr>
<th>Analytical packages</th>
<th>Parameters measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOCs Package: chlorinated and petroleum hydrocarbons</td>
<td>Chloroethenes, chloroethanes, chloromethanes, BTEX and petroleum derivatives</td>
</tr>
<tr>
<td>&quot;Anions&quot; Package</td>
<td>Chlorides, Nitrates, Sulfates</td>
</tr>
<tr>
<td>&quot;M-E-E&quot; Package</td>
<td>Methane, ethene et ethane</td>
</tr>
<tr>
<td>&quot;DOC-NPOC&quot; Package</td>
<td>Dissolved Organic Carbon (Non-Purgeable Organic Carbon: VOCs excluded, already measured in the VOCs Package)</td>
</tr>
<tr>
<td>&quot;Electrochemical&quot; Package (on-site measure)</td>
<td>Dissolved Oxygen (mg/L), pH, Redox Potential (mV), Temperature (°C), Conductivity (µS/cm)</td>
</tr>
<tr>
<td>&quot;Colorimetric&quot; Package (on-site measure)</td>
<td>Alkalinity (mg/L of CaCO3), Ferrous Iron (mg/L)</td>
</tr>
</tbody>
</table>

Table 1 - Description of the "analytical packages" required for the qualitative evaluation of the biodegradation of chlorinated hydrocarbons in groundwater.

Application example

The industrial site used as an example is located on a sandy alluvial aquifer, which has an average thickness of 5 m to 7 m, lying on top of a clay-loam substratum. The groundwater table is at a depth of about 2 m. The average hydraulic conductivity of the aquifer is $3 \times 10^{-4}$ m/s and the average pore velocity of the groundwater is about 1 m/d. Private individuals located down-gradient from the site use this groundwater for gardens and cattle (the closest wells are 300 m down-gradient from the source zone).

Pollution from chlorinated solvents has been present for about 30 years and is due to multiple overflows of a storage tank that is located in the basement of one of the workshops. The lateral extension of the main source zone is about 25 m$^2$ (Figure 8). The NAPL, consisting of a PCE/TCE mixture (about 60/40 molar fraction), was identified at the alluvial aquifer / substratum interface (with a maximum total concentration of about 60 g/kg dry weight). The plume of dissolved chlorinated compounds emitting from the main source extends over 650 m down-gradient with an end-point discharge in a river; the plume is also extremely wide, with a width of about 300 m near the river.

The data acquired for the qualitative evaluation of the biodegradation is shown in Table 2 and is compared with the recommended threshold values.
What is the nature of the organochlorinated pollution in the most contaminated zone?

At this industrial site, TCE is the main chlorinated compound in the aqueous phase (in MwA9 and MwA11), even though the main NAPL contaminant is PCE. The "initial" aqueous concentration of PCE cannot be measured because reductive dechlorination is extremely efficient in the source zone. Reductive dechlorination quickly leads to the production of large amounts of all metabolic intermediates, especially cis-DCE (in MwA11). Apparently, cis-DCE does not form a bottleneck in the source zone, since VC and ethene are also produced in large quantities. The calculated dechlorination rates are, therefore, quite high: 24 % and 53 % for MwA9 and MwA11, respectively. These values are averages of the PCE and TCE dechlorination rates.

It is important to note the high quantities of ethene and ethane produced (1100 µg/L of ethane in MwA11), which indicate efficient and complete reductive dechlorination.

Why is biological reductive dechlorination efficient?

Biological reductive dechlorination is efficient because the redox conditions are methanogenic at the presumed location of the source zone (MwA9). In this monitoring well, the concentration is slightly below the threshold value, but the monitoring wells located down-gradient and near MwA9 (MwA11 and MwA25) indicate considerable production of methane (17 to 21 mg/L), which is confirmed by strongly negative redox potentials (-86 to -265 mV) that correspond with conditions that are favorable for reductive dechlorination.

The sulfate reduction is not as efficient; there are high sulfate concentrations in the most contaminated zone. It is possible that the very high sulfate concentrations prevent even more complete dechlorination due to competition between sulfate-reducers and halorespirators for electrons.

Measurements of ferrous iron (6 mg/L to 18 mg/L in MwA9, MwA11 and MwA25) confirm reductive conditions with, in addition, the absence or near-absence of nitrates and dissolved oxygen at locations up-gradient from the source zone. Lastly, the alkalinity confirms high CO₂ production at MwA25 (the starting point of the plume).

Therefore, at this site, and at the most contaminated zones in particular, there is evidence of active biological degradation.
Why are the redox conditions strongly reductive?
The pollution caused by chlorinated solvents comes together with other carbon contamination, as shown by the high content of dissolved organic carbon that "fuels" the biological reactions. Methanogenesis will continue as long as carbon is available. The high production of ethene and ethane indicates that efficient dehalorespirators (in particular, *Dehalococcoides ethenogenes*) are present and benefit from suitable physico-chemical conditions.

Do the reductive conditions allow for attainment of the protection requirements at the receptor locations?
No. First, the spatial dimensions of the zone that shows strongly reductive conditions is too small to allow for a long enough residence time for the chlorinated contaminants and a complete reductive dechlorination into the harmless end-products ethene and ethane. In addition, cis-DCE and especially VC reach the identified receptors. Second, biological degradation of TCE, cis-DCE, and VC in the "remote" plume (more than 400 m away from the source zone) proves to be inefficient in aerobic conditions (results not shown).

<table>
<thead>
<tr>
<th>SITE A</th>
<th>UPGRADENT</th>
<th>SOURCE ZONE</th>
<th>DOWNGRADIENT PLUME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance from the center of the source zone (m)</td>
<td>0</td>
<td>10</td>
<td>65</td>
</tr>
<tr>
<td>Parameters</td>
<td>Threshold values</td>
<td>Average or measure</td>
<td>Measure</td>
</tr>
</tbody>
</table>

**CHARACTERIZATION OF CHLORINATED ALIPHATIC HYDROCARBONS BIODEGRADATION**

<table>
<thead>
<tr>
<th>Chloroethenes and metabolic intermediates (µg/L)</th>
<th>PCE</th>
<th>TCE</th>
<th>cis-DCE</th>
<th>trans-DCE</th>
<th>11-DCE</th>
<th>VC</th>
<th>Ethene</th>
<th>Ethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dechlorination rate (%)</td>
<td>&gt; 60%</td>
<td>de 40 à 60 %</td>
<td>53 (3)</td>
<td>de 20 à 40 %</td>
<td>24 (1)</td>
<td>de 5 à 20 %</td>
<td>39 (3)</td>
<td>&lt; 5%</td>
</tr>
<tr>
<td>Ethene + Ethane (µg/L)</td>
<td>20 à 200</td>
<td>0</td>
<td>61</td>
<td>1110</td>
<td>153</td>
<td>28</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Free chloride (mg/L)</td>
<td>&gt; twice background concentration (mg/L)</td>
<td>198 and 469</td>
<td>323</td>
<td>237</td>
<td>162</td>
<td>279</td>
<td>174</td>
<td></td>
</tr>
</tbody>
</table>

**CHARACTERIZATION OF IN SITU REDOX CONDITIONS**

| Methane (mg/L) | > 1 mg/L | 0 | 0,85 | 17 | 21,1 | 0,66 | 1,01 |
| Sulfates (mg/L) | < 20 mg/L | 55 and 100 | 95,2 | 73,2 | 22,7 | 128 | 36 |
| Ferrous Iron (mg/L) | > 2 mg/L | 1,2 | 6,3 | 10,2 | 18,1 | 2,08 | 0,14 |
| Nitrate (mg/L) | < 1 mg/L | 2 | 0 | 0 | 0 | 9,3 |
| Dissolved Oxygen (mg/L) | < 0,5 mg/L | 0,2 and 0,8 | 0,07 | 0 | 0,1 | 1,29 |
| Redox Potential (mV) | Eh < + 100 mV | 225 | 2 | -54 | 25 | 274 | 298 |
| Alkalinity (mg/L) | > twice background concentration (mg/L) | 160 | 200 | 260 | 1260 | 280 | 260 |

**CHARACTERIZATION OF CARBON SOURCES**

| DOC-NPOC (mg/L) | > 10 mg/L | 7 | 10 | 16 | 180 | 4,9 | 9,5 |
| VOC (BTEX + Alkyl-benzenes + naphtalene) (mg/L) | > 2 mg/L | 0,001 | 0 | 0,036 | 0,034 | 0,001 | 0,005 |

(1) PCE/TCE average. 35% for calculation based on PCE, and 13% based on TCE
(2) PCE/TCE average. 60% for calculation based on PCE, and 47% based on TCE
(3) Averages given for convenience, since the results are not relevant (the wells are not located in the most contaminated zone; metabolites are likely to have been transported by groundwater and degraded by aerobic oxidation in MwC)

The "0" values correspond to concentrations below the analytical quantification limit.

Table 2 – A qualitative evaluation of the biological degradation using the MACAOH methodology at site A.
6. Quantitative evaluation of the Natural Attenuation processes (step 3)

The method in the present work allows for the quantitative analysis of the proportional contribution of each process involved in NA (bearing in mind that, for example, attenuation via "dilution" is generally not accepted) and calculation of the (bio)degradation rates for the chlorinated hydrocarbons in the plumes. The results of this step will also be used as inputs for building and implementing the numerical model (step 4).

6.1. The source zone

In the source zone, the mass fluxes of dissolved (for the saturated zone) and gaseous (for the unsaturated zone) contaminants are evaluated using an analytical approach: plume transects that represent the source zone’s dimensions. The data acquired include the composition of the NAPL, the concentrations of dissolved and/or gaseous contaminants, and the gaseous mass fluxes at the ground/atmosphere interface (see Figure 9).

![Figure 9 – A schematic of the mass balance in the source zone.](image)

\( C_{\text{gw}} \) - groundwater concentration; \( M_\text{NAPL} \) - NAPL mass in the source zone; \( GW \text{ table} \) - groundwater table elevation; \( S_{\text{groundwater}} \) - control transect at the vadose zone/atmosphere interface; \( S_{\text{groundwater,downgradient}} \) - control transect in groundwater downgradient from the source; Sat. Zone: Saturated Zone; \( \Phi_{\text{dissolved}} \) - mass flux of dissolved contaminants in groundwater emitted by the source and transported by groundwater flow; \( \Phi_{\text{vapors}} \) - mass flux of gaseous contaminants emitted by the source towards the atmosphere.

6.2. The plume of dissolved contaminants

In the plume of dissolved contaminants, the mass flux balance is computed between two aquifer transects delineated by groundwater elevation contours and represented by a set of monitoring wells located in a plane perpendicular to the flow direction (Figure 10). This approach consists of an analytical evaluation of the proportional contributions from advection, volatilization, and vapor washout between two plume transects. The contributions of hydrodynamic dispersion, "dilution,” and biodegradation processes to concentration reduction are then computed by taking the difference. This method also allows for the calculation of biodegradation rates based on the site-specific data.
6.3. Application example: the plume of dissolved contaminants

A qualitative evaluation of the biodegradation processes (step 2) revealed methanogenic conditions from the source zone to \( x = 120 \) m, followed by aerobic conditions in the remote plume, the up-gradient region of the river. Three plume transects, perpendicular to the flow direction, were selected for the mass flux balance approach; their locations were 8 m (the down-gradient extension of the source zone), 120 m, and 650 m from the source zone.

Assuming a homogeneous biodegradation rate in all 3 control volumes (Figure 10), the approach mentioned above gives the following results (Figure 11):

- all contaminants show reduced dissolved mass fluxes when carried by groundwater between transect 1 and transect 2, except for ethane (inconsistent result);
- "dilution" is the most prevalent process in the central volume for all contaminants, except for ethane, accounting for 61 %, and up to 82 % depending on the contaminant, of the flux difference between the up-gradient and down-gradient transects. The second most prevalent process, except for ethane, is biodegradation, accounting for 9% to 35%;
• dispersion, even for overestimated values (results shown), gives a low contribution to the flux reduction (4% to 8% depending on the contaminant);
• the contribution from volatilization is very low, while the contribution from vapor washout is zero or nearly zero (largely due to the presence of industrial buildings and road asphalt);
• 1st order biodegradation constants given from mass balance calculations vary from 0.26 year⁻¹ for cis-DCE to 1.8 year⁻¹ for ethene.

The results of steps 3 and 4 are then used to predict the evolution of the NAPL saturations and the contaminant concentrations in the dissolved and gaseous plumes by modeling (step 4). Advice on performing modeling studies is provided in the MACAOH "Modeling" guide.

7. Implementation of Monitored Natural Attenuation: long-term groundwater monitoring specifications (step 5)

The implementation of Monitored Natural Attenuation (MNA) as a clean-up strategy calls for long-term site monitoring, which lasts, in theory, until the remediation objectives are achieved.

This method is based on the OSWER Directive 9200.4-17P [5], which describes the main 7 objectives of any long-term groundwater monitoring plan as:

• demonstrate that NA occurs as expected;
• detect changes in the environmental conditions (e.g., hydrogeologic or geochemical changes) that may reduce the efficacy of any of the NA processes;
• identify any potentially toxic metabolites;
• verify that the plume is not expanding down-gradient, laterally, or vertically;
• verify that the impacts to the down-gradient receptors remain acceptable;
• detect any release of contaminants into the environment that could affect the effectiveness of NA; and
• verify that the remediation objectives are achieved.

Using these objectives, the monitoring plan specifies the measurement locations, the parameters to be measured, the associated analytical techniques, the frequency of measurements, and the methods for data interpretation. These specifications are based on a conceptual model of the site that is developed from the data measurements and interpretations carried out during steps 1 through 4.

7.1. Network of measurement locations

It is impossible to define, a priori, the minimum number of measurement locations. As a general rule, the type, number, and position of the measurement locations must be sufficient to characterize the plume geometry with special attention given to measurements up-gradient from the source, at the source, and down-gradient from the source zone (Figure 12). Depending on the uncertainty in the data, the heterogeneities of the aquifer properties, and the distribution of contaminants, the measurement network may also include devices for the 3D characterization of the plume (e.g., multilevel groundwater sampling).

The network of measurement locations should include receptors at which the remediation objectives are defined, and there should be MNA control wells that allow for an evaluation of the evolution of the NA processes over time.
7.2. Parameters to be measured and the frequency of sampling

Groundwater monitoring for MNA includes two phases:

- **a short-term initial phase** designed to detect the impact of transient phenomena on the plume and source zone characteristics (e.g., concentrations and geochemical conditions),
- **a second, long-term monitoring phase** designed to evaluate the evolution of the NA processes over time and the concentrations reduction until the remediation objectives are achieved.

![Figure 12 - A monitoring network for MNA (view from top).](image)

7.3. Phase I: short-term monitoring

The list of recommended parameters is as follows: the hydraulic head, the pumping rates, the injection and infiltration rates, the water levels in neighboring streams and lakes, the meteorological conditions (especially effective precipitation), and the groundwater concentrations of dissolved chlorinated contaminants and biodegradation indicators (all 6 MACAOH analytical packages: VOCs, Anions, M-E-E, DOC-NPOC, Electrochemical, and Colorimetric).

The sampling frequency depends on the site context and the types of parameters measured. In all cases, it is recommended to implement this short-term monitoring plan **at least every three months** during the first two years of MNA. Based on these results, a **reference state** of the plumes will be defined and the reference month for the phase II measurements will be set.

7.4. Phase II: long-term monitoring

**Long-term monitoring of the source zone**

The list of recommended parameters is as follows: physical parameters (hydraulic head, water levels in streams and lakes, pumping and injection/infiltration rates, and effective precipitation), the NAPL composition, and the groundwater concentrations of dissolved contaminants in the zone immediately down-gradient from the source.

Depending on the situation, the following optional data could be collected: the mass flux of gaseous chlorinated contaminants at the ground/atmosphere interface above the source zone, the distribution of NAPL saturation, and the groundwater biodegradation indicators at the source zone.

Since the source zone evolution processes are very slow, **sampling should occur approximately every 5 years.**

**Long-term monitoring of the plume of dissolved compounds**

The list of recommended parameters is as follows: physical parameters (hydraulic head, water levels in streams and lakes, pumping and injection/infiltration rates, and effective precipitation), and the groundwater concentrations of dissolved chlorinated contaminants and biodegradation...
indicators (all 6 MACAOH analytical packages). Optional data include: the vadose zone concentrations of gaseous chlorinated contaminants and the mass fluxes of gaseous chlorinated contaminants at the ground/atmosphere interface.

This long-term monitoring plan should be implemented once a year or possibly once every several years.

7.5. Data interpretation

The collected data can be displayed in maps (for example, the hydraulic head and concentrations) and as graphs showing the evolution of the various measured parameters. The main objectives are to specify the plume geometry, to identify temporal trends in concentration changes, and to compare the measured data with the model predictions. The greatest difficulty associated with interpreting the data concerns detecting the effective reduction in concentrations, since various factors may generate wide variations in the measured data: especially the heterogeneities in the aquifer properties and in the distribution of contaminants, and the temporal variations in the aquifer hydraulic or geochemical conditions. These phenomena may potentially modify the measured concentrations by several orders of magnitude between two sampling events, and may hide the effective decrease in pollution (which is generally slow) caused by NA processes.

Other difficulties arise when accounting for the presence of multiple plumes generated by several source zones and the detection of new releases of contaminants during monitoring, and when evaluating the time required for source zone depletion, which governs, to a great extent, the reductions in the groundwater concentrations. It is thus recommended to implement other data interpretation strategies, i.e., more robust approaches than the graphical evaluations described previously. These may include finding mass balances in each compartment (the saturated zone, vadose zone, and surface water) or for each physical state (NAPL, water, gas, and sorbed phase), estimation of the mass fluxes through a plume transect, evaluation of pollution attenuation rates, and numerical modeling.

Data interpretation must lead to a conclusion on the effectiveness of using MNA as a groundwater remediation technique. In the case of a negative decision or negative results, a complementary or alternative clean-up strategy must be implemented.

8. Data acquisition and interpretation

For data acquisition and its initial interpretation (prior to the specific interpretations proposed in the guide), there are some key steps that guarantee the quality of the MNA feasibility study or its implementation. Some key points on these aspects are discussed below.

8.1. Data acquisition

- **Monitoring well installation**: since NAPL may be present at the aquifer/substratum interface (Figure 1), it is recommended to extend the monitoring wells a few decimeters into the substratum.
- **Multilevel water sampling**: differences of several orders of magnitude are often observed in chlorinated contaminant concentrations between water samples located a few decimeters apart vertically. It is thus recommended to conduct multilevel water sampling (examples in Figure 13). It should be noted that the concentration is highly dependent on the sampling strategy, since it introduces a bias with respect to the local concentration measured in the pore water.
- **Evaluation of gas transfers**: since data on the gas phase may present some statistical fluctuation problems, a simultaneous implementation of flux measuring chambers at the ground/atmosphere interface (gaseous mass flux measurements) and vadose zone monitoring wells at multiple depths (gaseous concentration measurements) is recommended.
- **Evaluation of biodegradation rates**: in general, laboratory data is not very representative. It is thus recommended to acquire biodegradation rates using data measured at the site.
8.2. Data interpretation:

- The soil concentrations must be interpreted in terms of the NAPL saturation (refer to the technical guide "Characterization of source zones").
- The water and gas concentrations must be compared to the equilibrium concentrations (i.e., the solubility if the pollution consists of a single species, or the product of the solubility and the molar fraction of each species in the NAPL for a mixture of several contaminants).
- The physical properties of the contaminants can be used to describe the phase mass transfers at thermodynamic equilibrium: the solubility of the NAPL/water transfer, the vapor pressure of the NAPL/gas transfer, Henry's constant for the water/gas transfer, and Kd, the partition coefficient of the solid/water transfer. For interpreting data, however, non-equilibrium transfer rates are often required to better describe real world scenarios. Accounting for transfer rates tends to produce lower concentrations and longer time periods (e.g., Figure 14 shows concentrations that are lower than the equilibrium concentration of 24 400 ppmV in the source zone even though the porous medium was considered to be homogeneous).
- Accounting for heterogeneities at different scales is a valuable aid when interpreting both the pollution data and the properties of the porous medium. For example, a hydraulic conductivity value measured in the laboratory using a decimetric scale may be radically different from a hydraulic conductivity value measured from a pumping test that is representative of a plurimetric or greater scale.
9. References


