SNOWMAN NETWORK
Knowledge for sustainable soils

State of the art concerning MNA in Europe – France

SNOWMAN network conference on monitored natural attenuation
November 7th 2011
Salon du Relais, Paris

Revised version

Inge Declercq

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1. Regulation and status

1.1. Regulatory context

The legislation concerning the management of contaminated soils in France is covered primarily by the law of 1976 concerning « Installations Classées pour le Protection de l'Environnement » (ICPE). Another law of importance to the subject of contaminated soils is the law from 15 July 1975 concerning waste removal and recuperation of materials. The national risk-based policy for the management of contaminated sites was established in the “Circulaire” from 3 December 1993. (Hazebrouck, Hulot & Bureau, 2006)

In general, the management of contaminated sites in France is determined by the future usage of the sites. In this context, NA is considered to be on the same level as active remediation measures. The “Circulaire” from 8 February 2007 from the Ministère de l'Ecologie et du Développement Durable (MEDD) mentions natural attenuation (NA) explicitly within the context of the national methodology for the management and supervision of contaminated sites and soils in France, but there is no official published definition of the concept of (monitored) natural attenuation ((M)NA). NA is not yet entirely considered as a management technique, but the use of “atténuation naturelle sous surveillance” (MNA) is not excluded either. Annex II of the Circulaire explains in some more detail the conditions for the use of natural attenuation as a management tool. The contamination has to be stabilised or has to be in regression. Furthermore, it has to be shown that the removal of the contamination is impossible or undesirable. Only when previous conditions are met and the residual levels of the contamination are in accordance with the envisioned use of the site, natural attenuation can be considered a remediation option, on the condition that it is accompanied by surveillance or monitoring.

A schematic model of the national methodology for the management of contaminated sites is presented in Figure 1. This model tells us e.g. that natural attenuation can only be applied once the sources and the impacts of the contamination are controlled for; that different management options have to be considered and that the choice must be justified based on costs and benefits.

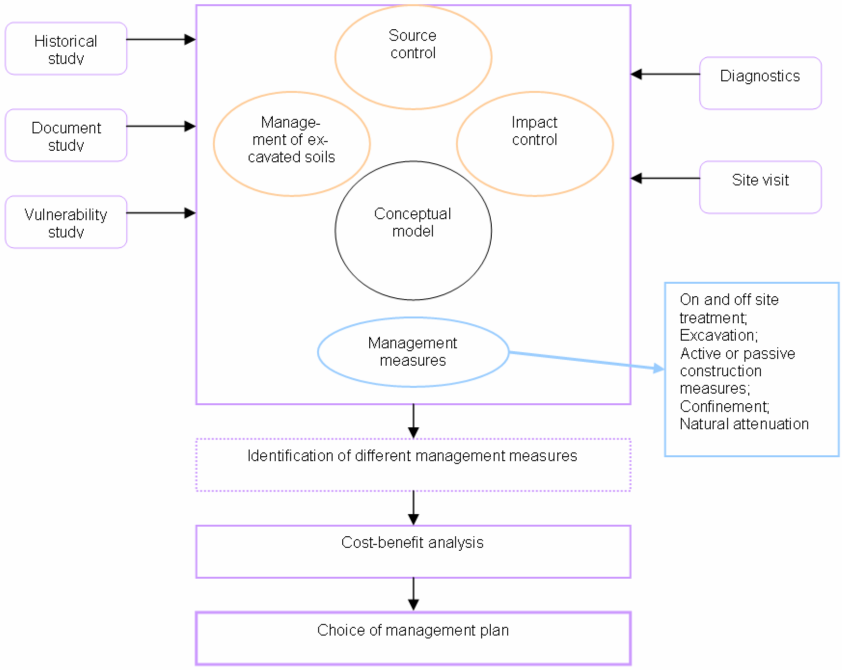

Figure 1. National methodology for the management of contaminated sites – France (MEDD, 2007, annex II, p.38)

The BRGM report of phase 2 of the ATTENA project[1] shows in more detail the place of NA within this methodology. A flowchart shows the national methodology for the management of contaminated sites (Figure 2); as can be seen, NA is an option for the management of impacts. NA can only be used for the management of the contaminant source once the source is under control. (Saada et al., in press)

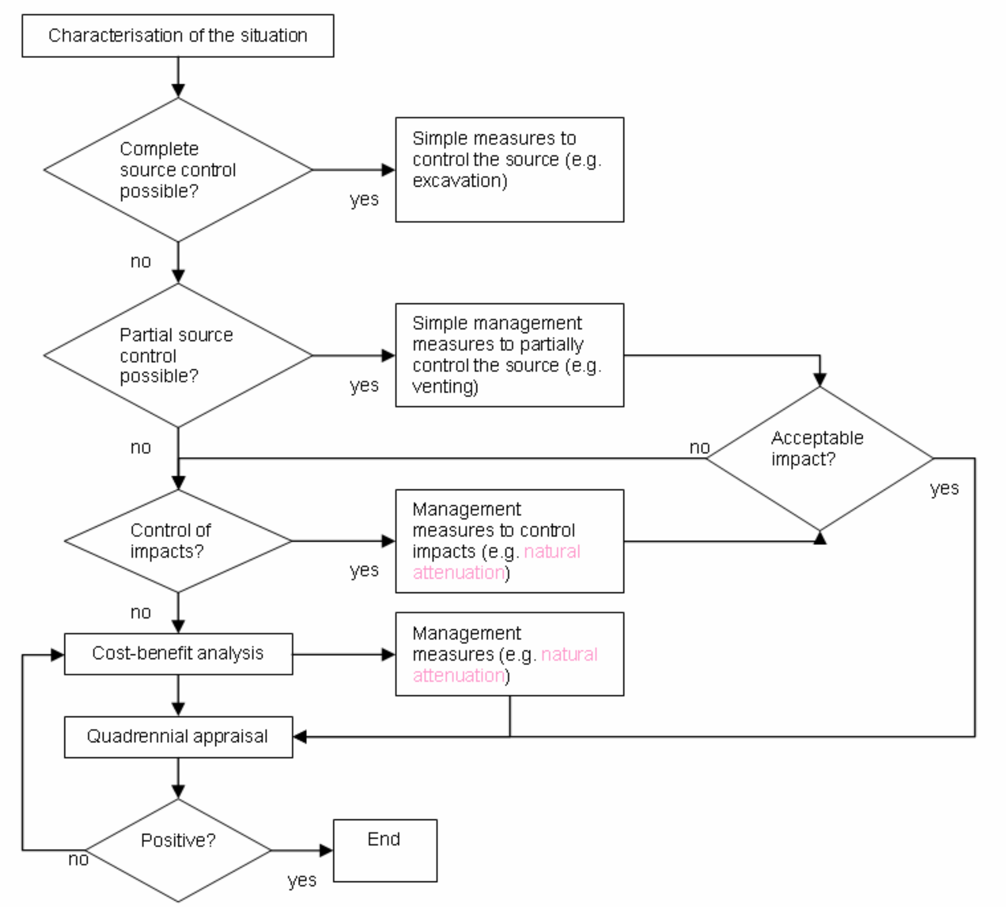

Figure 2. NA and the national methodology for the management of contaminated sites. (Y. Duclos, personal communication, 12 September 2009)

1.2. Status

1.2.1. Contaminated sites in France

According to data and statistics presented on the website of "Developpement Durable" (http://www.statistiques.developpement-durable.gouv.fr/), 4186 "sites et sols pollués" (polluted sites and soils) were known in France in July 2009. These polluted sites and soils are shown in orange dots on the chart of France in Figure 3. A "site pollué" is defined as a site that holds permanent risks for human health or the environment, resulting from current or past activities on this site. The contamination often has an industrial origin. Apart from the information available on the website of Developpement Durable, two databases provide information on contaminated sites in France. These inventories are BASOL (base de données des sites pollués) and BASIAS (inventaire d'anciens sites industriels et activités de service), containing former industrial and commercial sites without connotations on (possible) contamination.

[1] This project will be discussed in paragraph 2.2.2.

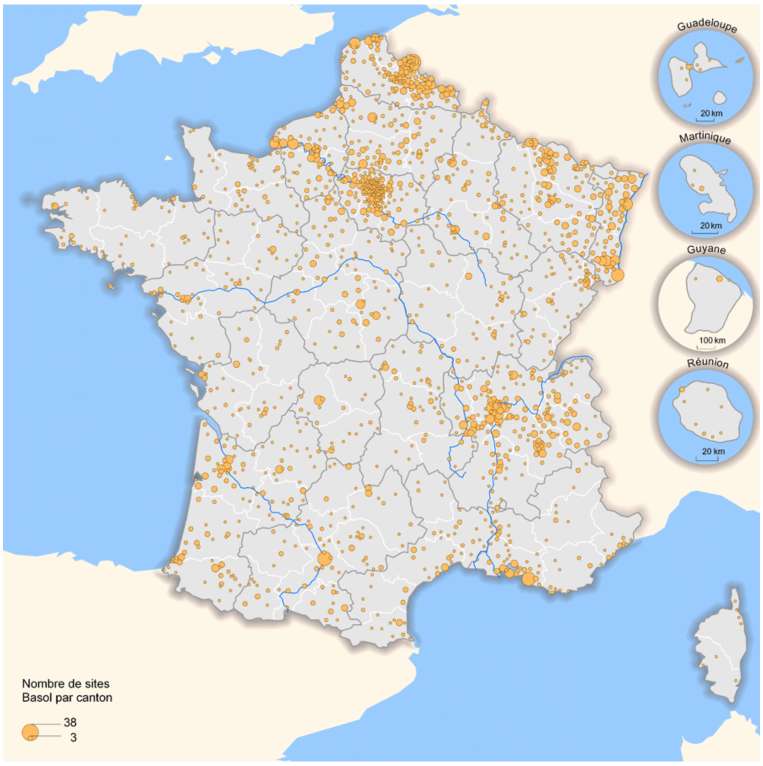

Figure 3. Chart of France: locations of contaminated sites in July 2009. (Website Developpement Durable)

1.2.2. Use of NA in France

In the BRGM (Bureau de Recherches Géologiques et Minières) report "Etat des connaissances sur l'atténuation naturelle des hydrocarbures" from January 2006 (RP-54183-FR), part of the objective was to gain insight into the extent to which natural attenuation processes are considered when making decisions for the remediation of contaminated sites in France. For this, an inventory of industrial sites (where natural attenuation processes are present) was drawn up. The RP-54183-FR report states that French administrations were aware of four sites identified as "having taken into account the natural attenuation processes in their contamination management". Secondly, by means of the BASOL database, another eleven sites were identified according to selection criteria such as 'surveillance of water in the underground', 'biodegradation' and 'attenuation'. Thirdly, a survey was sent out. The report states that "very little" contaminated sites take into account the NA-processes, but it doesn't state an exact number. (Saada, Nowak, Chartier & Coquereau, 2006)

Table 1. Overview of French sites from BRGM reports 54183 and 55981.

Report BRGM		***Contaminants***	***Management of the site***	***Source of information (if not confidential)***
RP-54183-FR	1.	CCl_4	NA processes ineffective	BASOL
	2.	COHV, BTEX, phenols, PAH, …		Confidential
	3.	BTEX, chlorinated ethenes	Study of NA	CNRSSP
RP-55891-FR	1.	BTEX	MNA – active NA	NICOLE, 2005
	2.	Chlorinated ethenes	Hydraulic confinement – MNA not favoured (risks)	NICOLE, 2005
	3.	Lindane	Cover + MNA	ADEME, 2004
	4.	Chlorinated ethenes	Study and follow-up of NA	ADEME, 2004
	5.	Chlorinated ethenes	Study of NA	ADEME - MACAOH, 2004
	6.	Chlorinated ethenes	Study of NA	ADEME - MACAOH, 2004
	7.	PAH	Study of NA	GISFI
	8.	Chlorinated ethenes	Site proposed for MNA – active NA	Study bureau
	9.	BTEX, PAH	Site proposed for MNA – active NA	Confidential

In the report BRGM/RP-55891-FR from December 2007, BRGM answers the request from the ministry MEEDDAT (Ministère de l'Ecologie, de l'Energie, du Développement Durable et de l'Aménagement du Territoire) to supply insight into the use of natural attenuation as a remediation technique in France. The inventory begun in 2006 and was completed through a survey that included large industrial organisations, research groups, study bureaus and providers that conduct studies and/or remediation of contaminated sites. The authors mention that during the collection of information, a confidentiality issue occurred. This resulted in the fact that the inventory cannot be used to evaluate the current situation for the application of natural attenuation, as it was intended, because only limited information was gathered from certain sites. The report states that as a result of the survey, nine sites were found where NA was considered or investigated as a remediation option. The three sites that were the subject of BRGM/RP-54183-FR are not included in this report. (Archambault & Saada, 2007)

An overview of the French sites as discussed in the BRGM reports of 2006 and 2007 is given in Table 1.

With regard to the overall use of (M)NA in France, the BRGM report number 58609 from 2010 states that the application of MNA in France is "currently rising", but it doesn't specify or give information as to how many times it actually has been chosen as a remediation technique. Furthermore, it is mentioned in the report that MNA is mostly applied for contaminations which are located in the saturated zone. (Colombano et al., 2010)

In 2008, ADEME (the French agency for environmental and energy management) initiated a survey to collect information on the used remediation techniques in France. The report mentions how many times a remediation technique was indicated as "being applied" by the contacted enterprises[2]. The results of the survey showed that MNA was applied zero times. (ADEME, 2011) This survey was repeated for the period 2010-2011. Results concerning MNA hadn't changed: the number of MNA-applications is still '0'. (Y. Duclos, personal communication, 30 September 2011)

[2] 60 Enterprises were contacted; however, only 28 responded to the inquiry.

2. Documents and projects

2.1. Existing Documents

This document listing includes regulatory outlines, existing methodologies (which will be discussed in further detail in paragraph 3), research reports concerning the use of NA in France and a report on cost-benefit analysis of remediation techniques.

2.1.1. Regulatory outline

Ministère Français. (1975). *Loi n°75-633 du 15 juillet 1975 Relative a l'élimin ation des déchets et a la récupération des matériaux*.

Ministère Français. (1976). *Loi n°76-663 du 19 juillet 1976 relative aux instal lations classées pour la protection de l'environnement*.

Ministère Français de l'Environnement. (1993). *Circulaire du 3/12/1993 relative à la "politique de réhabilitation et de traitement des sites et sols pollués*".

Ministère de l'Ecologie et du Développement Durable (2007). *Note du 8 février 2007 – Sites et sols pollués – Modalités de gestion et de réaménagement des sites pollués*. Consulted online in august 2011 http://www.developpement-durable.gouv.fr/Note-du-8-fevrier-2007-Sites-et.html

2.1.2. Guide for the application of MNA at waste deposit sites (2001)

As requested by the Ministère de l'Aménagement du Territoire et de l'Environnement (MATE), BRGM and the Pollutions, déchets & Environnement division (POLDEN) published a guidebook concerning the use of MNA at waste deposit sites in France. This guidebook will be discussed in paragraph 3.1.

Guyonnet, D., Jucker, C. & Méhu, J. (2001). *Guide pour l'implantation de stockages de déchets monoproduits – BRGM/RP-50417-FR*. Orleans : BRGM.

2.1.3. NA-processes for metals (2004)

The 2004 BRGM report discusses the NA of cadmium, lead, mercury and arsenic in the non-saturated zone. In particular the process of precipitation is discussed. The "recommendations guide" from 2004 (paragraph 3.2) is followed by a final report on this subject in 2005.

Blanc, P., Burnol, A. & Guyonnet, D. (2004). *Atténuation naturelle des métaux de la liste de substances prioritaires dans la zone non saturé – Guide de recommandations, rapport final BRGM/RP-53096-FR*. Orleans : BRGM.

Jourdan, B., Plantone, P., Lerouge, C. & Guyonnet, D. (2005). *Atténuation naturelle des métaux à l'aval de sites de stockage de déchets – synthèse bibliographique. Rapport final BRGM/RP-54417-FR.* Orleans : BRGM.

2.1.4. MACAOH program technical guides (2001 – 2006)

Three technical guides were published as a result of the MACAOH R&D program (Modelling, Attenuation, and Characterization in Aquifers of Organo Halogenated compounds, cfr. Paragraph 2.2.1) initiated by ADEME (l'Agence de l'environnement et de la maîtrise de l'énergie). The guidebooks concern the topics of modelling, characterization and natural attenuation. The guidebooks are the topic of paragraph 3.3.

Côme, J.M., Ropars, M., Kaskassian, S., Razakarisoa, O., Quintard, M., Schäfer, G. & Haeseler, F., & Mouton, C. (2008). MACAOH R&D Project (2001-2006). *Natural attenuation of chlorinated solvents in aquifers – Technical Guide: extended abstract*. France: ADEME.

ADEME (2006). Programme R&D MACAOH (2001-2006). Volum*e I : Caractérisation de la zone source et transfert de la pollution – expérimentations menées en laboratoire et sur le site contrôlé SCERES à Strasbourg.* France: ADEME.

ADEME (2006). Programme R&D MACAOH (2001-2006). Volume *II : Modélisaton du devenir des composés organo-chlorés aliphatiques dans les aquifères : situations à modéliser, analyse critique des outils de calcul disponibles, programme d'intercomparison.* France: ADEME.

Côme, J.M., Kaskassian, S., Ropars, M., Razakarisoa, O., Quintard, M., Schäfer, G. & Haeseler, F. (2006). Programme R&D MACAOH (2001-2006). *Caractérisation dans les aquifères d'une zone source constituée d'organo-chlorés aliphatiques – guide méthodologique.* France: ADEME.

Côme, J.M., Ropars, M., Kaskassian, S., Quintard, M., Vogel, T., Razakarisoa, O., Nex, F., Schäfer, G. & Haeseler, F. (2006). Programme R&D MACAOH (2001-2006). *Atténuation naturelle des composés organo-chlorés aliphatiques dans les aquifères – guide méthodologique.* France: ADEME.

Côme, J.M., Quintard, M., Schäfer, G., Mosé, R., Delaplace, P., Haeseler, F. & Mouton, C. (2006). Programme R&D MACAOH (2001-2006). *Modélisation du devenir des composés organo-chlorés aliphatiques dans les aquifères – guide méthodologique.* France: ADEME.

2.1.5. Guidebook for modelling: PAH (2005)

This guidebook was published by INERIS and offers a guide of 'good practices' for the acquisition of necessary information for the analytical or numeric modelling of poly aromatic hydrocarbons (PAH).

Rollin, C., Quiot, F., Denys, S. & Bureau, J (2005). *Rapport d'étude 66244-DESP-R01 : Hydrocarbures aromatiques polycycliques – guide méthodologique*. France : INERIS.

Rollin, C., Quiot, F., Denys, S. & Bureau, J (2005). *Rapport d'étude 66244-DESP-R02 : Hydrocarbures aromatiques polycycliques – données d'entrée des modèles analytiques ou numériques de transferts dans le sol et les eaux souterrains : synthèse bibliographique relative aux paramètres Kd (sorption) et $T_{1/2}$ (biodégradation)*. France : INERIS.

2.1.6. Guidebook for modelling: metallic trace elements (2006)

This guidebook was published by INERIS and offers a guide of 'good practices' for the acquisition of necessary information for the analytical or numeric modelling of metallic trace elements.

Rollin, C., Quiot, F., Badreddine, R., Bour, O. S. & Bureau, J (2005). *Rapport d'étude INERIS-DRC-06-66246/DESP-R01a : Eléments traces métalliques – guide méthodologique*. France : INERIS.

2.1.7. The use of NA in France

BRGM studied the knowledge concerning the use of NA in France, as well as its actual application for the remediation of contaminated sites. This resulted in two reports from 2006 and 2007.

Saada, A., Nowak, C., Chartier, R. & Coquereau, N. (2006). *Etat des connaissances sur l'atténuation naturelle des hydrocarbures. Rapport final – résultat de la phase 2. BRGM/RP-54183-FR*. Orleans : BRGM.

Archambault, A. & Saada, A. (2007). *Utilisation de l'atténuation naturelle dans la gestion des sites pollués en France. Rapport final – BRGM/RP-55891-FR*. Orleans : BRGM.

2.1.8. Cost-benefit analysis for remediation methods (2010)

In 2010, BRGM published a report on cost-benefit analyses of the existing remediation methods in France. This report is the result of a study requested by MEEDDAT. It describes several in-situ, ex-situ and on-site remediation methods, including MNA.

Colombano, S., Saada, A., Guerin, V., Bataillard, P., Bellenfant, G., Beranger, S., Hube, D., Blanc, C., Zornig, C. and Girardeau, I. (2010). *Quelles techniques pour quels traitements – analyse coûts-bénéfices. Rapport final BRGM/RP-58609-FR*. Orleans : BRGM.

2.1.9. ATTENA project 2007 – 2012: towards a protocol?

The ATTENA project (paragraph 2.2.2) coordinated by BRGM aims to publish a protocol for the application of NA in France. So far, a first draft of this protocol has been published in 2008. This first draft is discussed in paragraph 3.4.

Saada, A., Béranger, S., Blanchet, D., Benoit, Y., Rollin, C., Périé, F., Charbonnier, P., Delloye, T. & Zornig, C. (2008). *Ebauche de protocole en vue d'une étude de caractérisation de l'atténuation naturelle : projet ATTENA phase 1. Rapport BRGM-RP-56383-FR.* Orleans: BRGM.

Béranger, S., Rollin, C. & Saada, A. (2008).*Synthèse des données historiques collectées en vue d'une étude de caractérisation de l'atténuation naturelle : Projet ATTENA phase 1. Rapport BRGM-RP-55943-FR.* Orleans: BRGM.

Saada, A., Benoit, Y., Guérin, V., Blanchet, D., Béranger, S., Gourry, J.C. & Zornig, C. (2008). *Expérimentation de terrain en vue d'une étude de caractérisation de l'atténuation naturelle : projet ATTENA phase 1. Rapport BRGM-RP-56194-FR.* Orleans: BRGM.

2.2. Research projects

2.2.1. MACAOH program

MACAOH is a research and development project initiated by ADEME with the cooperation of a study bureau and three research organisations. Its focus lies on the behaviour of aliphatic organic chlorinated solvents in aquifers, including chloromethanes, chloroethanes and chloroethenes. Over a period of five years (from 2001 until 2006), the project conducted experiments at laboratory scale and at pilot scale (in a basin) at two industrial sites and modelling studies. (ADEME Guidebook for natural attenuation, 2006) The costs of this project were 1.900.000€. (Duclos, 2011) This program resulted in three guidelines concerning the topics of natural attenuation, modelling and characterisation (paragraph 3.3).

The industrial sites consisted of alluvial deposits of sand and stones (with strong biodegradation at the scene) at one site, alluvion of loam and clay (and weak biodegradation) on the other.

(ADEME Guidebook for natural attenuation, 2006)

2.2.2. ATTENA project

The ATTENA research project is coordinated by BRGM, with partners from both the public and industrial domain. The overall purpose of this project is to set up an operational protocol for the use of natural attenuation in the regulatory context in France. This requires the collection of results from both on site and laboratory measurements, to allow insight into relevant parameters for understanding natural attenuation processes and the behaviour of contaminants. The project includes the use of a model which integrates biological, geochemical and transport aspects of natural attenuation. This will allow to predict the evolution of contamination plumes. The costs of this project were 1.970.000€. The project resulted in a first draft protocol, as discussed in paragraph 3.4.

Three sites were available for the collection of information: the first site consists of a former quarry that has been exploited for its limestone (until 1949) and which became a waste dump site afterwards (1963-1973). The drainage water is contaminated with different types of organic chlorinated solvents. The second site is an old cokes factory (operational during the period 1921-1973) where the contamination consists of BTEX, PAH's and phenols. The third site is a depot of petroleum products (from 1972 till …) where the water has been impacted by light hydrocarbons and petroleum additives. However, only the second site was found suitable and will be maintained for further research concerning natural attenuation. The two other sites were rejected because of the failure to meet the requirement that the source is under control (1st site) and because NA had already occurred (3rd site). These two sites were then replaced by two others: a former treatment factory (alluvial deposit contaminated by chlorinated solvents) and a gas station contaminated by hydrocarbons (loam).

(Béranger, Rollin & Saada, 2008; Duclos, 2011; Saada, Benoit, Guérin, Blanchet, Béranger, Gourry & Zornig, 2008 ; V. Guérin, personal communication, 14 November 2011)

2.2.3. Project ANTELIX

This project started in 2009 and is expected to last 30 months. It studies the NA-processes present in groundwater contaminated by leachate from waste deposit sites. The project will include one test site. The project aim is to provide a methodology for the use of MNA for the management of former waste deposit sites. (Guyonnet & Chevrier, 2009; V. Guérin, personal communication, 14 November 2011)

3. Guidebooks and methodologies

3.1. Use of MNA at waste deposit sites

The guidebook was published by BRGM in 2001. It describes the characterisation of the source zone and an approach to demonstrate that MNA can be used for the remediation of waste deposit sites. The guidebook also includes recommendations to create a surveillance network to monitor the water quality.

3.1.1. Conceptual model

In order to evaluate the impact that NA will have on the contamination, it is necessary to have enough information on the situation. In other words: a conceptual model has to be created. For this, the following information is required:

- Behaviour of the source zone;
- Geometry of the site;
- Flow directions of the groundwater;
- Transfer parameters and their spatial differences;
- Limiting conditions;
- The initial state of the site;
- Measuring points.

This conceptual model can then be used to create a mathematical model in order to evaluate NA-processes.

3.1.2. Monitoring network

The guidebook offers several recommendations with relation to the implantation of measuring points. It mentions furthermore that a long term monitoring plan should be established.

(Guyonnet, Jucker & Méhu, 2001)

3.2. NA of metals

The 2004 BRGM guide of recommendations discusses a few characteristic parameters for the evaluation of NA-processes of metals:

- Chemical composition of fluids;
- pH;
- Oxidation-reduction potential;
- Partial pressure of gas in the fluid (particularly CO2).

Furthermore, the report discusses specific elements related to cadmium, lead, mercury and arsenic.

The 2005 follow-up document recommends not only to calculate the total concentration of metals but also to determine the form under which they occur. Furthermore, a necessary element of physical-chemical examinations appears to be the mineralogy of the soil.

(Blanc, Burnol & Guyonnet, 2004; Jourdan, Plantone, Lerouge & Guyonnet 2005)

3.3. MACAOH guidebooks

The research program MACAOH resulted in the publication of three guidebooks. The topics concerning organic chlorinated solvents are: the characterisation of a source zone, natural attenuation in aquifers and modelling in aquifers.

3.3.1. Characterization

Overall, the characterization of a contamination encompasses several stages, as presented in Figure 4:

1. Pre-diagnostic: document study and field investigations
2. Characterization of the source zone
   a. Determination of the composition of the contaminant: is there a mobile organic phase? This requires exploratory drilling in the soil or sampling through piezometers;
   b. Estimation of the volume of both the source zone and the organic phase (method 1) OR estimation of only the volume of the source zone (method 2).

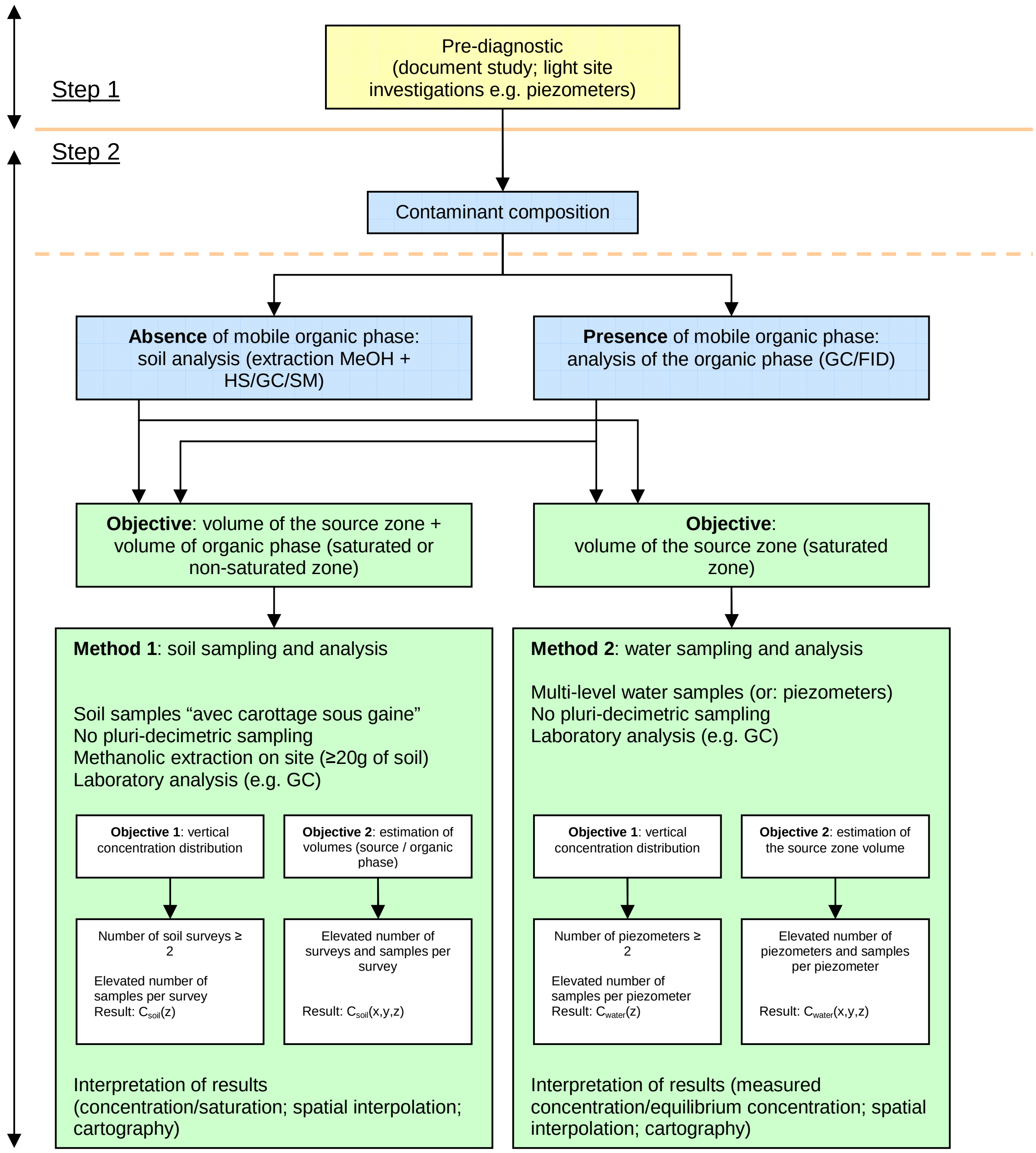

Figure 4. Characterisation of a source zone. (ADEME Guidebook for characterization, 2006, p.2)

(ADEME Guidebook for characterization, 2006)

3.3.2. Natural attenuation

The methodology for evaluating the suitability of monitored natural attenuation is made up of the following steps:

1. Data analysis to specify the spatial and temporal aspects of the contamination
2. Qualitative evaluation of the biodegradation mechanisms in the plumes consisting of dissolved and gaseous compounds
3. Quantitative evaluation of natural attenuation processes in the source zone and in the plumes
4. Prediction of the temporal evolution of the source zone (non aqueous phase liquid (NAPL) saturations), as well as prediction of concentrations in the dissolved and gaseous plumes

After the completion of these steps, it must be decided whether MNA is feasible as a remediation strategy. It can be implemented as a stand-alone technique or in combination with an 'active' technique. For this, cost and benefits have to be taken into account, as well as various possible constraints such as technical constraints, social impact, health and environmental protection, etc. The fifth step of the management of the contaminated site is then - when the decision has been made to accept MNA as a remediation technique – to include long-term monitoring of the situation until the remediation objectives are met.

(ADEME Guidebook for natural attenuation, 2006)

3.3.3. Modelling

This guidebook deals with several aspects of modelling: how to choose a calculation tool, how to perform the modelling process and how to choose between different available models.

- *Choosing a calculation tool*

The selection of a calculation tool starts from a schematic presentation of the contamination problem. In general, three steps lead to the selection:

1. Analysis of the 'functionalities' necessary for the physical model
    a. Functionalities concerning movement of the phases (e.g. single, two or three phases, immobile phases)
    b. Functionalities concerning transport of the compounds (including biodegradation, dissolution and volatilisation)
2. Choice of a physical model: eight possibilities (presented in Figure 5)
    a. Physical model 1: single phase (gas) transport in the non-saturated zone in the presence of two immobile phases (water and organic phase) while taking into account volatilisation.
    b. Physical model 2: single phase (water) drainage in the saturated zone associated with transport resulting from biodegradation processes.
    c. Physical model 3: single phase (water) drainage in the saturated zone in the presence of an immobile organic phase in the saturated zone and taking into account transport due to dissolution and biodegradation processes.
    d. Physical model 4: single phase water drainage, immobile organic phase which is located in the saturated and in the non-saturated zone, immobile gas phase in the non saturated zone and taking into account dissolution, biodegradation and volatilisation.
    e. Physical model 5: two phased (water + gas) drainage, immobile organic phase in the saturated and in the non-saturated zone and taking into account dissolution, biodegradation and volatilisation.

f. Physical model 6: “complete model” including three mobile phases and transport processes of dissolution, biodegradation and volatilisation.

g. Physical model 7: three mobile phases and transport processes of dissolution and volatilisation.

h. Physical model 8: three mobile phases.

3. Choice of a calculation tool

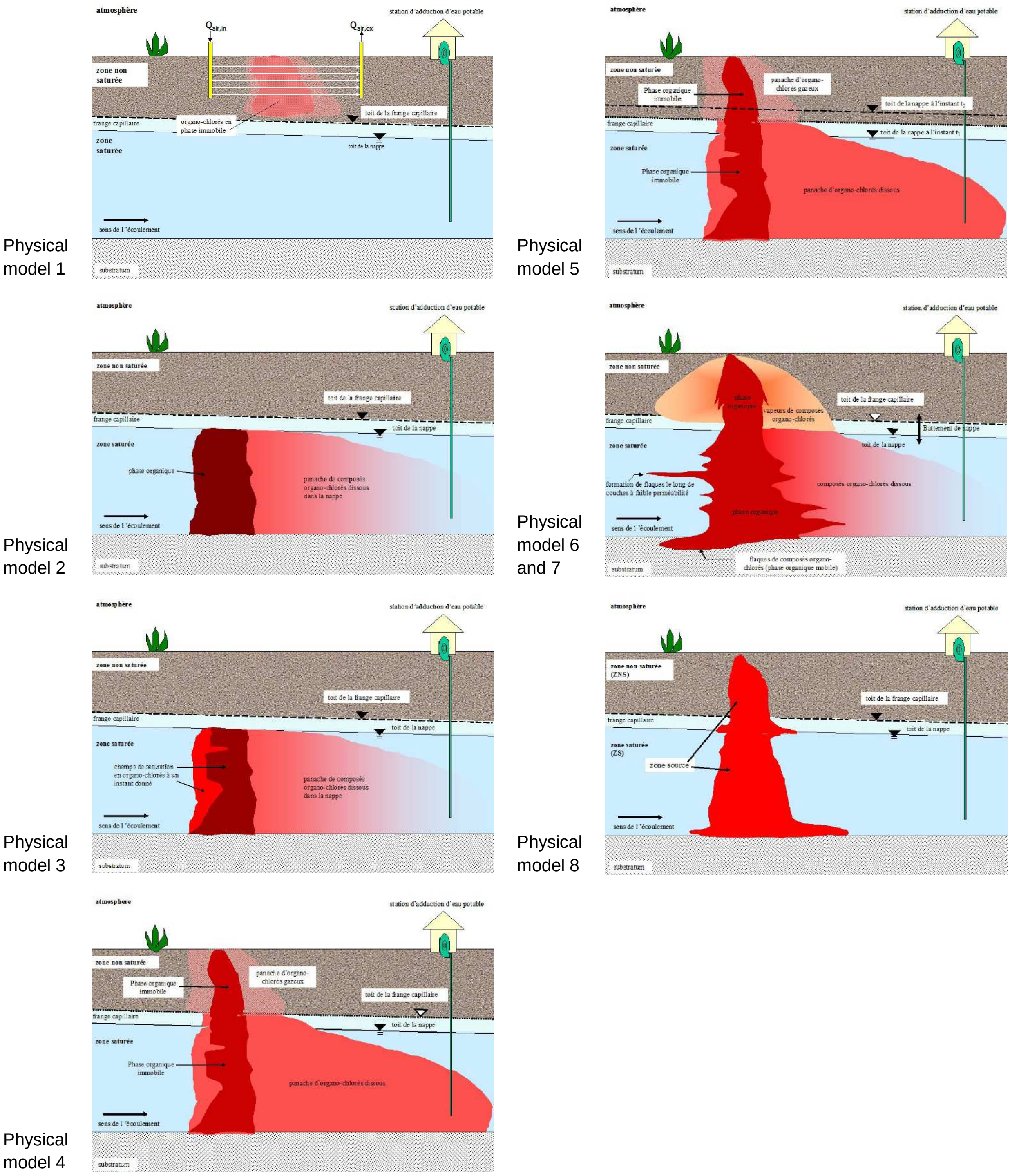

Figure 5. Modelling: eight physical models. (ADEME Guidebook for modelling, 2006, pp.46-53)

- *Modelling*

The modelling itself consists of several stages as well:

1. Presenting the problem in a schematic way: fixing the geometric format of the model; identification of NA processes and their mathematical representation; …
2. Construction of a numeric model (formulation of the mathematical code)
3. Implementation of the numeric model including necessary adjustments, sensitivity analysis and simulations

- *Realisation of modelling: how to choose between models?*

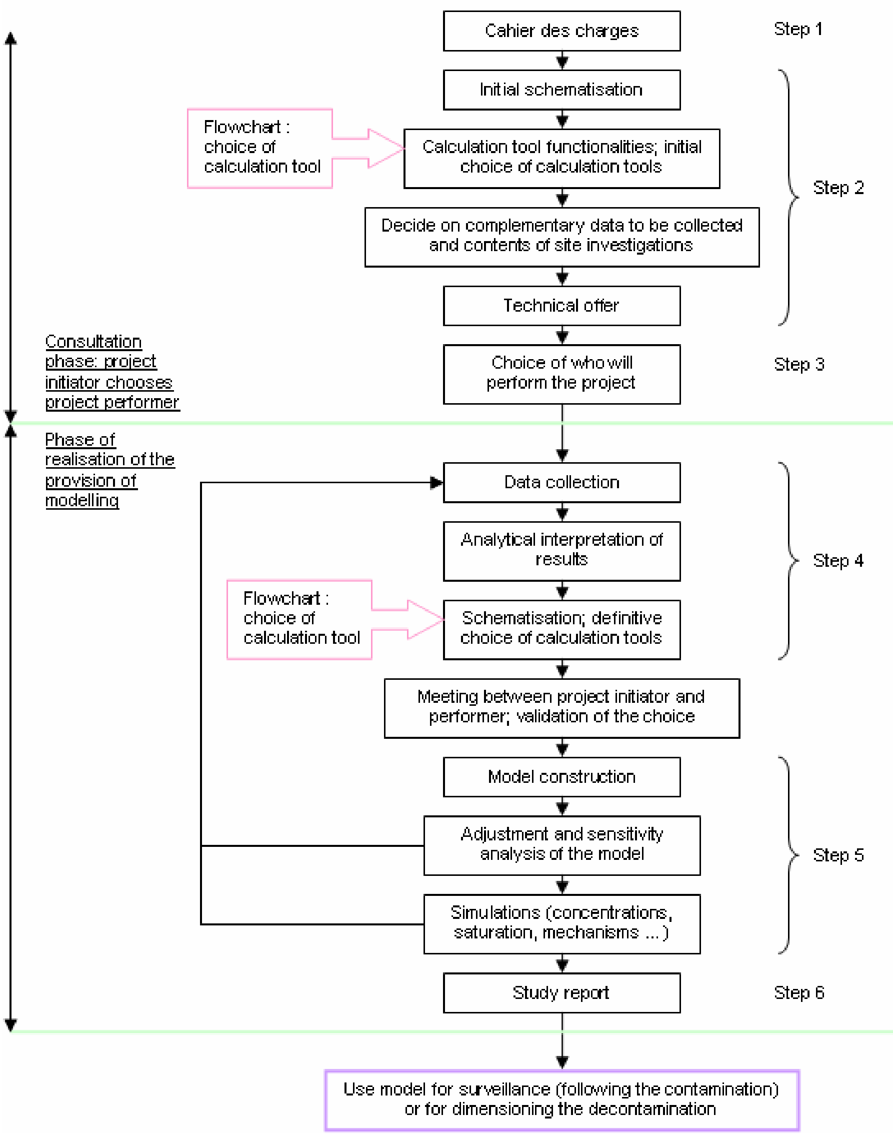

Figure 6. Flowchart for the decision making with regard to choosing the model. (ADEME Guidebook for modelling, 2006, p.65)

In order to assist project initiators in their choice of different available models, the guidebook offers a decision process (Figure 6). (ADEME Guidebook for modelling, 2006) This includes the following steps:

1. "Cahier des charges": which objectives have to be reached?
2. Initial schematisation and elaboration of technical offers from the consulted partners (concerning calculation tools)

3. The project initiator chooses which partner will perform the study
4. Collection and interpretation of information; development of a schematic interpretation of the problem and choice of calculation tools
5. Construction of the model based on the chosen calculation tools and implementation of the model
6. Study report including collected information; calculation tools; schedule and modelling efforts

3.4. Protocol for the use of natural attenuation in France

The ATTENA project drew up a first draft of a protocol, aiming to result in an operational protocol for the use of natural attenuation in the regulatory context in France. It is based on existing protocols of the United States of America and the European Union[3] and will be completed during the second phase of the project.

Five stages have been defined for the validation of natural attenuation as a remediation measure:

1. Characterisation of the situation
2. Exploration of qualitative elements
3. Exploration of quantitative elements
4. Interpretation of collected information
5. Establishment of a surveillance plan

After each phase, the continuation of the management of the site and the need for intervening measures has to be evaluated. This will allow comparison between the use of natural attenuation versus the use of other, more traditional methods for the management of contaminated sites.

(Saada, Béranger, Blanchet, Benoit, Rollin, Périé, Charbonnier, Delloye & Zornig, 2008)

At the moment, this first draft of the protocol is being modified in order to publish the operational protocol within a few months. In a draft version of the report, it is explained that the operational protocol will include four stages (in stead of the original five):

1. Characterisation of the situation
    a. Characterisation of the contamination (history, behaviour, …)
    b. Collection of information concerning the hydro-geological context; the site equipment (piezometers) and the possible receptors (e.g. water wells for private or public use)
    c. Pre-evaluation of the feasibility
2. Feasibility study: is NA applicable?
    a. Comparison between expected plume length and determined plume length
    b. Demonstration of favourable hydrogeochemical conditions for NA
    c. Additional tests to prove the existence of NA-processes (e.g. isotope analysis and microbiological studies)
3. Project study: quantification of the efficacy of NA
    a. Quantification of the source zone and the plume
    b. Quantification of NA-processes
    c. mass balance: decrease of contaminant mass

[3] American protocols used are those of the US EPA (1998; 1999; 2005 & 2007). European protocols are those from the UK (Caret et al., 2000); from Germany (HLUG, 2005) and from France (MACAOH program).

   d. Evolution of the contaminant concentrations (e.g. by using tracers)
   e. Application of analytic or numeric models
   f. Ratio between electron donors and acceptors
4. Establishment of a surveillance plan

Again, after each phase the continuation has to be evaluated in order to choose between MNA and other measures for remediation. The protocol will include a cost-benefit analysis to facilitate this choice.

(Y. Duclos, personal communication, 12 September 2011)

3.5. Techniques

3.5.1. Biodegradation of chlorinated solvents

A few methods to prove the existence of biodegradation of chlorinated solvents is described in a publication from INERIS. The document mentions:

(1) Determination of physical-chemical parameters;
   - Soil measurements of e.g. total organic carbon, Fe(III) and BTEX
   - Groundwater measurements of e.g. BTEX, dissolved oxygen, nitrates, …

(2) Isotope characterisation in the aquifer.

The results of these methods can then be incorporated into a model to predict the evolution of the contamination.

(Denys, 2004)

3.5.2. MACAOH program

During the MACAOH program, several techniques were used covering the different themes that are incorporated in the program (characterisation, natural attenuation and modelling). Laboratory analysis as well as field tests were performed. (ADEME Volume I, 2006)

- *Characterisation*

The characterisation methods include e.g. laboratory tests to determine (residual) saturations of the organic phase; cartography of concentrations in the water and of saturations of the organic phase and the “déconvolution” method (variant to the cartography of concentrations).

(1) Pre diagnostic techniques to characterise a source zone
   - Geoprobe/MIP: combination of a penetrometer and a membrane interface probe

(2) Operational techniques to characterise a source zone
   - “Integral investigation” method: analysis of water samples downstream of the source zone;
   - Penetrometer in combination with spectroscopy Raman;
   - Optical measures of refraction;
   - Dissoluble tracers: PITT method.

(3) Techniques to determine the composition of an organic phase
   - when there is a mobile organic phase: two possibilities for sampling (followed by laboratory analysis)

  - pump placed at the bottom of a piezometer, sampling at low flow capacity so that the organic phase won't mix with the water from the saturated zone
  - Discrete interval samplers
- when there is no mobile organic phase: soil sampling, extraction on site and laboratory analysis

(4) Techniques for the extraction of interstitial water at advancement

- Waterloo Ground water Profiler;
- Manual extractor of IMFS/IFARE;
- Geoprobe Groundwater Profiler.

(5) Techniques for multilevel water sampling

- Waterloo Multilevel System;
- Continuous Multichannel Tubing Multilevel System;
- Vegas sampler;
- Discrete level Multi-Layer Sampler;
- Passive Diffusion Bags.

(6) Instruments for the extraction of the organic phase

- Discrete interval samplers

(ADEME Guidebook for characterisation, 2006; ADEME Volume I, 2006)

- *Qualitative evaluation*

(1) Laboratory tests to describe the dissolution process of the TCE/PCE mixture;

(2) Laboratory tests to describe the adsorption process;

(3) Simulation of the migration and transfer of contaminants (SIMUSCOPP).

(ADEME Volume I, 2006)

- *Quantitative evaluation*

(1) Transfer of the contamination:

- In the three compartments of the aquifer;
- To the atmosphere: application of the Fick's law and "chambre à flux".

(2) Mass balance;

(3) Multi-sampling techniques to verify vertical distributions of concentrations in the water of the saturated zone: VEGAS; DMLS; PDB or the operational mode from IMFS/IFARE.

(ADEME Volume I, 2006)

- *Modelling*

Another technique applied during the MACAOH program, is the modelling of the natural attenuation of organic chlorinated solvents in order to be able to predict their future evolution in the aquifer. The modelling is based on numeric schemes. Different methods exist to resolve a parabolic or elliptic equation: DF (final differences), EF (final elements) and VF (final volumes). The latter is a variation of the DF-based schemes. There exist direct, semi-direct and iterative methods for calculation. (ADEME Guidebook for modelling, 2006)

3.5.3. ATTENA project

Piezometers were installed for measurements at the three sites. These were used to follow concentrations of contaminants and physicochemical parameters such as conductivity, pH, temperature, anions and cations.

Also as a part of the ATTENA project were several (in-situ) methods used to study industrial sites within the framework of natural attenuation.

(1) Geophysical methods

- Electrical resistivity tomography (« resistivity panels », Syscal Pro - Iris Instruments, OhmMapper - Geometrics);
- Induced polarisation (GDP32 II - Zonge);
- Self potential.

(2) Geochemical methods

- Diagraphy with an Idronaut IDRO302 probe to measure several parameters such as the oxidation-reduction potential; conductivity; temperature and dissolved oxygen;
- Diagraphy with a fluorimetric probe to measure polycyclic aromatic hydrocarbons;
- Passive sampling of groundwater (Exposmeter type lypophilic, SPMD).

(3) Gas-analysis

- Ecoprobe 5 to measure e.g. unsaturated hydrocarbons, COHV, methane, CO_2, …);
- Chromatography (Micro GC SRA P200).

(4) Microbiological and complementary laboratory analysis (of soil, water and gas)

(Béranger, Rollin & Saada, 2008 ; Saada, Benoit, Guérin, Blanchet, Béranger, Gourry & Zornig, 2008)

3.5.4. ANTELIX

This project aims to demonstrate NA in groundwater contaminated by leachate from waste deposit sites. (Guyonnet & Chevrier, 2009) In the first progress report from 2009, a few techniques are described:

(1) Chemical tracers

- Organic elements e.g. dissolved organic carbon;
- Wide range of elements or inorganic traces e.g. sulphate and cadmium;
- Volatile organic compounds and contaminant from pharmaceutical products.

(2) Isotope tracers

- Tracer for water (^{3}H, $^{18}0$; $^{86}Sr/^{87}Sr$);
- Tracers for NA-processes ($^{12}C/^{13}C$, ^{34}S, Zn, ^{7}Li).

(3) Analysis of the solid matrix to identify e.g. the anthropogenic soil fraction

4. Lessons from the application of NA

The 2010 BRGM report summarises some aspects related to the use of MNA, including information on advantages and disadvantages of the technique; costs and duration. (Colombano et al., 2010) Weak and strong points of NA are also presented in a publication from ADIT (2006).

- *Performance of MNA*

Furthermore, the 2010 BRGM report mentions briefly the performance of MNA as a remediation technique. It states that the decontamination efficiencies are very diverse, but nonetheless, outputs of more than 70% can be obtained under ideal circumstances. (Colombano et al., 2010)

- *Costs*

The 2010 BRGM report is the result of a cost-benefit study performed for several existing remediation techniques, including MNA. According to this report, the costs for MNA can vary between €12 – €65 per square metre treated water. (Colombano et al., 2010)

- *Advantages of MNA*

Some advantages of MNA as a remediation technique (Colombano et al., 2010) are:

- the significant results and the reliability of results when the optimal conditions are met;
- the cost advantage in comparison to other, active, techniques;
- the technique can be used as a supporting technique in combination with active measures;
- the technique can be used for a great number of contaminants;
- the minimal disturbance of the soil and low impacts on the environment when using MNA;
- it can be used for contaminations at great depth and under buildings.

Strong points of the MNA technique according to ADIT are economical (as mentioned: low costs); technological (avoids the excavation and transport of contaminated soil); sanitary (limited contact between operators and contaminants) and environmental (as mentioned: no waste production).

- *Disadvantages and limitations*

Some disadvantages and limitations (Colombano et al., 2010) are:

- the effectiveness is severely impacted by the dispersion of the contaminants and the permeability of the soil, both of which can be very heterogeneous;
- very variable results, depending on site-specific aspects;
- long treatment durations;
- social and political elements have to be taken into account as early as possible;
- transparency and informing stakeholders is of importance;
- because NA-processes are slow and thus require time to remediate contaminations, it is possible that some contaminants migrate before they are degraded;
- possibility of the production of toxic degradation products;
- MNA cannot be used for a number of organic compounds;
- the technique requires monitoring of the dispersion of contaminants and thus quality control measures;
- MNA cannot be used for high concentrations of metals or metalloids;
- the technique requires analytical follow-up and interpretations;

- the soil and groundwater cannot be used during treatment;
- soil where clay or organic matter is present generate higher adsorption levels of contaminants onto the soil matrix, which lowers the efficiency of the treatment;
- low temperatures decrease the efficiency.

Weak points of the method according to ADIT which are also mentioned by Colombano et al., are the need for long time monitoring and follow-up; the formation of toxic degradation products which can inhibit the microbiological community and the migration of contaminants when the NA-processes are slow. Furthermore, ADIT mentions the low efficiency when contaminant concentrations are high as a weakness of the NA concept.

5. Return on experience

The return on experience refers to the results from MNA for the remediation of contaminated soils in practice. However, seeing that there are no known cases of real-life application of MNA in France, there is also no return on experience.

6. Timeline

Figure 7 represents the timeline for France, as can be seen: research projects in France are still being performed; methodologies were published until 2006. The ATTENA protocol is expected for 2012-2013. Until now, no remediation projects exist where MNA is applied.

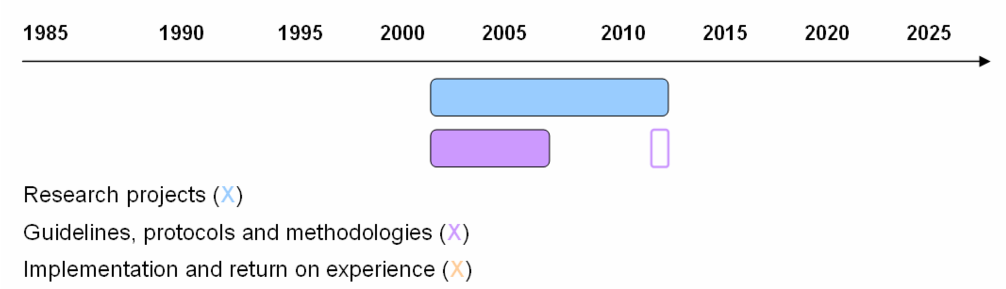

Figure 7. Timeline for France.

7. Additional references

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Websites

Developpement Durable http://www.statistiques.developpement-durable.gouv.fr/.

8. List of abbreviations

ADEME	l'Agence de l'environnement et de la maîtrise de l'énergie
BASOL	base de données des sites pollués (http://basol.ecologie.gouv.fr/)
BRGM	Bureau de Recherches Géologiques et Minières
BTEX	benzene, toluene, ethylbenzene and xylene (volatile organic compounds)
CNRSSP	Centre National de Recherche sur les Sites et Sols Pollues
COHV	composés organo halogénés volatils (chlorés)
ETBE	ethyl tertiary butyl ether
GISFI	Groupement à Intérêt Scientifique sur les Friches Industrielles
ICPE	Installations Classées pour le Protection de l'Environnement
INERIS	Institut National de l'EnviRonnement Industriel et des RisqueS
MATE	Ministère de l'Aménagement du Territoire et de l'Environnement
MEDD	Ministère de l'Ecologie et du Développement Durable
MEEDDAT	Ministère de l'Ecologie, de l'Energie, du Développement Durable et de l'Aménagement du Territoire
(M)NA	(monitored) natural attenuation
MTBE	methyl tertiary butyl ether
NAPL	non aqueous phase liquid
PAH	poly aromatic hydrocarbons
POLDEN	Pollutions, déchets & Environnement devision of INSAVALOR