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Monitored Natural Attenuation

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Preliminary Remarks

One of the responsibilities of the Scientific-technical Association for Environmental Remediation and Brownfield Redevelopment – Ingenieurtechnischer Verband Altlasten e.V. (ITVA) – as defined in its articles of association is the elaboration of regulations, recommendations and technical guidance on “contaminated sites”. The many different issues involved are analyzed in detail by the association’s technical committees.

The draft of this technical guidance was published by ITVA in December 2004 after four years of intensive analysis and discussion. The over 40, in part, very detailed positions expressed by numerous stakeholders including the German Environment Ministry, the Federal Environment Agency, state ministries, state agencies, BUND, members of the KORA priority funding project of the Federal Ministry for Education and Science, as well as many other experts, clearly highlights the need for a broad debate on this issue. A state agency in Germany commented appropriately that this was a “highly charged issue”. We would like to use this opportunity of thanking all those who supported the work of the ITVA, and for the many constructive ideas for additions and revisions.

Although the scientific base for understanding this issue is still in its infancy and we therefore still have some distance to go before arriving at state-of-the-art technology; and although it is currently not possible to clarify all of the regulatory and technical issues, we nevertheless decided to term this report “Technical Guidance” because it not only reflects the current status of the discussions undertaken by ITVA, but also acts as a useful guide to the elaboration of MNA concepts.

The technical guidance concerns the examination and possible incorporation of natural attenuation processes (NA processes) when searching for ways to deal with groundwater contamination caused by contaminated sites or harmful soil changes (hereinafter referred to together as “contaminated sites” for the sake of simplicity). Because not enough is currently known about NA processes in unsaturated zones, this topic is not looked at further here. The technical guidance is intended to support problem owners, regulators and their advisors, who are professionally involved in the management of contaminated sites. This technical guidance is also intended to raise awareness of the possibility of taking NA processes into consideration in the management of contaminated sites. Another aim is also to highlight that the use of NA processes is gaining increasing acceptance amongst regulators when dealing with contaminated sites, particularly where they comply with statutory objectives.

Ongoing research projects (e.g. the BMBF KORA priority funding project the joint project of the Bavarian science association “Sustainable remediation of contaminated sites taking into consideration natural attenuation processes”, and individual research projects in the various federal German states etc.) will deliver new information and findings when they have been concluded. These can then be incorporated in the revised version of this technical guidance or in other technical guidance still to be elaborated. Use of this technical guidance is completely unconditional. Legal claims arising from their application are excluded.

1 Summary

In addition to defining the terms natural attenuation (NA), monitored natural attenuation (MNA) and enhanced natural attenuation (ENA), the authors of this technical guidance also summarize the current status of the discussions in Germany, and use this as a basis for elaborating the preliminary legal classification.

After first discussing an MNA concept which describes the integrated and process-oriented means of assessing the behavior of contaminants in the saturated zone, subsequent chapters deal with the part NA processes play in the systematic management of contaminated sites.

A large part of this technical guidance is dedicated to presenting the MNA concept. This report summarizes and discusses the decision-making criteria important for the implementation of MNA. The implementation of these concepts in practice and the associated procedures then round off this technical guidance with a discussion of a multi-stage investigation programme which successively builds up a more detailed picture of the NA processes.

The proportionality study is particularly important for decisions on whether to proceed with the implementation of MNA, as well as for the approvals issued by the responsible government agencies. The proportionality study includes a comparison of different options and a cost-benefit analysis.

The comprehensive appendix to this technical guidance contains the known fundamentals and publications providing an overview on the principles for understanding and investigation of NA processes. In addition to explanations of the different processes involved (biodegradation, sorption, etc.), the appendix also includes a compilation of the influencing factors with comments on the currently available investigation methods. Technical guidance is also given on preparing predictions by modelling the behavior of the contaminants in the saturated zone. The technical guidance is rounded off by a chapter on the monitoring involved in MNA which is used to measure the changes in contaminants and to verify and validate the predictions.

Because a great deal of research activity is currently being undertaken on natural attenuation in Germany at a federal and a state level, the procedures presented in this technical guidance – and the discussion of the investigation methods currently available – merely reflect the current level of understanding within ITVA. It will therefore be necessary in a few years to revise this technical guidance to include the new findings and experience gained from ongoing research activity and practical implementation.

2 Introduction

2.1 Background and objectives

Research on natural attenuation (NA) has been conducted for over 20 years now in the United States of America. There are also comments in German references beginning in the 1950s that also refer to the phenomenon of natural attenuation. Ambitious research projects have now also been started in Germany (e.g. the BMBF priority funding project "KORA – Kontrollierter natürlicher Rückhalt und Abbau von Schadstoffen bei der Sanierung kontaminierter Grundwässer und Böden" (Retention and degradation processes to reduce contamination in groundwater and soil) [1]; the Bavarian research association project "Nachhaltige Altlastenbewältigung unter Einbeziehung des natürlichen Reinigungsvermögens" (Sustainable remediation of contaminated sites by incorporating natural attenuation) [2]; research activities in Baden-Württemberg and other federal German states investigating the subsurface processes involved. Consideration is already given in many cases here to incorporating natural attenuation processes in the remediation of contaminated sites and pollution incidents. Making allowance for NA processes is currently the subject of intense discussions in Germany and has led to a large increase in the number of inquiries submitted to the regulators.

The current discussion on natural attenuation and the absence of appropriate regulations – particularly with respect to the identification and evaluation of NA processes, and acceptance in the management of contaminated sites – underlines the urgent need to deal with this issue by issuing technical guidance, and the need to provide the urgently needed support. A more detailed understanding of the processes involved and the implementation of systematic procedures is required to break down the existing barriers to their implementation.

This ITVA Technical Guidance on Monitored Natural Attenuation (MNA) is primarily aimed at the problem owners, the regulators and their advisors responsible for managing and dealing with contaminated sites and pollution incidents. The intention of this technical guidance is to make a valuable contribution to the implementation of NA processes in dealing with contaminated sites, help break down existing barriers standing in the way of their implementation, and provide support for the implementation of NA processes as alternative or complementary method to conventional active remediation measures.

2.2 Obstacles to the acceptance of NA processes

NA processes are only rarely taken into consideration in the remediation of contaminated sites primarily because of problems in understanding and acceptance. The main reasons and problems include:

- Equivocal definitions of natural attenuation, monitored natural attenuation and enhanced natural attenuation (ENA)
- Differences in categorizing (M)NA as a process, site factor, investigation measure, remediation measure, protection or restriction measure[1]
- Differences in interpreting the legal position particularly with respect to the Federal Soil Protection Act (BBodSchG) [3], Federal Water Act [4] and EC Water Framework Directive [5]. Other problems include the future liability of the problem owner if the specified remediation objectives are not achieved (“residual risk” if contingency measures are required),
- The scientific state-of-the-art on (M)NA in published works is not yet reflected in the state of technological development, which largely prevents its use in the public sector
- The absence of benchmarks for evaluating costs and benefits
- Uncertainties concerning the implementation of (M)NA may be an obstacle to after-use decisions and authorizations.

2.3 Technical guidance content

In addition to the discussion of the legal framework in Germany and definition of terms, information is also provided on the basis of the various stages of contaminated site and pollution incident evaluation, and on the potential acceptance and incorporation of NA processes, including the recommended procedures.

The comprehensive appendices discuss in detail the subsurface processes occurring on the basis of the current level of understanding, provide information on the investigation methods, and comment on the suitability of these methods. Additional chapters provide detailed help on the options available for predicting the behavior of the contaminants over time, and the monitoring options.

3 Definitions

3.1 Natural attenuation (NA)

In this technical guidance, the term natural attenuation (NA), as adapted from the US EPA OSWER Directive 9200.4-17P [6], is defined as the different physical, chemical and biological processes taking place without any human intervention and which under certain conditions can lead to a reduction in the mass, toxicity, mobility, volume and concentration of contaminants in soil and groundwater. These processes include:

- Biodegradation (mineralization, humification, co-metabolic breakdown)
- Precipitation
- Physico-chemical breakdown (e.g. radioactive decay, iron oxidation)
- Sorption (e.g. adsorption, absorption)
- Dilution (dispersion, diffusion)
- Volatilization (evaporation, sublimation).

These NA processes have various effects including the immobilization, destruction or transformation of contaminants. The importance of the non-destructive processes (sorption, dilution, volatilization) in the acceptance of MNA is discussed in Chapter 6.3.2.

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[1] protection or restriction measure = institutional control

3.2 Monitored natural attenuation (MNA)

Monitored natural attenuation (MNA) is the monitoring of NA processes by time-series monitoring and the verification of predictions. In our opinion, the investigation of NA processes and assessment of the future contaminant behavior precedes monitoring and is therefore not part of MNA.

3.3 Enhanced natural attenuation (ENA)

Enhanced natural attenuation (ENA) is the stimulation or initiation of natural processes by supplying substances to enhance natural reactions in the subsoil environment. ENA is an *in-situ* remediation measure that enhances the NA processes occurring in the subsurface.

In-situ remediation measures are understood in accordance with the Contaminated Site ABC dated 1992 (page 34 in [7]) as those methods used to remediate environmentally hazardous substances already present in the subsurface without physically, chemically or biologically moving the soil or the ground with the aim of removing the contaminants from the soil, converting them into innoxious substances or preventing their spread.

4 Legal framework

4.1 Federal Soil Protection Act

4.1.1 Discussion of the various legal interpretations

An intense and heated debate has continued for several years in Germany on the engineering, scientific, regulatory and environmental legislation positions on the specific classification of NA, MNA and ENA within the definitions laid down in the German Federal Soil Protection Act (Bundes-Bodenschutzgesetz - BBodSchG) which came into force on 01.03.1999 – particularly because the previous public discussions have not always differentiated rigorously enough between NA and MNA. The details discussed in Chapter 4 highlight the crucial importance of differentiation for proper classification.

Some of the legal positions published to date are discussed in the following.

- Some are of the opinion that NA and MNA as remediation measures in the sense of Section 2 Para. 7 Number 1 BBodSchG must actually be classified as decontamination measures [8, 9, 10, 11, 12]. The advocates of this interpretation justify their position by saying that there is no difference whether natural contaminant breakdown processes are harnessed or whether active remediation measures are implemented to remove or reduce the contamination. Another argument put forward is that measures in the sense of MNA are not so much concerned with the technical or scientific processes involved but rather the regulatory framework [13].

- Others are of the opinion that NA and MNA should be classified as institutional controls in the sense of Section 2 Para. 8 BBodSchG [14, 34], which pursuant to Section 4 Para. 3 Sentence 3 BBodSchG can be implemented as an alternative by the problem owner, if active remediation measures are not practical or considered unreasonable.
- Criticism of the former interpretation is primarily based on the view that remediation or institutional controls in the sense of Section 2 Para. 7 and Para. 8 BBodSchG are always associated with active human involvement or a technical method. NA is exclusively understood as involving natural subsurface processes that take place even without any human involvement [14, 15, 16, 17, 18]. MNA should therefore not be classified as remediation. Although it is true that measures (investigations, predictions, evaluations) are undertaken to demonstrate the natural remediation effects, monitoring cannot be seen as a technical remediation method having an influence on the remediation success, but merely demonstrates that NA processes are actually occurring. MNA should therefore be classified in terms of Soil Protection Law as an investigation measure pursuant to Section 15 Para. 2 BBodSchG [19].
- Other opinions state that natural attenuation processes occurring in the subsurface should be taken into consideration at the various phases of contaminated site management [17]. If monitoring is conducted to observe and control the processes, MNA can also be seen as a part of the risk assessment process [14].

4.1.2 Position of the authors on the legal classification and significance of NA, MNA and ENA

NA, MNA and ENA are not defined in the current federal or state soil protection or water acts. They are also not defined in the subordinate regulations. It should therefore come as no surprise that problem owners, consultants, and soil protection and water regulators face considerable uncertainty with regard to the legal classification and implementation of NA and MNA.

4.1.2.1 NA as a site parameter

NA is the total of the physical, chemical and biological processes taking place in the subsurface which, without human intervention, can reduce the mass, toxicity, mobility, volume and concentration of soil and groundwater contaminants. It is not possible to classify these natural processes as remediation measures in the sense of the definitions in Chapter 3 because the remediation of contaminated sites is understood as the implementation of regulatory and technical measures [20]. The legislative also appears to take this view because the term remediation is defined in Section 2 Para. 3 BBodSchG as a measure, and because decontamination measures are further defined pursuant to Section 5 Para. 1 Sentence 1 BBodSchV as technically implementable measures whose suitability for the environmentally compatible removal or reduction of contaminants has been proven in practice.

NA is neither a technical method nor a regulatory measure. The authors of this technical guidance are therefore of the opinion that NA can neither be considered as remediation pursuant to Section 2 Para. 3 BBodSchG nor as a protection or restriction measure pursuant to Section 2 Para. 8 BBodSchG. As a natural subsurface process, NA must be considered as a site parameter which must be taken into consideration at every stage of contaminated site management (investigation, risk assessment, remedial investigation/feasibility study, remediation, after-care) in just the same way as the other site parameters and conditions [35].

4.1.2.2 MNA as a measure

MNA is by definition the monitoring of NA processes, and provides documentary evidence in the form of measurement data to answer the question of whether the predicted retention and breakdown of contaminants actually occurs. The MNA concept (cf. Chapter 5) comprises investigations which can be taken into consideration as part of: detailed investigation, risk assessment, determining the remediation measures and objectives, remediation planning, remediation plan elaboration design, and after-care. An MNA concept can therefore be seen as a package of measures usually subject to regulatory control. Unlike NA processes, an MNA concept involves technical and regulatory measures. Against the background of the ongoing legal debate on this subject, the authors of this technical guidance leave open the question of whether MNA can be legally interpreted as a remediation, institutional controls, or a monitoring measure.

Whichever way MNA is classified, implementation critically depends on elaborating decision-making criteria (cf. Chapter 5.3.2) to enable NA processes to be taken into consideration as part of an MNA concept.

4.1.2.3 ENA as a remediation measure requiring water utilization approval

ENA involves active intervention in the processes taking place naturally underground with the aim of stabilizing contamination within soil or enhancing the natural attenuation processes. ENA will be classified in this context as a remediation measure pursuant to Section 2 Para. 3 BBodSchG.

Because the initiation and stimulation of NA usually involves the artificial emplacement of substances within the saturated zone, it is classified as a controlled water utilization measure. It therefore requires statutory authorization pursuant to Section 7 Federal Water Act

(WHG) because Section 3 Para. 1 Number 5 WHG regulates the application of substances to groundwater as utilization of water in the sense of WHG.

A situation is also defined as controlled water utilization if substances are added to the unsaturated zone and when the substance is capable (in the sense of Section 3 Para. 2 Number 2 WHG) of causing permanent or not inconsiderable harmful changes to the physical, chemical or biological properties of the water. This has to be verified on a case-by-case basis.

4.2 Water legislation

In the past, NA processes have primarily been taken into consideration in dealing with groundwater contamination, i.e. when dealing with contaminant plumes in groundwater. This raises the question of whether this complies with the current water legislation or whether remediation measures have to be carried out in all cases of groundwater contamination.

The first point to note is that unlike the Federal Soil Protection Act, the water legislation neither defines nor even refers to remediation, remediation obligations, or institutional controls measures. However, these terms are defined in the soil protection legislation which means that when treating contaminated groundwater caused by harmful soil changes or contaminated sites, the question of remediation of groundwater contamination is covered by the Soil Protection Act pursuant to Section 4 Para. 3 BBodSchG. There can therefore only be one standardized remediation term independent of whether the remediation measure involves the unsaturated or the saturated zone.

Although Section 4 Para. 4 Sentence 3 BBodSchG does refer to the water legislation with respect to the specifications which need to be fulfilled when remediating groundwater pollution caused by a contaminated site, neither WHG nor the state water laws define specific requirements or statutory and therefore obligatory limits. The trigger values laid down for groundwater in BBodSchG only concern leachate trigger values – these should not be confused with groundwater trigger values [21]. Even though the “insignificance thresholds” laid down by the Working Group on Water issues (Bund/Länder-Arbeitsgemeinschaft Wasser - LAWA)[2] play an increasingly important role in enforcement, it is still important to remember

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[2] The LAWA is the German Working Group on water issues of the Federal States and the Federal Government represented by the Federal Environment Ministry. The Working Group on water issues (LAWA) was set up in 1956 as an amalgamation of the ministries of the States of the Federal Republic of Germany responsible for water management and water legislation.

that in a legal sense, these are neither general mandatory limits, nor remediation or intervention limits, because the insignificance thresholds[3] are not legally defined.

The German water legislation traditionally concentrates on preventative water protection and gives the water regulators a great deal of regulatory discretion [21]. For instance, if groundwater has been contaminated or groundwater is at risk, it is up to the regulator to make further decisions. This concerns decisions to implement measures (”Entschließungsermessen”) as well as determining the remediation objectives and the choice of specific measures (”Auswahlermessen”).

The EC Water Framework Directive 2000/60/EC dated 23.10.2000, and the Groundwater Directive still to be adopted, pursue a very broad management approach with respect to river basin units and groundwater bodies. Groundwater protection places slightly more emphasis on the idea of preventative groundwater protection and specifies phased management objectives for the water regulators. Section 4 Para. 1 lit.b) EC Water Framework Directive (converted to German water legislation in 2002 by amending Section 33 a) Federal Water Act) obliges EU member countries and thus the national water regulators to e.g. comply with the following environmental objectives with respect to groundwater:

- Implement measures to prevent any deterioration in the condition of groundwater bodies,
- To protect, improve and remediate groundwater bodies with the objective of achieving good quantitative and chemical groundwater conditions by 2015 or at the latest by 2027,
- Reversing all significant trends revealing an increase in the concentration of contaminants, and to reduce the contamination of groundwater step-by-step.

Because the EC Water Framework Directive pursues a broad management approach, the aforementioned objectives apply to groundwater bodies and do not apply directly to “point sources”, i.e. contaminated sites. It is not currently possible to assess whether and which direct consequences may arise from further specifying the management objectives in the programme of measures and management plans to be elaborated for each groundwater body by 2009.

In conclusion, neither the German water legislation nor the provisions laid down in the EC Water Framework Directive exclude the incorporation of NA processes.

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[3] LAWA 2004: Determination of insignificance thresholds for groundwater

5 The MNA concept

An MNA concept is defined in this technical guidance as those measures required at each stage of the site investigation, from planning and achieving the agreed objectives, which are necessary to take into consideration NA.

The concept, aimed at describing in as much detail as possible the transport behavior and contaminant attenuating processes, can be subdivided as follows:

MNA concept

Analysis, evaluation and assessment on the basis of the decision-making criteria (phase 1)

- Documenting the existing situation (step 1)
- Analyzing the processes (step 2)
    - Qualitatively (step 2a)
    - Quantitatively (step 2b)
- Estimate/prediction (step 3)
- Proportionality study (step 4)

MNA plan (phase 2)

- Summarized phase 1 documentation
- Determine the monitoring programme
- Describe the contingency criteria and scenarios

MNA (phase 3)

- Continuous compliance monitoring to monitor the estimated/predicted future contaminant behavior (MNA)

After-care (phase 4)

- Monitoring after achieving the objectives.

The MNA plan should be elaborated on the basis of the decision-making criteria after analysis, assessment and evaluation of NA processes. The MNA plan can also be part of a remediation plan by incorporating active remediation measures. Legal certainty on the part of the problem owner and the regulators can be achieved by regulating the procedures to be conducted at the site in the form e.g. of a public law agreement. The monitoring of the estimate/prediction is then carried out (MNA). After-care begins when the agreed objectives have been achieved. This after-care is carried out in an analogous way to the after-care following active remediation measures.

5.1 Taking natural attenuation processes into consideration in pre-emptive groundwater protection, soil protection and contaminated site management

The following discussions are intended to show whether and in what way NA processes can or should be taken into consideration at the various stages of contaminated site management (cf. Figure 5.4).

Contaminated site management is normally divided up in accordance with BBodSchG/ BBodSchV[4] into the following steps, although each step can merge into the next step or jump a step:

- Preliminary investigation
- Detailed investigation
- Risk assessment
- Remedial investigation
- Remediation plan
- Remediation implementation / execution phase
- After-care.

5.1.1 Preliminary Investigation

As soon as the regulator suspects the existence of harmful soil changes or the presence of a contaminated site, it is obliged to execute suitable measures to determine the situation pursuant to Section 9 Para. 1 BBodSchG. This includes investigations looking in particular at the type and concentration of the contaminants and the possibility of their spreading in the environment. These investigations are termed preliminary investigations in Section 3 Para. 3 BBodSchV alongside Art. 1.1 of Appendix 1 BBodSchV. The law regulates that the preliminary investigation is paid for by the regulator – as also deducible in reverse from Section 24 Para. 1 Sentence 1 BBodSchG.

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[4] Federal Soil Protection and Contaminated Sites Ordinance
(BBodSchV), dated 12 July 1999

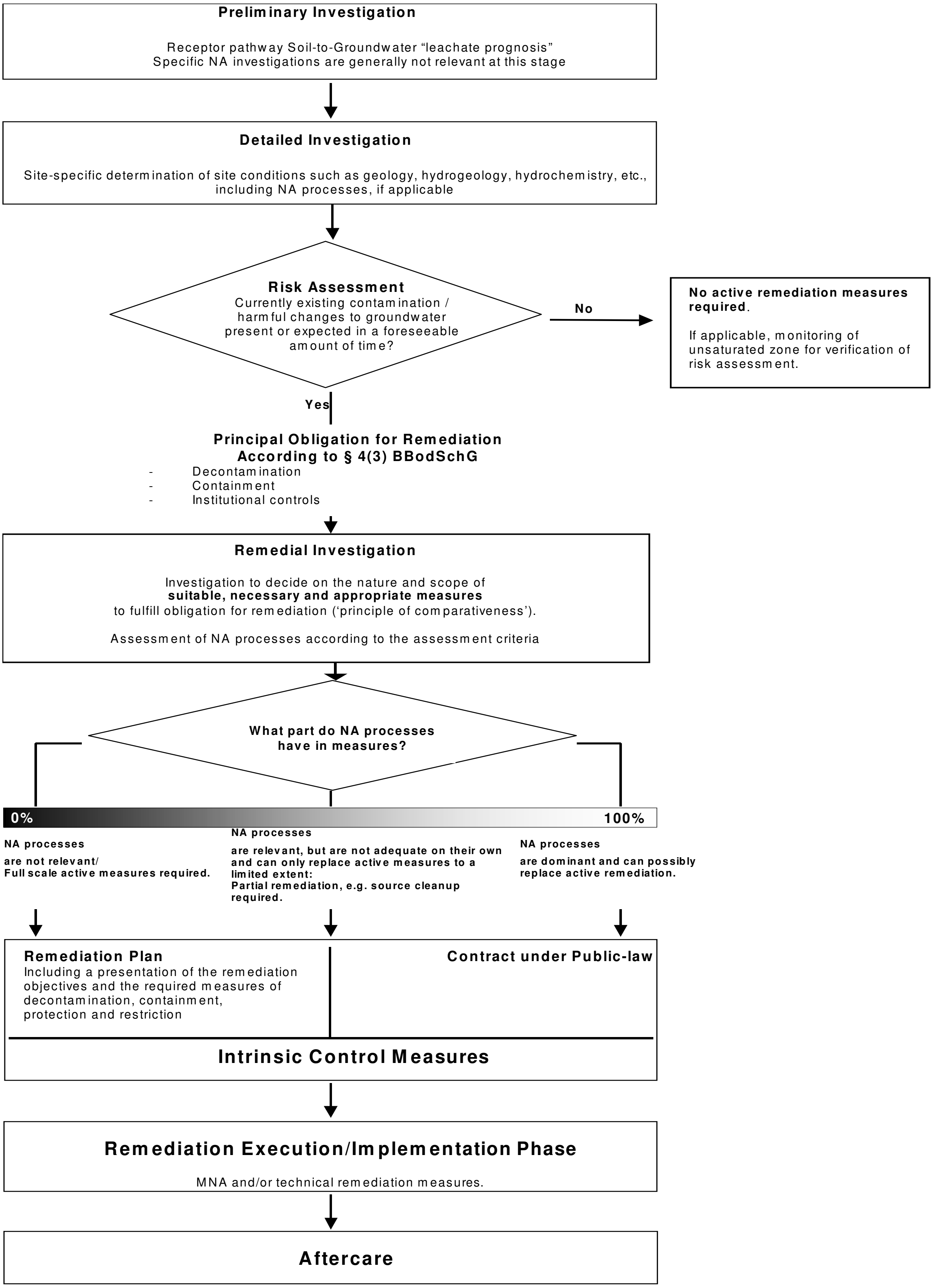

Fig. 5-1: Incorporation of natural attenuation processes in contaminated site management

The preliminary investigation is conducted to assess the situation further and to carry out site investigations to assess whether the initial suspicion is unfounded or whether the suspicion of the presence of a contaminated site is confirmed to the extent that a subsequent detailed investigation is required. Because the investigations necessary to confirm the efficiency of NA processes usually require a great deal of time, and considerable expense, it is not considered appropriate to start at the preliminary investigation stage with investigations of the presence of potential NA processes.

5.1.2 Detailed Investigation

The detailed investigation following on from the preliminary investigation is discussed in Section 9 Para. 2 BBodSchG and defined in more detail in Section 3 Para. 3 BBodSchV together with Art. 1.2 of Appendix 1. A detailed investigation is primarily aimed at ascertaining whether the concentration of contaminants represents a risk to receptors such as individuals or the public at large, as well as e.g. the groundwater. The cost distribution is regulated by Section 24 Para. 1 Sentence 1 BBodSchG.

Because detailed information on the nature and extent of the contamination and any potential risks should already be acquired during the detailed investigation stage, it is considered prudent at this stage of the contaminated site evaluation to include an assessment of the NA potential within the scope of the investigation in suitable cases. Guidance is also provided here by Appendix 1 BBodSchV. Art. 3.3 which describes in more detail the procedure for estimating the immissions entering the groundwater from a suspected contaminated site. Art. 3.3 also states that the NA processes in particular should also be taken into consideration in the unsaturated (vadose) zone. The crucial aspects here include the mobility and the degradability of the contaminants identified in the unsaturated zone. It therefore makes sense for the investigations to also include the NA processes when a relevant NA potential is considered to be present.

5.1.3 Risk Assessment

The regulator assesses on the basis of the information from the preliminary investigation and the detailed investigation whether there is a risk to individuals or the general public, and what these risks are. This risk assessment step is the sole responsibility of the regulators, who usually base their evaluation on investigation reports and expert reports. The risk assessment must also include an evaluation of any potential risks to conservation resources at the site such as groundwater. It is generally understood that a risk is a concrete situation which, if allowed to progress unchecked, will in all probability cause damage to a receptor, e.g. to humans or to groundwater. In terms of the time scale involved, it is sufficient that damage is probable at some time, possibly after several years or several decades. The time period should not, however, be too long. Determination of the relevant length of time is defined on a case-by-case basis.

If the preliminary investigation or the detailed investigation reveal that the relevant values defined in Appendix 2 BBodSchV are not exceeded, the suspicion of the existence of a contaminated site or harmful soil changes are ruled out in accordance with Section 4 Para. 2 BBodSchV. On the other hand, exceeding a certain value alone does not necessarily mean that the case involves a contaminated site or harmful soil changes. The suspicion that a hazard exists still needs to be clarified by more detailed investigations. If the BBodSchV appendix does not define any limits for a particular contaminant at a specific site, use must be made of the methods and benchmarks defined in Section 4 Para. 5 BBodSchV to derive the limits. These are published for the soil-human receptor pathway and the soil-plant receptor pathway in Federal Gazette number 161a dated 28/08/1999. Reference is made to e.g. [36] with respect to the soil-groundwater receptor pathway.

If the investigations reveal that there is a definite risk or even damage, the problem owner is obliged pursuant to Section 4 Para. 3 and Para. 6 BBodSchG to remediate the contaminated site and the associated groundwater contamination, and to permanently remove all risks, significant disadvantages and significant nuisance for individuals or the public at large. The regulator can issue a notice for the necessary measures to be conducted in accordance with Section 10 Para. 1 BBodSchG. This means that the authority has the discretion to decide whether and in what form the problem owner exercises its remediation obligations.

If relevant information exists, it is prudent to take NA processes into consideration at this stage in the management of a contaminated site. Generally, however, the NA potential is only evaluated as part of a remediation study when comparing alternatives with active remediation methods.

5.1.4 Remedial Investigation

The regulators have to bear in mind the generally applicable proportionality principle when analyzing the need for action, and if so, which risk mitigation measures are needed. The principle of proportionality means that the stipulated measures must be suitable, necessary and appropriate. Whether and when this is the case must be looked at in more detail as part of the remedial investigation conducted pursuant to Section 13 BBodSchG. Appendix 3 of BBodSchV also refers to the need to include a proportionality assessment in the remediation investigation: Art. 1 in Appendix 3 states that the remediation investigations of contaminated sites must determine suitable, necessary and appropriate measures to fulfill the remediation obligations.

In addition to the investigation steps stipulated in Art. 1 Appendix 3 BBodSchV, the remediation investigation also looks in more detail at the following, particularly with reference to NA processes:

- Which remediation measures are suitable to avert risks and how much time and expense will be involved?
- What is the relevance of NA processes, and how much time is required to reduce values below the risk threshold over which specific area?
- Is it possible to accelerate the NA processes by artificial stimulation? How much expense over what period of time is required for ENA?
- Are the NA processes adequate to replace an active remediation measure or to complement an active remediation measure?
- What is the estimated expense and time required for monitoring?

5.1.5 Remediation plan: Public-law agreement

When conclusions have been reached on how the contaminants will behave in the subsurface (assessment/prediction), as well as the type of NA processes if any which can be taken into consideration, the nature of the monitoring which should be carried out, and which additional remediation measures are required, the next recommended step is the elaboration of a remediation plan detailing all of these findings and conclusions. An application should then be made to the regulator pursuant to Section 13 Para. 6 BBodSchG to have the remediation plan officially authorized. Even though the remediation plan is basically only a non-binding proposal, the commitment declaration, which corresponds to environmental-law authorization, legally binds the problem owner, the regulators and other stakeholders (e.g. neighbors).

Elaborating a remediation plan is particularly recommended in such cases and is also demanded by the regulators pursuant to Section 13 Para. 1 BBodSchG when:

- Harmful soil changes or contaminated sites affect a significant area
- Co-ordinated action is required because of the diverse range of measures required.

Co-ordinated action is particularly important in the case of ENA and MNA because of the long monitoring periods usually required.

Art. 1 Appendix 3 BBodSchV lists in detail the information and documentation that should be included in the remediation plan. Art. 2.1 stipulates that this also includes a description of the planned remediation objectives. ENA and MNA should be dealt with in a special chapter containing details that should include the following:

- Summary of the investigation results and the prediction with respect to the relevant NA processes: what period of time is required to break down or retain which contaminant mass or contaminant flux, and which metabolites with what risk potential does this generate, etc.?
- Investigation time and expense for MNA as a performance control measure, and definition of the investigation methods and parameters.
- Discussion of the performance control measures as part of the after-care phase.
- Discussion of any additional remediation measures which may be required.
- Definition of the quality targets whose achievement correspond to successful MNA
- Definition of criteria to withdraw from the MNA concept and initiate an active remediation measure
- Definition of safety aspects if required.

Because the remediation plan is not intended to clarify other questions (e.g. exemption from measures which go beyond those defined in the remediation plan, the acquisition of construction rights, the involvement of other legal or natural persons such as local authorities, house owners, investors, financing banks, insurance companies, etc.) it is recommended in such cases that a public-law agreement be closed. The remediation agreement as a special form of public-law agreement became legally recognized when BBodSchG came into force (Section 13 Para. 4). The remediation agreement provides the contractual parties with greater legal security and can include customized and flexible solutions.

5.1.6 Remediation execution / implementation phase

The planned remediation measures and MNA are realized in the implementation phase.

Section 5 Para. 2 BBodSchG stipulates that the regulators can demand the implementation of performance control measures if required, especially soil and water analysis, as well as the installation and operation of observation wells. The performance control measures can be stipulated after execution of the remediation or containment measures, or in parallel to these measures. The results of the performance control measures must be recorded and archived for at least five years. Appendix 3 Art. 3 BBodSchV states that the performance control measures serve to monitor proper implementation, control the effectiveness of the planned measures, and must be specified in the remediation plan.

An MNA in which the NA processes are monitored by periodic investigations, and during which tests are carried out to check the predicted degradation or retention of contaminants, is basically nothing more than a package of performance control measures in the sense of Section 15 BBodSchG.

It is not unusual for the efficiency of active remediation measures to decline after a certain operational period, and for the remediation objectives defined at the start of the remediation programme to prove to be unrealistic or only partly achievable over a reasonable time period. The problem owner and the regulators must ask themselves in such cases whether the active remediation measures should be phased out even though they have failed to achieve the remediation objectives. Consequently, under these circumstances, it may be beneficial to initiate an investigation of the NA processes. If these investigations reveal that the NA processes are efficient enough to prevent an increase in the existing (residual) damage to the downstream groundwater, or that the degradation processes even cause a reduction in groundwater contamination, this should be taken into consideration when reaching a decision on which measures now need to be implemented. According to the decision-making criteria defined in this technical guidance, it may be prudent to terminate ongoing remediation measures in such cases. MNA is then required to monitor the predicted NA processes.

5.1.7 After-care

When the regulators agree that the defined objectives have been achieved, management moves into the after-care phase. Performance control measures can be demanded during this phase by the regulator pursuant to Section 15 Para. 2 BBodSchG – this usually involves soil and water analysis. The performance control measures may also be demanded independent of the remediation measures that were executed.

General information on the planning and implementation of the after-care phase are detailed in various technical guidances published by the German states as well as in the ITVA manual “After-care and monitoring of remediated contaminated sites” dated 2003 [22]. Please note that MNA is not dealt with in the latter manual.

5.2 Procedural analysis for conventional contaminated site management

5.2.1 Target analysis

Specifications for investigations and the characterization of groundwater contamination within preliminary investigations and detailed investigations are described in numerous technical guidances, regulations and manuals. Their main conclusions are similar and are presented here using as an example the nationally agreed recommendations from the Working Group on Water issues (LAWA) for the investigation, evaluation and treatment of groundwater contamination [23]. This manual defines the required site information to properly evaluate the situation with the aim of assessing the need, urgency and extent of any remediation measures. This information is determined in the "main investigation" (Chapter 6 of the LAWA report) which corresponds here to the "detailed investigation". According to the LAWA recommendations, a detailed investigation should present the following findings:

1. Nature, volume and risk of the contaminant (risk potential)
2. Location of the contaminant source
3. Local conditions - especially the hydro geological conditions
4. Stratification, protective barriers, covers
5. Presence of emissions, contaminant migration taking into consideration the contaminant properties and the hydro geological and other local conditions
6. Nature and extent of the spatiotemporal spreading of soil and groundwater contamination
7. Affected current or planned utilization (e.g. drinking water supply)
8. Other effects on the environment
9. Polluter.

The detailed investigation is followed by a risk assessment that basically corresponds to the evaluation of the aforementioned findings

5.2.2 Performance analysis

There is no standard procedural practice for defining the extent of the investigation measures, and they rarely match the originally defined scope of the target analysis. In practice, remediation measures are demanded and begun after identifying "unusual" concentrations of contaminants exceeding the relevant "reference values" and taking into consideration the regulations stipulated in each German state. All of these measures usually begin using a database which is neither adequate at the beginning nor during the remediation process to describe the actual damage to the subsurface, or document the changes taking place.

A remediation programme is already considered a success in many cases if a large amount of contaminants have been removed from the soil or the groundwater even though little is known about the total amount of contamination originally in place or the residual concentration or mass. An objective analysis of the remaining concentration of contaminants in the subsurface and comparison with the prediction and the remediation objectives is needed to reveal if targets have been reached. It is therefore clear that conventional groundwater remediation measures cannot be implemented successfully without adequately investigating the situation beforehand (see Chapter 5.2.1).

5.2.3 Target / performance analysis conclusions

If groundwater contamination is properly investigated and analyzed, and if an appropriate monitoring programme has been initiated, it is possible at any time during a remediation programme to assess the success to date and the probability of achieving the objectives. This is impressively demonstrated in practice. Reliable data and their continuous evaluation not only help permanently optimize the ongoing measures, they also support the implementation of a proportional response taking into consideration the economic aspects.

A remedial investigation according to Section 13 BBodSchG for instance only includes those investigations necessary to determine the nature and extent of the necessary measures. Section 13 BBodSchG and Appendix 3 BBodSchV also stipulate that the remediation plan must include an evaluation confirming the suitability of the chosen remediation measures taking into consideration the remediation objectives defined by the regulators.

5.3 MNA-specific procedure

5.3.1 General

Implementing MNA is usually a response to a specific case analysis and can usually only be regulated to a limited extent using standardized process steps. Critical parameters are the hazard situation (involving the receptors specifically affected), the types of contaminants (mobility, toxicity, degradability), and the site conditions (e.g. hydrogeology, hydrochemistry, current and planned site use – cf. Chapter 5.2.1). The decision to use MNA at a specific site should be based on the analysis of the available and possibly also additionally acquired data. This analysis and discussion of the situation should take place with a view to achieving unanimous agreement between the problem owner and the regulator and should be guided by defined decision-making criteria (cf. Chapter 5.3.2). This involves analysis to determine whether:

a) Other receptors are at risk

b) The predicted time frame of MNA is acceptable

c) The contaminant load can be permanently reduced.

d) There is any risk of further spreading of the contaminant plume

e) MNA is a mild measure compared to active remediation measures

f) Remediation of the contaminant source is feasible using reasonable (proportional) means.

Elaborating and reporting these decision-making criteria enables the stakeholders to assess the processes at the site capable of reducing the level of contamination, and to reach a firmly –based decision on the feasibility of MNA. Although it can be considered an alternative method in principle, MNA is usually implemented alongside conventional active remediation measures.

The decision to use MNA should be reached step-by-step in practice (cf. Chapter 5.3.3). The results of these investigations should then be incorporated in the MNA plan. In addition to discussing the decision-making criteria, the MNA plan also covers the future monitoring of the NA processes. A contingency plan should exist in case the performance deviates from the prediction.

5.3.2 Decision-making criteria

The following criteria can be used to support the decision-making process when deciding whether and under what circumstances NA should be taken into consideration within the context of averting risks.

1. Risk to other receptors

   The contaminated groundwater should not pose a risk to other receptors when the risk can be prevented by the implementation of simple measures (e.g. institutional controls

2. Duration

   NA processes can be taken into consideration if it is acceptable for the identified groundwater contamination to remain for a predicted and foreseeable period of time. It is not currently possible in the opinion of the authors to define a generic time frame. The acceptable time frame depends on various aspects including the groundwater management objectives (cf. Chapter 4.2) as well as on the decision reached by the regulators in each specific case, and on the planned use of the property expressed by the landowner.

3. Permanent flux reduction

   The NA processes should result in a permanent reduction of the flux of all contaminants including toxic and persistent metabolites, so that an effective reduction in risk is achieved independent of the additional remediation measures (cf. Criterion 6 “Remediation of the contaminant source”). This criterion does not allow non-destructive processes (e.g. dilution) to account for the majority of the effect when assessing the acceptance of MNA.

4. <u>Further spread of the contaminant plume</u>

   It is necessary to prevent the contaminant plume from spreading further so that there is no additional increase in the amount of groundwater contamination. It therefore has to be “quasi stable” within the framework of natural flow variations (flow rate, direction) as well as the reaction conditions (nutrient input, biodegradability, etc.).

   These and the previous flux criterion (Criterion 3) lie at the heart of the process-related evaluation. A combination of these two criteria restricts the emissions.

5. <u>Milder measure</u>

   MNA is worth considering as a milder measure compared to active remediation measures. This is determined by a proportionality study comparing active remediation measures and MNA (cf. Chapter 5.4). If an active remediation measure passes the proportionality test, it should generally be given priority.

6. <u>Remediation of the contaminant source</u>

   To prevent additional contamination entering the groundwater, source remediation to the extent practicable is usually required using appropriate measures (cf. Chapter 5.4). This reduces the length of time a contaminant plume exists.

5.3.3 Implementation of an MNA concept in practice

When the problem owner completely or partially turns down active remediation and chooses instead to use MNA as a milder measure to avert the potential risks, it is necessary to justify this decision in the MNA concept report.

Reaching a decision on whether to implement MNA should follow a step-by-step approach to identify at an early stage on whether this option is a promising alternative at the site from a technical as well as from a regulatory point of view. The procedure should be approved by the responsible authority on a case-by-case basis so that a decision can be made after each step of the phased investigation of the feasibility of MNA. This is the best approach for optimizing the costs involved and avoiding unnecessary additional investigations. Parallel to the NA-specific steps the necessary investigations for the remedial investigation should be conducted. Provided that reliable data exist, the criterion “MNA as a milder measure to avert hazards” can be assessed during the proportionality study.

Recommendations for specific NA investigations are largely confined to English references [24, 25, 26].

Phase 1: Analysis, assessment and evaluation of NA processes on the basis of the decision-making criteria.

The first phase of elaborating the MNA concept consists of analysis, assessment and evaluation of the local NA processes based on the decision-making criteria. This procedure should take place in the following stages:

Step 1: Investigation of the current status

Step 2: Analyzing the processes

- (2a) Qualitatively
- (2b) Quantitatively

Step 3: Estimation and forecast

Step 4: Proportionality test

Liaison with the regulator is required after each step to clarify acceptance problems and constraints early on and be able to directly proceed to the analysis of alternatives if required.

The **first step** is to assess the current site status and review and prepare the available data. In particular, this involves an assessment of the conditions required for realizing MNA. The aim of this step is to elaborate the information required for the two decision-making criteria:

1) “Hazard to other receptors
2) “Duration” – i.e. the time required for MNA if realized should be in proportion to the groundwater management objectives.

A positive assessment at this stage moves the process on to step 2.

The **second step** deals with the processes. To optimize the costs involved, the assessment should initially be restricted to the qualitative assessment (2a). If this produces a positive result, the process can be moved on to the second step (2b) which looks at the quantitative aspects. The assessment of the available data not only considers the concentrations (comparison with guidance values), but also the NA processes. A conceptual site model should be prepared for this purpose. If there are adequate qualitative indicators for the relevant NA processes, quantification of the NA processes should then take place to estimate or predict the decision-making criterion (3) “Permanent reduction in mass flux” and (4) “Further spread of the contaminant plume”. The assessment of the processes is therefore focused on:

- Analysis and evaluation of the spatiotemporal development of the contaminant plume
- Analysis and evaluation of evidence for natural attenuation processes (identification of degradation products, consumption of electron donors, dilution, etc.)

- Analysis and evaluation of the NA potential of the contaminants under the site conditions (literature search on sorption and degradation properties of the contaminants, etc.).

This does not necessarily involve any new or additional investigation methods on top of those conducted in the detailed investigation (Chapter 5.1.2) and specified in the relevant regulations. However, because there are often shortcomings in the detailed investigation with respect to qualitative NA assessments (e.g. inadequate information on geology, hydrogeology, hydrochemistry, contaminant potential and changes (forecast)) it may be necessary to conduct additional investigations (e.g. plume mapping, additional chemical analysis, clarifying the hydrogeology, starting systematic time-series monitoring).

This is particularly valuable when it is empirically known from a certain type of site and these types of contaminants that effective NA processes are likely to be present. These deficits also generally need to be resolved to support the successful planning of other remediation options as part of the remediation investigation and remediation planning.

Quantifying the NA processes will be divided into two stages to save time and costs. The first quantification stage is aimed at the aggregate total of pollutant reduction. If this already describes decision-making criterion 3 to the required degree of accuracy, it is not necessary to move on to the possible second step of quantifying the individual processes. This is, however, required if the aggregate total is unclear, and quantification needs to be broken down into the - individual processes (dispersion, breakdown, sorption, etc.). This usually requires additional process-specific investigations to be carried out (see Appendix A) which exceed the usual standards for contaminated site investigations (e.g. tracer tests, sorption tests, microbiological lab tests, isotope fractionation).

At this stage of the evaluation it is usually necessary to go beyond the conceptual site model (Step 2a) [27] to assess how best to model the site conditions and identify any associated data gaps. Deficits may be in the development and precision of the site model (geology, hydrogeology, contaminant risk) or in the need to evaluate and differentiate the separate processes. Table 5-1 shows which processes may be relevant to each contaminant group and which need to be assessed in more detail if necessary in specific NA investigations.

Table 5-1: Matrix for NA investigations for specific contaminants

Process / Contaminant Group	**Biodegradation (Appendix A-2)**	**Precipitation (Appendix A-3)**	**Sorption (Appendix A-5)**	**Dilution (Appendix A-6)**	**Volatilization (Appendix A-7)**
PAHs	0	-	x	0	-
Naphthalene	x	-	x	0	?
CHCs	x	-	0	0	x
TPH	x	-	0	0	0
BTEX	x	-	0	0	x
Heavy metals	-	x	x	0	-
MTBE	0	-	-	0	x
TNT	x	?	x	0	-

X necessary 0 in individual cases - usually not relevant ? unknown

As a general rule, the need to identify and quantify individual processes increases with the increasing importance of NA as a hazard aversion measure.

The aim of the second step of phase 1 of the MNA concept is to describe in detail the contaminant attenuation processes within the contaminant plume. Quantification of the individual processes and their combination to determine the aggregate total usually requires modeling. This in turn needs to be validated by field data, although these only measure the total of the processes.

The **third step** in the first phase of implementing an MNA concept concerns the estimation and prediction of the NA processes within the context of the decision-making criterion *Permanent reduction in mass flux* (criterion 3) and *Further spread of the contaminant plume* (criterion 4). The predictions should be discussed taking into consideration the modeling uncertainties, and assessed after consultation with the regulator. The uncertainties which are identified have a direct impact on the “monitoring plan” because the lower the reliability of the prediction, the higher the amount of field data (frequency and/or scope) which needs to be acquired to monitor the results. In this context, the evaluation of the contaminant attenuation processes needs to highlight the processes and the data acquisition necessary for monitoring.

The NA process estimation and prediction also provides an indication at this phase of the evaluation of the amount of time required for the NA processes to reduce the risks below the acceptable limits. This is the point in the evaluation for defining the length of time the groundwater body remains in a contaminated state, and the regulators should reach a decision on the decision-making criterion *Acceptance that the identified groundwater contamination will exist over the predicted time period* (Criterion 2).

The **fourth and last** stage of phase 1 of the implementation of an MNA concept is the proportionality study. The results of the remediation investigations must be complete at this stage to enable a comparison to be made between the remediation measures and MNA with respect to the proportionality criteria *suitability, necessity and appropriateness.* The proportionality assessment also requires cost estimates on the planned monitoring as well as the available active remediation measures.

Another aspect analyzed at this stage is the decision-making criterion: MNA represents a "*Milder measure compared to active remediation measures*" (criterion 5). This is also the latest stage for discussing the means of "*Remediating the contamination source*", because this is another important decision-making criterion (criterion 6). The suggested method for dealing with the contamination source is also part of the remediation investigation.

Phase 2: MNA plan

If MNA is demonstrated to be technically feasible, and if all the parties involved give their consent to MNA, it is recommended that the further plan of action at the site is described in an MNA plan. This should include the following:

- A description of the results of phase 1
- Description of the planned monitoring to monitor performance
- Elaboration of a contingency plan in case MNA fails. This requires definition of the criteria on a case-by-case basis.

Phase 3: MNA

Phase 3 of the MNA concept represents the implementation of the MNA plan. It is important here to continuously monitor compliance with the prediction: Monitoring should not be limited to comparing the measured concentrations with the predicted concentrations, but also the processes identified in phase 1. Deviations from the prediction should be assessed and evaluated with respect to the process. This should take into consideration the accuracy of the prediction and should lead to a revision of the prediction if necessary. Adjusting the groundwater model should also be part of MNA if required.

Phase 4: After-care

After-care in the form of performance control measures begins when the remedial objectives have been achieved. Essentially, this means continued monitoring, which is no longer focused on the NA processes, but rather on identifying any potential risks. This change of focus usually reduces the costs involved. The aim of after-care is to verify that the agreed remedial objectives for the site are maintained in the long term.

5.3.4 Conclusions

In conclusion, realization of MNA is possible in practice and can be implemented in a cost-optimized way by following systematic procedures. Proceeding step-by-step avoids unnecessary costs but requires that the problem owner and the regulator responsible to analyze the probability of success of the approach at each stage of the investigation, and support each subsequent step of the investigation. It is important to note here that implementing MNA will continue to be decided on a case-by-case basis in the foreseeable future.

5.4 Discretion and proportionality

5.4.1 General

Section 4 Para. 3 Sentence 1 BBodSchG stipulates that where there are contaminated sites or harmful soil changes, the problem owners must remediate the soil and the contaminated site and any contamination of the groundwater caused by the harmful changes to the soil or the contaminated site. Legislation does not specifically define what remediation actually means in detail. Although Section 4 Para. 3 Sentence 1 BBodSchG stipulates that it is an immediately valid obligation, it is also an **abstract remediation obligation** which requires further definition by the regulations laid down in BBodSchV, as well as regulatory enforcement, e.g. in the form of a remediation notice (according to the justification behind Section 4 Para. 3 BBodSchG [28]). Without further precise definition by the regulators, the problem owner does not know which measures in detail need to be implemented in such cases.

The soil protection regulator has a great deal of **discretion** at its disposal in this context. This is expressed in Section 10 Para. 1 Sentence 1 BBodSchG, which stipulates that the regulator can decide on the necessary measures needed to fulfill the remediation obligations arising from e.g. Section 4 Para. 3 BBodSchG. Discretion means that the regulator must use objective considerations to comprehensively justify its decisions. Discretion here involves “whether” as well as “how”. The conclusion drawn from this is that the regulator is not obliged in each case to issue a notice for remediation, protection or limitation measures to be implemented pursuant to Section 2 Para. 7 and Para. 8 BBodSchG. Such measures can be dispensed with under certain circumstances.

When examining the measures, the regulator has to take into consideration the principle of proportionality laid down in the constitution (P. 389 in [29]). The proportionality test comprises three steps [30]. A measure is only considered proportional in this context if it is:

- **feasible** achieving the desired objective – i.e. the remediation objective – (feasibility test)

  and

- **necessary**, i.e. if no other suitable measure (e.g. MNA) is available which has less impact on the stakeholders and the general public

  and

- is **appropriate**, i.e. is not out of proportion to the desired objectives (cost-benefit analysis).

The proportionality test usually involves a comparison of alternatives (e.g. a comparison between a pump-and-treat measure and NA monitoring) as an integral part of a remediation investigation.

5.4.2 Cost-benefit analysis

The aim of the cost-benefit analysis of alternatives is to rank the range of appropriate measures. This should be carried out reflecting the usual methods used for conventional remediation techniques ([31], [32]) and taking into consideration the information available on potential NA processes. The different measures can only be ranked after individual evaluation of the costs and benefits of each alternative.

The costs of each measure are determined independent of the benefit analysis. Net present value costs should be divided up into non-recurrent investment costs and operational costs with the relevant conversion factor [31] and calculated for each scenario. Other cost calculation or valuation methods may also be suitable which e.g. can also be oriented to DIN 219 [33] or the specific expertise of the planner. Care must be taken here to ensure that the planner is also liable for the cost assessment as one of the scheduled sections in a contractual work package.

The costs and benefits of each alternative measure should be derived taking into consideration the specified after use. This is then followed by the cost-benefit analysis. The cost-benefit analysis incorporates aspects on costs and benefits, which explains why this is the analysis method which is usually applied. The individual cost-benefit ratios of the suitable alternatives are derived from the cost-benefit analysis.

It is recommended to conduct a quantification of benefits according to [31]. The quantified benefit is determined in this way on the basis of the criteria: effectiveness, impact and quality of the property. The effectiveness is assessed from the indicators: fulfillment of remediation objectives, effective time, monitorability, renaturization and sustainability. The impacts are relevant in terms of the impairment of the stakeholders, impairment of the environment, and the generation of waste. The quality of the property is assessed on the basis of the indicators: potential uses, marketing possibilities, security of liability, and urban planning functions.

6 Outlook

The analysis of the legal framework and the discussion of the technical principles reveal that in the case of some contaminated sites, and under certain circumstances – which need to be specified further on the basis of further discussions – NA processes can be acceptable. The level of understanding documented in this report is based on the relevant scientific methods that have largely existed for a long time. The legal interpretation takes into consideration the different opinions on this subject. Another finding is that NA processes can be accounted for at each stage of the classic process of contaminated site assessment and management.

Ongoing research projects (e.g. the BMBF KORA priority funding project, the joint project of the Bavarian science association, the and individual research projects in the various federal German states etc.), and the results of the ad hoc “Natural Attenuation” sub-committee constituted in 2003 by the Contaminated Site Committee (ALA) of the Working Group of Soil Protection Issues (Bund/Länder-Arbeitsgemeinschaft Bodenschutz – LABO), will deliver new information and findings when they have been concluded. These can then be incorporated in a future revised version of this technical guidance.

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APPENDIX

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Appendix A Description of NA processes

A-1 Introduction

As per the definition in Chapter 3, this technical guidance refers to the following processes as natural attenuation:

- biodegradation (mineralization, humification, co-metabolic decomposition),
- precipitation,
- physico-chemical decomposition (e.g. radioactive decomposition, iron oxidation),
- Sorption (adsorption, absorption, desorption, complexation),
- dilution (dispersion, diffusion),
- dissolution (evaporation, sublimation).

Dissolved substances are mainly transported in the groundwater advectively because of the flow (direction and velocity) of the water. However, the aforementioned NA processes influence advective transport. As solute transport components, they determine the behavior of the substances in the groundwater. The combination ultimately causes the contaminants in the aquifer to “advance” leading to the spatiotemporal development of contaminant plumes down gradient of contaminant sources. The interaction of the individual processes and the related development of the contaminant plume are shown in Fig. A-1.

The amount of contaminants dissolved in groundwater is generally determined by the release rate from the contaminant source (source term). A contaminant plume will therefore persist (e.g. by dissolution from a residual phase) until the contaminants are completely dissolved/technically removed from the contaminant source (e.g. by excavating the contaminant source) or migration is technically prevented.

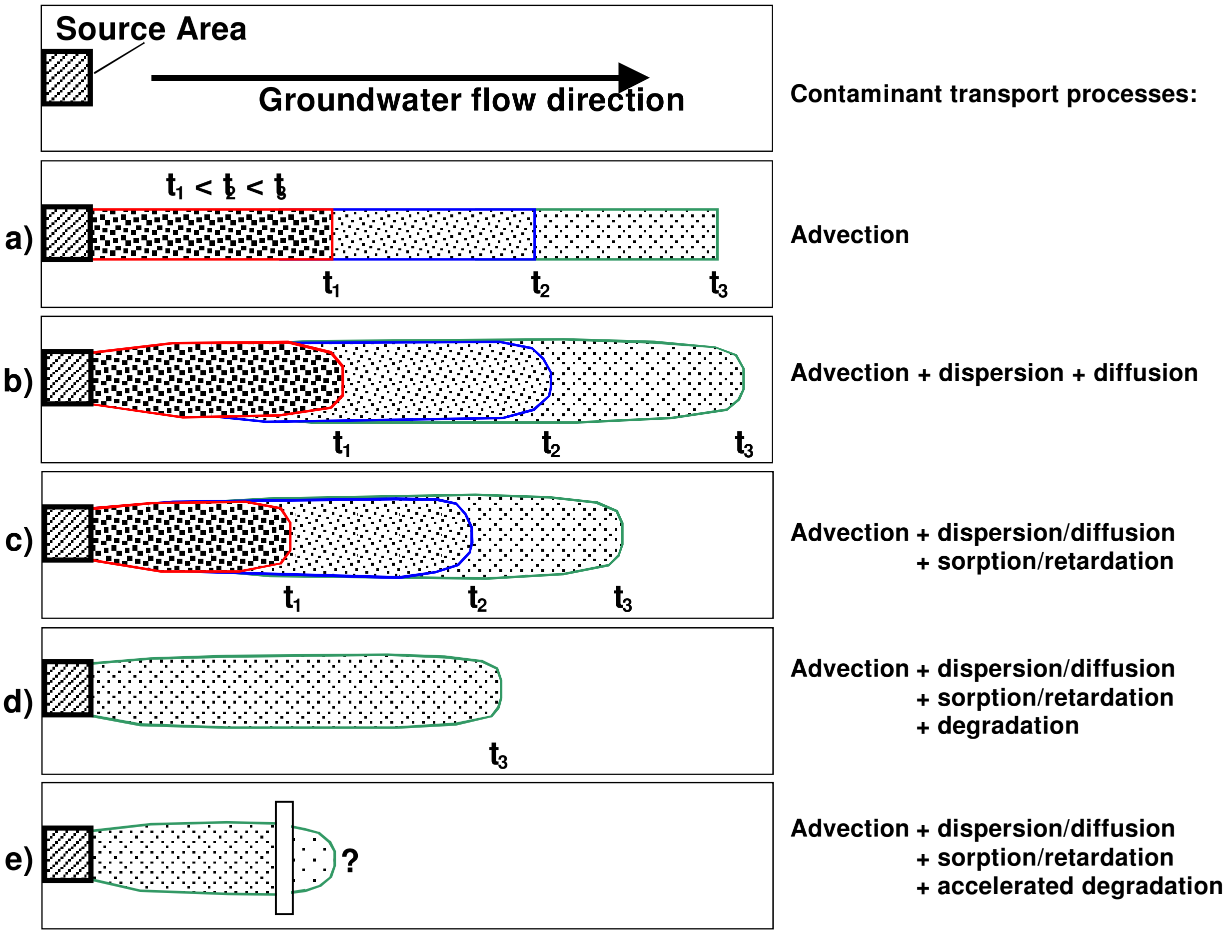

Fig. A-1: Development of contaminant plumes in groundwater over time. t_1 - t_3: various times; d) and e) excluding t1 and t_2. (Modified after [1], **[2]).**

The non-destructive transport rate of contaminants, which is controlled by advection, dispersion, diffusion, dissolution and sorption in the aquifer, can be neutralised by simultaneous destructive processes suc as biodegradation, decomposition and transformation of the substances (Fig. A-1, example d). This means that despite the permanent presence of a contaminant source, contaminant plumes in groundwater usually only spread to a limited extent and assume a stable dimension and may even shrink. It should be noted here that contaminant plumes do not generally follow straight lines, but frequently have vertical or horizontal sections depending on the flow conditions. Mapping the contaminant plume should take this aspect into account where applicable.

The following describes the individual components of contaminant transport of NA processes in the sense of the aforementioned definition, and methods to monitor them. A final comment describes the state of the art of the current implementation methods as part of an MNA concept.

A-2 Biodegradation

The biological degradation of contaminants in soil and groundwater can be considered sustainable. In principle, all contaminants which are biodegradable and are treated by biological remediation processes will also be eliminated under natural conditions in the soil and groundwater. Frequently, biodegradation is the result of successive enzymatically catalysed equilibrium reactions. The degradation velocity is determined by the slowest individual reaction step.

The determination of degradation rates is currently problematic because of the uncertainties in extrapolating lab results to actual field conditions. A standardised method for the measurement of degradation rates in the field (field measurement) is not yet available.

When assessing microbiological degradation, it is necessary to take into account the possible accumulation of toxic and possibly more mobile degradation products because this may increase the overall toxicity despite the elimination of the original contaminants. If toxic degradation products can be accurately identified, they can be determined directly as individual compounds (such as vinyl chloride (cf. A-2.2.2). Alternatively, toxicity tests may provide indicators e.g. when degradation products are not sufficiently understood or difficult to quantify.

The relevant microbiological transformation processes in soil for reduction in contaminant concentrations can be classified according to physiological aspects:

Type 1: Complete metabolisation and mineralization of contaminants

Complete metabolisation and mineralization involves the almost complete degradation of contaminants and has only been described for bacteria in the case of many contaminant groups. The substances involved are metabolised by the microorganisms using various substrate-specific enzymes. The substance can be used as a carbon source to grow biomass, or as an energy source by mineralisation to CO_2 and water.

Even if the contaminants are completely metabolised, there may be temporary accumulations of minor quantities of metabolites if there are limitations along the metabolic path. These metabolites are also found outside the cells in the medium under certain conditions, or may even appear in the environment.

Type 2: Co-metabolic transformation of contaminants

The main criterion for this type of degradation is that the substances cannot be used as the sole source of carbon or energy, and the microorganisms therefore cannot grow on them. Apart from a possible detoxification function, this type of degradation has no significant growth advantage for the organisms. The organisms are therefore dependent on additional substrates (co-substrates, auxiliary substrates) to maintain their metabolism and growth.

In this process, the contaminants are often fortuitously metabolised by the enzymes which catalyse a specific reaction when degrading the co-substrates. Because the transformation is indirect, co-metabolic degradationis normally incomplete (transformation, partial degradation, conversion). Transformation products produced and released in this manner may be further metabolised by other microorganisms or completely mineralised.

Type 3: Humification of contaminants

The biodegradation of all organic substance in soils involves decomposition and transformation reactions, which redistribute the initial substance into various compartments. Aside from metabolisation and mineralization (with formation of biomass), part of the carbon is fixed in the organic soil matrix. During the decomposition of natural substances, these processes are termed humification. Contaminants and their metabolites are analogously included in the reactions.

A-2.1 Influencing factors

Various factors in the soil and groundwater greatly influence the rate and of biological contaminant transformation or degradation. The conditions may be unfavourable or become so unfavourable that decomposition comes to a complete standstill. Some of these factors are discussed in the following.

Redox potential. The aforementioned metabolic functions include redox reactions (reduction oxidation reactions) and therefore depend on the respective redox potential of the environment (soil, water, microhabitat). The redox potential therefore influences the utilised organic compounds and the end products. Depending on their metabolic type, microorganisms require various redox potentials. The composition of bacterial communities therefore also shifts depending on the changes in living conditions, which are recognisable from the redox potential.

The oxidation of organic compounds (substrates) by microorganisms involves the oxidation of carbon. The energy released by this process is utilised by the organisms for growth. Hydrogen (protons and electrons) is transferred successively to electron acceptors with decreasing redox potential: Oxygen ($O_2 \rightarrow H_2O$), nitrate ($NO_3^- \rightarrow N_2$), manganese ($MnO_2 \rightarrow Mn^{2+}$), nitrate ($NO_3^- \rightarrow N_2$), iron ($Fe^{3+} \rightarrow Fe^{2+}$), organic substances, sulfate ($SO_4^{2-} \rightarrow S^{2-}$), and carbonate ($CO_2 \rightarrow CH_4$).

pH. Most soil bacteria grow best in a range from pH 6.5 to 8. If the buffer capacity of the soil is not sufficient, pH values can change as a result of the formation of partial degradation products, geochemical processes taking place after pollution incidents, and in the course of biological activity. Shifts in pH influence the solubility of minerals, metal salts and heavy metal salts, and the conformation – and thereby bonding behaviour – of humin substances.

Temperature. In general, the rate of bacterial transformation increases with temperature even though the participating enzymes have their specific optimal temperatures. Temperature influences the solubility of electron acceptors and contaminants. Under aerobic conditions, the soil and groundwater temperatures can also rise due to the decomposition activity of microorganisms.

Bioavailability. The bioavailability of contaminants is influenced by water solubility, volatility, surface area, sorption and inclusion, as well as the age of the contamination. Because only bioavailable contaminants can be transformed, this is often the limiting factor in biological degradation.

Water content. Because bacteria absorb contaminants over the water phase, and educts and products are transported via the water phase, the water content significantly affects bioavailability. The adsorbed water around and between soil particles is generally sufficient to support bacterial life.

Carbon sources. Other nutrients and co-contaminants may encourage microorganism growth. In the event that a contaminant can be mineralised by the microorganisms (Type 1, see above), the presence of other carbon sources can be considered unfavourable for the remediation process because they can be preferentially degraded instead of the contaminants and consume the available electron acceptors. If co-metabolic degradation is involved, additional carbon sources are essential because contaminant degradation only starts in their presence.

A-2.2 Contaminant groups

A-2.2.1 Petroleum Hydrocarbons

Principles of biological degradation: Petroleum products largely consist of aliphatic and aromatic hydrocarbons. The degradability of the aliphatic hydrocarbons depends on chain length, degree of branching and degree of molecular saturation. Toxic metabolites are not expected from degradation by the mineralization of the contaminants. Preferred degradation takes place under aerobic conditions, but degradation also occurs much more slowly under anaerobic conditions. Short-chain aliphatic hydrocarbons are volatile and have a toxic effect on many petroleum hydrocarbon-degrading bacteria. Long-chain and especially branched hydrocarbons on the other hand are persistent. The hydrocarbon compounds biodegradable are aliphatics with chain lengths of C_{10}-C_{16}.

The degradation of mono-aromatic hydrocarbons in petroleum products (benzene, toluene, ethylbenzene, o- and m-xylene and phenol) is facilitated under aerobic conditions. Toluene and ethylbenzene decompose well under anaerobic conditions. Benzene degradation appears possible particularly under iron reducing conditions. The anaerobic degradability of xylenes varies with the position of the substituents.

The following shows the potential degradability ranking of hydrocarbons under aerobic conditions [3]:

Aliphatic hydrocarbons:

n-Alkane > Isoalkane, Alkene > Cycloalkane

Aromatic hydrocarbons:

Toluene > Ethylbenzene > Benzene, Xylene

Bioavailability. Petroleum hydrocarbons migrate in the unsaturated zone or pool as generally coherent phases at the water table (LNAPL). Pendular and insular residual saturations hinder bioavailability. Bioavailability is restricted partly because (longer chained) aliphatic hydrocarbons do not dissolve well in water, and partly because they also sorb strongly to soil particles and humic substances. Bioavailability decreases with age of the contamination because the contaminant spectrum shifts, reducing the more volatile and water-soluble components, and because there is sequestration (inclusion) of contaminants in high molecular matrixes.

Proof of microbiological degradation: The significant consumption of electron acceptors (O_2, NO_3^{2-}, Fe^{3+}, SO_4^{2-}, CO_2), causes the establishment of up to five individual redox zones down gradient of a contaminant source. These zones and the consumption of electron acceptors can be assessed. Degradation produces the bacterial communities to change in favor of bacteria which can utilize the aliphatic and aromatic contaminants. This can sometimes be documented by molecular biological methods.

Suitability for MNA: With regard to natural attenuation, the petroleum hydrocarbons (TPH) are the group with the highest natural degradation potential because the petroleum hydrocarbon consumers are ubiquitous, and because the intermediate products are not more toxic than the original substances, and degradation is productive (with energy gain). Within this group, the BTEX aromatics are the best researched. They are the only internationally accepted substance group whose general suitability for MNA has been confirmed to date.

A-2.2.2 Chlorinated hydrocarbons

Principles of biological degradation: This contaminant group depends more than any other group on the environmental conditions described above for the transformation of aliphatic chlorinated hydrocarbons (CHCs: chloroethene, chloroethane and chloromethane) and the possible accumulation of transformation products. Degradation is usually co-metabolic. Only the discovery of (reductive) dehalorespiration showed that an energy gain can also be linked with dechlorination under specific conditions. The higher the degree of chlorination, the more likely degradation will be anaerobic (and vice versa). The biological degradation of chlorinated aromatic hydrocarbons is slow and usually only leads to lower chlorinated compounds. This may be due to the toxic effects of many chlorine aromatics. However, the latter have a lower toxicity than the more highly chlorinated compounds.

Bioavailability. Most CHCs are heavier than water, relatively water soluble and volatile. Water solubility and volatility increase with decreasing numbers of chlorine atoms. The monochlorinated compounds of vinyl chloride, monochloroethane and monochloromethane are gases form at room temperature and correspondingly less water soluble. The CHCs spread in the soil, water and (soil) gas in characteristic ways depending on their properties. Dissolved CHCs sorb reversibly to organic substances in the soil. Within the chlorinated aromatic hydrocarbons, volatility and water solubility decrease in a substance group with increasing chlorination, while persistence and stability increase.

Proof of microbial degradation: Because the degradation of aliphatic CHCs is strongly dependent on environmental conditions, microcosm studies are needed to assess the natural attenuation potential and determine the influencing factors. Microcosm studies involving anaerobic tests are very expensive and time consuming. However, the metabolites can generally be proven in the groundwater because degradation takes place by the successive splitting off of the chlorine atoms. In microbial degradation, trichloroethene is preferentially transformed to 1,2-*cis*-dichlorethene, rather than 1,2-*trans*-dichlorethene. A comparison of the ratios of the two isomers may provide an indicator of microbiological degradation. A reduction in TOC can also be used as an indicator of microbiological activity (but this does not necessarily indicate degradation).

Reversible adsorption down gradient of contaminant sources produces a chromatographic effect because the different substances are transported at different velocities in the groundwater plume. In down-gradient direction, there are shifts in the contaminant ratios. This effect must not be misinterpreted as degradation.

Suitability for MNA: At older contaminated sites, primarily chloroethenes have a natural degradation potential which is not to be underestimated; provided that the subsurface, as in many contaminated sites, is anaerobic and contains sufficient organic nutrients. However, the accumulation of vinyl chloride can be problematic, owing to its persistence under anaerobic conditions resulting in slow degradation. Chlorine aromatics are only biodegraded in situ at extremely low rates, making this contaminant group generally unsuitable for MNA.

A-2.2.3 2,4,6-Trinitrotoluene

Principles of microbiological degradation: While many nitro aromatic compounds can be biodegraded both aerobically and anaerobically through gaining energy [4], TNT (2,4,6-Trinitrotoluene) and other higher nitrated aromatic compounds are only transformed co-metabolically, that is, without an energy link. Under in-situ conditions, biological and abiotic transformation produces free metabolites (such as aminonitrotoluenes), “polar metabolites”, and sequestered metabolites, which are irreversibly incorporated into the organic soil fraction. This process is termed humification. On the other hand, there is no significant mineralization.

Bioavailability. TNT is present as a solid in the soil, ranging in size from dust to large lumps. Due to its slow dissolution from the solid phase, TNT is very persistent.

Proof of microbiological degradation: investigation of contaminant retardation in column and lysimeter tests, because texture has a major influence on retardation. Proof of known metabolites in soil and groundwater. Stable isotope investigations [15N]

Suitability for MNA: Even though irreversible fixation in the humic fraction is an acceptable process for TNT detoxification, balancing the material flows is currently not possible. With the data and analytical techniques available today it is necessary to warn against simply assuming Monitored Natural Attenuation will solve the problem of explosives contamination without conducting further research. The example of polar metabolites which were only discovered in 1997, and then detected at nearly all examined sites, shows that there is still a great deal more to find out about the natural processes occurring in the subsurface.

A-2.2.4 Polycyclic aromatic hydrocarbons

Principles of microbiological degradation: Polycyclic aromatic hydrocarbons (PAHs) are a heterogeneous group of condensed aromatic structure. PAH elimination takes place productively with an energy gain and biomass formation by mineralization or humification within the organic soil matrix. The initial degradation reaction is an oxidative attack on the ring structure. This step requires oxygen. More highly condensed PAHs (3 to 4 rings) are generally degraded slowly and only after the degradation of more easily accessible aromatic compounds (naphthalene or monoaromatics). The degradation of simple PAH is also reported under nitrate and sulfate reducing conditions. Even though the degradation of high molecular PAH (>4 rings) has been described in lab studies, their degradation in the field is significantly limited by their low water solubility and their strong sorption to the soil matrix.

Bioavailability. Tar oils and gasworks sludge are present in the subsurface as solids or phases and have been continuously seeping into the groundwater for decades. The contaminants sorb more strongly to the soil matrix and have a poor bioavailability particularly in C_{org} rich sediments. Sorption, transport and bioavailability, as well as degradation, also depend on co-contaminants.

Proof of microbiological degradation: Degradation tests in microcosms or columnar tests from material obtained from the site. Proof of oxygen consumption in the field. Possible identification of metabolites.

Suitability for MNA: Because PAHs are less mobile in the subsurface and the plumes are short and stable because of the low water solubility, sorption and degradation, PAH contamination appears suitable for MNA measures under the premise “retention". PAH contamination from tar oils and gasworks frequently contains other mobile contaminants, which continuously dissolve from the phase. BTEX prevent the degradation of PAH and also act as a solvent catalyst. The co-contaminants of the groups of N, S and O-heterocyclic compounds are also of special interest. The environmental behavior of these much more water soluble and mobile compounds is only now being researched in terms of mobility, toxicity and degradation.

A-2.2.5 Heavy metals

By nature, heavy metals are non-biodegradable. Biological systems can, however, influence redox conditions in the subsurface so that there is quasi irreversible precipitation of heavy metals, leading to their immobilization. However, this requires high microbiological activity.

A-2.2.6 Recalcitrant or non-degradable contaminants

Recalcitrant or non-degradable contaminants exert a significant influence and often constrain the option of taking NA processes into account in contaminated site management. Contaminants with low solubility and good adsorption rates (such as PAHs) spread slowly in a restricted zone around the contamination source. However, the life time of such contamination is, predicted to involve generally unacceptable time periods (sometimes > 1000 a).

Another problematic group involves contaminants which do not break down well but are highly water soluble and mobile. They can be largely responsible for the maximum extent of a contaminant plume, for the current plume status (expanding, stable or shrinking) as well as for the time required before the plume becomes stable or starts to shrink.

In this group, the focus is particularly on methyl tertiary butyl ether (MTBE), a gasoline additive. It is highly water soluble (approx. 50 g/l), does not biodegrade well, and is poorly retarded during subsurface transport, i.e. has the qualities of a conservative tracer. Another contaminant group contains the heterocyclic aromatic compounds related to PAH contamination.

Due to many factors affecting the success of biodegradation in natural attenuation and the restricted influence on subsurface biological processes, no general statements can be made about the degradability of a specific contaminant. The ability to degrade must either be tested under the prevailing conditions, or indicators for biodegradation activity must be gathered. Aside from the indicators previously discussed, molecular biological methods can be used to detect specific enzyme activities or changes in the bacterial communities. Toxicity tests may also indicate the presence of poorly detectable toxic metabolites in the plume.

A-3 Precipitation

A-3.1 Precipitation reactions

Precipitation is a chemical reaction that changes substances dissolved in the water into insoluble or poorly soluble substances. This is either due to changes in equilibrium conditions (temperature, pH, redox conditions) or to the addition of electrolytes (changes in ionic strength). In most cases, causes the solubility product of the compounds dissolved in the water to be exceeded and therefore leads to their precipitation in the form of crystals, flakes or drops. This is regardless of whether the chemical composition of the substance being precipitated is changed or not [5].

A-3.2 Influencing factors

The most frequent precipitation form found at contaminated sites is the transformation of dissolved metal ions into poorly soluble metal hydroxides, carbonates, or sulphides. This requires redox processes and suitable pH conditions. Furthermore, the formation of anionic salts has to be accounted for.

A-3.3 Data Collection

Precipitation reaction data are easily collected by measuring E_H-pH values under lab conditions (fast reaction times). In groundwater systems, precise determination is often affected by errors because of the existing microbiological activity, long reaction times and redox measurement methods. The viability of the results is often adequate for simple problems, but can often be limited when special problems are involved.

A-3.4 Comment

The effect of binding contaminants by precipitation has already been described for heavy metals (e.g. in sediments), where the precipitation as poorly soluble sulphides may bind the contaminants. Under specific conditions (such as changed redox conditions), precipitated products may redissolve. The role of precipitation reactions should be looked at on a case by case basis to determine to which extent contaminants can be sequestered or the general influence of precipitation on the hydro chemical equilibrium.

A-4 Physicochemical breakdown

Radioactive decay as an example of physical breakdown plays no role in contaminated site management in NA investigations, with the exception of issues concerning radioactive repositories. The element-specific decay constants and conditions are known and found in the literature. Radioactive decay causes the destruction of the initial material, even though this leads to the production of contaminants as daughter products of some decay processes.

Another example of natural physico-chemical decomposition is the reaction of organic substances on geogenic iron.

A-5 Sorption

A-5.1 Description

Transport of dissolved contaminants (contaminant plume) in the aquifer is more or less retarded (delayed) due to sorption processes (sorption and subsequent desorption). Sorption, i.e. interaction between substances dissolved in the water and aquifer minerals such as grain matrix, particles and already sorbed additives (organic substances), is substance-specific. In general, poorly soluble compounds sorb relatively strongly and desorb relatively slowly, and are retarded correspondingly. Because sorption is rapid compared to the time scale of advection, equilibrium can be assumed in practice between dissolved and sorbed substances. The relation between dissolved and sorbed portions is described by the sorption isotherm, which is a linear function in its simplest form:

adsorbed concentration C_S *= distribution coefficient* $K_d \bullet$ *dissolved concentration C*

The result is a retardation in transport without altering the substance mass.

In the case of hydrocarbons, sorption is mainly determined by the proportion of organic substances (humic substance, peat, lignite etc.) in the aquifer. This is defined as f_{OC}, which is determined as the quotient of bound organic carbon and the total sample weight. In practice, a proven measure of sorption of hydrocarbons is the octanol/water distribution, termed K_{OW}.

There is an empirical relation between the distribution coefficient K_D and K_{OW} which applies to nearly all relevant contaminants:

$$K_D = A \bullet f_{OC} \bullet K_{OW}$$

with A as the substance specific factor. With a high share of clay minerals, the latter approach can also be complemented by expansion with the sorption proportions of sesquioxides (Fe, Al and Mn oxides). This is done by adding the latter formula to the product of the distribution coefficient clay/water (62,785 $S^{0,81}$) and the correction factor T_k where

$$T_k = 0.2 \bullet (\text{clay content} - 20) / 100)$$

for the clay and sesquioxide content. *S describes the solubility of the organic substance.*

Also, two other isotherms are frequently used:

- the Freundlich isotherm:

  $C_s = K_d \bullet c$

- the Langmuir isotherm:

  $C_s = (a_{L1} \bullet c) / (a_{L2} + c)$

A-5.2 Data Collection

Sorption and the related desorption are determined from the aforementioned derivative via aquifer parameters and their empirical relations to each other. In mixtures, competing reactions play a role. Sorption should therefore be determined in lab tests (batch or column tests). This also decides what isotherms should be used in each specific case.

A-5.3 Comment

Sorption can play a significant role in NA processes: When proven, it should be further examined and quantified as a non-destructive process. In the case of high sorption and low desorption rates (PAHs), these processes do not lead to mass reduction, but do reduce acute risks. In this case, the risk assessment should give more consideration to the term “foreseeable time period". Specific lab tests can complement the sorption and desorption rates reported in the literature because they can vary significantly in individual cases. If the relevance of sorptive processes is established, lab data should be provided as part of the NA investigation, particularly when mixtures are involved. In a first approximation, the empirical formulas should be used.

Sorption can also be significant in connection with possible microbiological degradation. Despite low microbiological degradation rates, these may possibly be sufficient for complete biodegradation of the dissolved substances as a result of sorption of the substances on the subsurface matrix and the associated retarded transport,

A-6Dilution (dispersion and diffusion)

Dilution of the contaminant plume is the result of hydrodynamic dispersion and molecular diffusion. The concentration of the contaminants changes without altering the substance mass. Together with sorption, these processes are also included in non-destructive NA processes. In major contaminant plumes, dilution occurs particularly at the periphery of the plume.

A-6.1 Dispersion

A-6.1.1 Description

Dispersion in contaminant transport processes in the groundwater generally refers to hydrodynamic dispersion, which includes all the mechanical mixing processes during the transport of water constituents. It is caused by microscopic variations in flow velocity in the pores. Variability is a consequence of the irregular velocity profile within a pore, differing pore cross-sections and/or deviations from the mean flow direction. The velocity of each water particle is always higher in the centre of a pore than near a mineral grain. Hydrodynamic dispersion draws out the contaminant plume, reducing the concentration gradient in flow direction. Dispersion takes place both in the flow direction (longitudinal) and orthogonal to the flow direction (transverse).

Its absolute value is therefore direction dependent. Transverse dispersion is generally one magnitude lower than longitudinal dispersion. Mathematical analysis of dispersion therefore depends on the dimensionality of the flow field, which has to be assessed within the framework of the hydrogeological concept model. If dispersion is a dominant NA processes, the hydro geological model should take these conditions into account.

Apart from the aforementioned small scale effect of hydrodynamic dispersion, natural inhomogenities in aquifers, e.g. clay and silt lenses, result in macro dispersion to be more important for contaminant distribution in the aquifer even after a flow distance of a few meters. As the flow distance increases, the influence of these heterogeneities grows, and the scale-dependent macro dispersion determines the mixing processes in the groundwater.

A-6.1.2 Data Collection

Dispersion is quantified by the dispersion coefficient, which is expressed as a product of aquifer dependent dispersivity and the average groundwater seepage velocity. Dispersivity related to grain structure is an aquifer parameter which generally increases with decreasing porosity, decreasing roundness and increasing unevenness. Dispersivity can be determined in the lab. It varies from 0.01 – 1 cm. It can also be determined from tracer tests [6]. However, field-derived dispersion values can be much higher because they are affected by macro dispersion [7]. Generally valid formulas derived from lab parameters are therefore unavailable.

A-6.1.3 Comment

Because dispersion determined in the lab is not representative, and it is difficult to determine dispersion in the field, formulation of the hydro geological model and its assessment should use the contaminant distribution in the plume (molar ratio of CHCs or distribution of BTEX) and empirical data to estimate whether dispersion plays a significant part in NA. In this case, a tracer test under controlled field conditions should be considered, e.g. during a pump test. On the other hand, a tracer test with active groundwater transport in contaminated areas is difficult and therefore expensive.

A-6.2 Diffusion

A-6.2.1 Description

Diffusion, or more precisely “molecular diffusion”, is the mixture of gaseous, liquid or solid particles which arise from concentration gradients produced under the influence of Brownian motion. Under stable conditions, it is described by

1. Fick's Law

$$F \;=_{.} \tilde{D} \bullet \square c/\square x \quad [kg/sm]$$

It is independent of the direction and vector norm of the flow field.

A-6.2.2 Data Collection

Measuring diffusion is difficult. It is generally estimated from empirical formulas or obtained from literature sources and tables. The role of diffusion in contaminant transport is generally very small and can be ignored if the groundwater flow velocity is large ($v_a > 0.1$ m/d). However, it can become a relevant transport component in low permeability layers (siltstone or clay stone).

A-6.2.3 Comment

The significance of diffusion in NA should be assessed depending on the lithology, and taken into account in the transport formula if applicable on the basis of figures from the literature. Site or substance specific determination is therefore not part of NA-specific investigation.

A-7 Volatilization

The volatilization of substances is determined by their vapor pressure. This is element specific and can be obtained from the literature insofar as it is largely involves single substances. The values for mixtures may differ from the literature values. Vapor pressure plays a role in chlorinated hydrocarbons as well as in short-chained aliphatic and aromatic (BTEX) hydrocarbons. This should be taken into account in the site investigation by conducting soil gas measurements. If volatilization is not taken into account under specific conditions (e.g. high permeability soil, no paving over) this may lead to an overestimation of microbiological or sorptive processes in the aquifer, and thus erroneous interpretations of long-term behavior.

Appendix B Prediction of spatiotemporal changes

Groundwater models can be an important tool in developing an MNA concept. Relevant NA processes can be modeled with the help of analytical and numerical models. Hydro geological models are mathematical models that can provide a simplified view of a conceptual subsurface interpretation. They are therefore only as good as the information available, but can show data deficits. The input data are the hydro geological, hydro geochemical and biogeochemical data obtained at the respective site. Numerous models of varying complexity are available depending on the data situation, the level of site investigation, and the required precision of the evaluation. This technical guidance aims to provide an overview of the possible uses, expected information gain, and limits in assessing NA.

B-1 Model term

The principles and applications of groundwater modeling are adequately described in many textbooks (e.g. [8], [9], [10], [11], [12], [13], [14], [15]). There is a principal differentiation between "analytical models" and "numerical models". Both model approaches are based on the general equation of groundwater flow, the Laplace formula (a partial differential equation system which can be solved by using boundary conditions). This is derived from the connection between the continuity conditions and the DARCY formula (e.g. in [12]. Various tests showed that the DARCY formula applies equally well to high permeability and poor permeability layers [5, 9].

The formula system can be solved both by analytical and by numerical routes, however both solutions always require a computer. Analytical models can only describe homogeneous porous media, while input data with numerical models may be subject to spatial variation.

In the **“analytical models”,** the choice of simple boundary conditions or geometries enables explicit solution of the flow equation. Analytical models are a quick and simple means of modeling NA processes when only a small amount of field data is available or the hydro geological conditions at the site are easily described (see Fig. B-1).

Such simplified boundary conditions are generally not applicable for complex (i.e. nearly all) flow conditions. The flow equation is therefore equally complex and must be solved with **“numerical models”,** that is, by applying iteration processes. The framework conditions are discretized spatially, and in the case of non-steady-state flow, also temporally. The most widespread procedures are currently the finite difference method and the finite element method (see Fig. B-1).

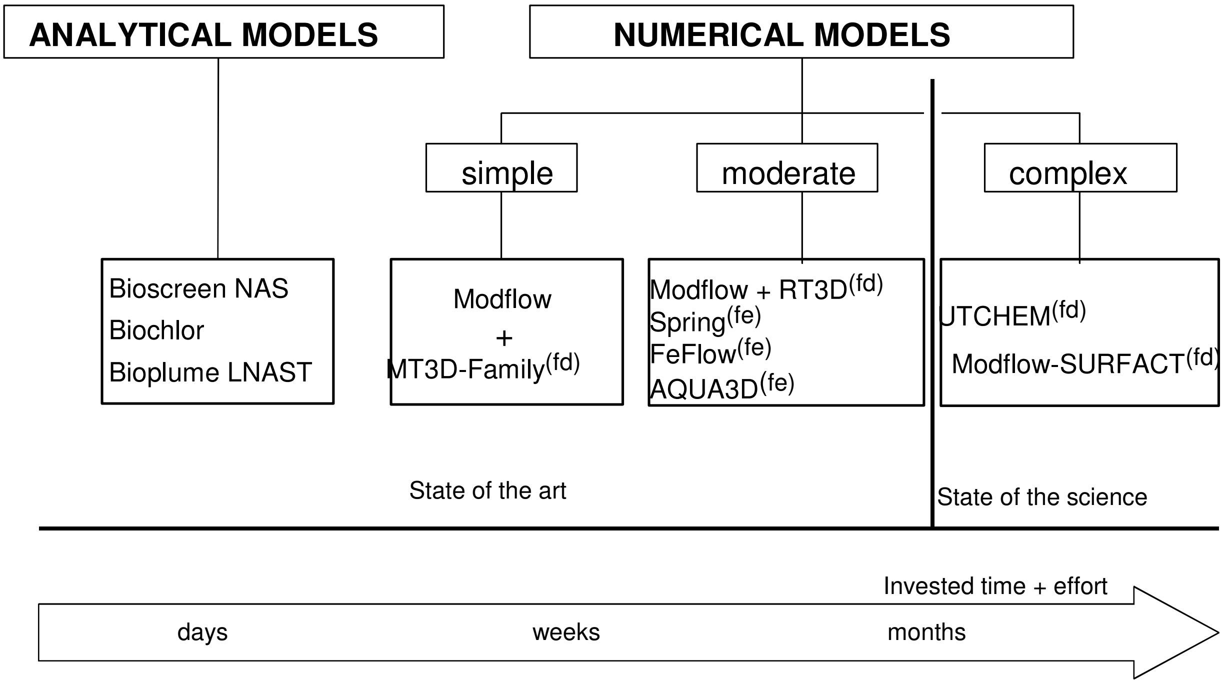

Fig. B-1: Overview of a selection of mathematical models.
Model systems, references and authors – see Appendix B-7.1.
Legend: (fe) finite element method; (fd) finite difference method

Both methods are equally suitable in the majority (99%) of modeled aquifers. Errors resulting from the respective method in solving the mathematical formula are insignificant compared to the errors in obtaining data, and do not represent exclusion criteria for one or the other method.

B-2 Goals when using models

The use of models in MNA mainly serves as an interpretation tool for the prognosis of plume geometry and the spatiotemporal change in concentrations of monitored contaminants. This means that suitable models can produce a prognosis. For instance, a calculation of how far a contaminant plume will spread or what time periods can be expected until the desired contaminant concentration is reached at a fixed observation point.

Apart from these two basic questions, models can also be used to improve process and system understanding, e.g. by comparing field data and model values. Consideration of site-specific conditions and the incorporation of new data enable continuous improvement in the model’s predicting accuracy. The model results also serve as a planning basis, e.g. to optimize the monitoring programme by setting up new observation wells.

It is important to emphasize that the use of models is a tool for the further interpretation of field data. Models and model results must never be used in isolation, but must always be critically verified within a previously created CSM and on the basis of new field data.

B-3 Model use

The use of models is generally prudent and helpful at every stage of contaminated site management. Basically, the requirements (data and expense) for models increase with expectations and accuracy.

B-3.1 Detailed investigation

A first opportunity for the use of supporting models is the qualitative assessment of NA processes in detailed investigations after confirming contamination at a site, unless the concept model (or a critical detail assessment) is enough to answer this question. The question of whether the contaminant plume is quasi-steady-state, and which processes allowed this state to develop, can sometimes be answered by using a “simple model” at the stage. An analytical model (Bioscreen or Biochlor etc., see Fig. B-1) or a simplified numerical model is generally sufficient, because the need for precision is lower. This first simplified abstraction must, however, be supported in principle by the site-specific conditions. The use of a "simple model" is not possible if the heterogeneity of the local conditions does not permit this level of simplification at this stage of contaminated site management.

Basically, a model in the detailed investigation is generally used for acquisition and visualization, as well as being useful for the identification and assessment of NA processes. It is not as suitable for precise quantification and reliable prediction. It should show which kind of models or model systems would be useful in further contaminated site management and what additional data are needed for this purpose.

B-3.2 Remediation investigation

If the detailed investigation identifies NA processes, the NA-specific site conditions must be specifically examined during the remediation investigation to provide improved input data for modeling. The data acquisition program must be adapted to the information requirements. Because of the detailed data acquired and the resulting complexity and heterogeneity of the site, only numerical models are usually useful at this stage of contaminated site management. However, they require significantly more input parameters. The related degrees of freedom in modeling require more competence and responsibility both in making the model and in assessing the results.

This becomes particularly important when one considers that only sufficient quantification of NA processes will produce a decision to realize MNA. Documentation of temporal variations of degradation rates can, however, also be provided through continuous monitoring, usually for many years.

The in-depth follow-up investigation during the remediation investigation is followed up by the main development of the model, its calibration for sensitivity to parameter variations (**sensitivity analysis**), and its validation by means of a different dataset to the one used for calibration. Only then can it be used for prediction and therefore in the remediation decision-making process. Quantitative assessment of NA processes in the remediation decision will usually not be possible if it proves impossible to create a sufficiently accurate model for the specific site. If it is possible to establish an accurate model, it is used to predict how the contamination will behave and to elaborate the monitoring programme, which may possibly replace active remediation. The further **validation** of the model then takes place during monitoring.

Even if NA processes often cannot wholly replace active remediation at a site, the model helps to determine and assess the remediation alternatives in the course of the remediation investigation. For instance, consideration of source remediation in combination with MNA for the contaminant plume requires a model. The comprehensibility and verifiability of the model on the basis of field data plays a role in deciding the acceptance of model results.

B-4 Model components

The first step in creating a model is always the formulation of a conceptual site model [16], regardless of what model or model software will be used later on. The conceptual model combines all available information about the geological, hydro geological and hydraulic onsite characteristics in a model, which is, if possible, already three-dimensional. Furthermore, all information about the contamination situation is included (e.g. the scope and type of contaminants, position and geometry of the source, and if applicable, the plume; receptors at risk, etc.). A lot of the data included in the conceptual site model initially has a purely qualitative character. However, it is mandatory that the conceptual data model is continuously adapted as the data become more accurate because it is the starting point for all other model components. It is at this early stage of model formation that the decision of whether an analytical model is sufficient or a more complex numerical model is needed is generally made.

In the next processing step, based on the conceptual site model, the preferred model software is used to create a three-dimensional hydraulic model. In this phase, it is important to specify the site-specific hydraulic conditions, including the associated important boundary conditions, and calibrate the model both in stationary terms (groundwater system at rest) and in non-stationary terms (e.g. using pumping test data). It should be noted here that in theory, a large number of pairs of parameters on hydraulic conductivity (K) and down gradient groundwater (Q) are required to calibrate the model, and that the number of parameter pairs can only be reduced by carrying out a plausibility assessment (such as a flow network analysis) or by using pumping tests (Fig. B-2).

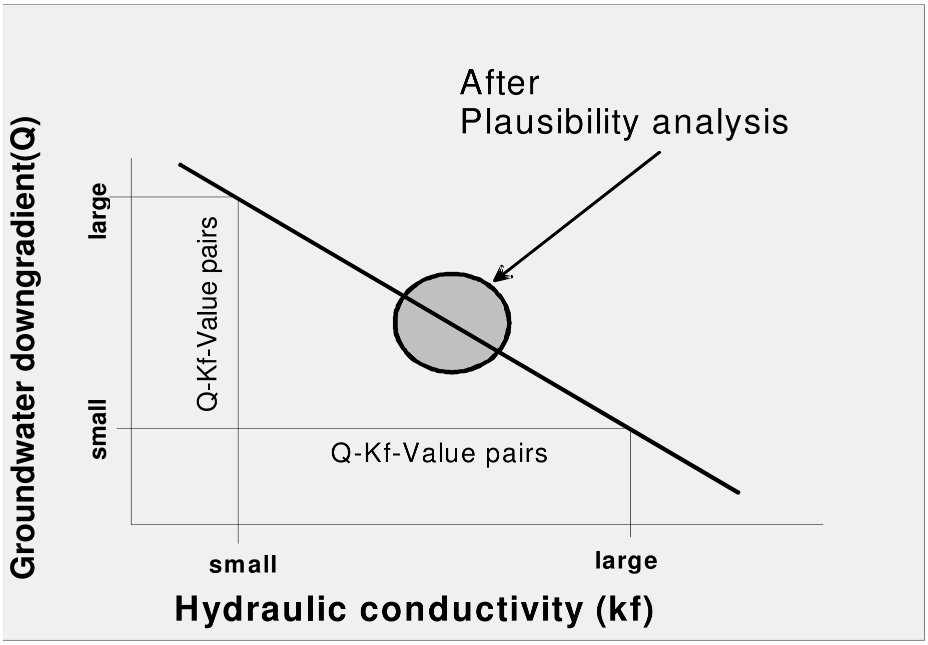

Fig. B-2: **Prognosis of a hydraulic model modified after [17]**

It is important to note here that higher predictability is not given by those models which divide the model cells into various small scale hydraulic permeability sections, but by those models which leave the hydraulic conditions relatively homogeneous across the model grid [18].

After calibration of the hydraulic model, the next step involves production of a **contaminant transport model** based on the calibrated and validated hydraulic model (groundwater model). Calibration of a transport model is clearly more difficult than that of a hydraulic model, because the contaminant concentrations often involve variables with much higher variability. With sufficient knowledge of the contaminant plume and the time contamination began, calibration can be accomplished using the present contaminant distribution. Another calibration option is associated with the temporal change in the contaminant plume. Calibration gives the first information on the retention and break down of contaminants, and the time from the start of contamination to the last plume monitoring.

The first step in the variant calculations is conservative advective material transport modeling – i.e. degradation or other retarding processes are not initially included in the material transport calculation. Among other things, this clarifies the influence of NA processes on contaminant spread, allowing it to be taken into account more precisely in further calculations.

In the second phase, the NA processes are implemented in the material transport model. This involves inclusion in the model of the data first obtained or calculated onsite (calibration) or in the lab, such as the degradation rates, retardation constants and other data. The contaminant sources are generally only taken into account in a very abstract manner because the complex solution processes of contaminant phases are difficult to quantify. With the exception of the multi-phase models, contaminant sources can only be entered as:

- constant source,
- temporally varying source,
- precipitation source,
- point source,
- source of increased concentration due to evaporation.

The parameterization of material transport models is often not possible on the basis of site parameters alone because their acquisition costs are comparatively high. It is therefore also necessary to obtain data from the literature. The literature contains extensive information on the retardation of contaminants, mostly derived from laboratory experimentation. However, there is significantly less data on the biodegradability of various organic contaminants – degradation tests under onsite conditions should be carried out here if applicable.

The degradation parameters can be entered either as time constants (but spatially variable) such as in MT3D (Modflow Program) or as reaction balances between two different contaminants (PER/TRI/CIS/VC/ETH), as in e.g. RT3D (Modflow Program). Such modeling is highly complex because the input figures required frequently have to be estimated or determined expensively in the laboratory. However, the additional expense should always to be seen in relation to the possible improvement in the accuracy of the forecast.

B-5 Model selection

Before a model is created for a site, it is necessary to clarify whether a model is necessary and helpful. If, for instance, there is historic data on contaminant development, and it can be seen from the development over time that there is no further contaminant spread, the use of a model is generally not required unless statements are needed on the change over time until complete degradation of the plume, e.g. with regard to present use and planned after use.

If, however, the contaminant plume is already near a possible receptor (such as a waterworks) and there is no information on the developmental history of the plume, the use of a model with the inclusion of new data may be helpful for the risk assessment.

Therefore, modeling is not necessary for every contaminated site for which NA processes are to be assessed. The use of models in contaminated site management is determined, among other things, on the basis of the following:

- the state of the respective investigation (--> existing data density)
- the requirements for model accuracy (→ description or prognosis),
- site-specific attributes (→ heterogeneity of the subsurface as well as contaminant distribution / composition)
- specific goals in further site processing (--> Deepened investigation programme, remediation).

Therefore, the general framework conditions for NA models are not significantly different from those of established flow and transport models. Regardless of which model approach is used (simple analytical Excel table or highly parameterized complex numerical model), the underlying site-specific concept model and the hydro geological model must be plausible and supported by field data. The decisive responsibility here lies with the geoscientific staff and modeling staff. In the simplest case, an analytical approach to the remediation investigation can be enough to provide a reliable prognosis of the site development. In the "*worst-case*", even a costly numerical model fails to provide the precision required for the MNA concept to be accepted.

Fig B-3 shows the characteristics and uses of the various models. No recommendation is made for individual software products. An overview of selection criteria and possible uses when selecting models for NA processes is provided in ASTM (1999) [19]. Please note however that developments in the software market are rapidly advancing and even this report no longer contains all current model systems.

It must also be noted that all models are subject to the "model paradox" which states that no model can combine all three attributes of "Quick", Inexpensive" and "Good". This basically means that the selection of a model must always be adapted to the respective state of knowledge, project purpose and available budget.

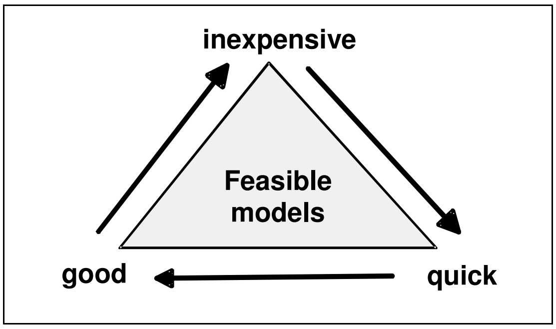

Fig. B-3: Model paradox

B-6 Limits of modeling

When assessing the natural contaminant reduction potential of a site, two core questions are generally asked:

- in what spatiotemporal condition is the contaminant plume in the groundwater? (definition of reaction space) i.e. has the maximum expansion of the contaminant plume been reached?
- How long will the contaminant plume exist? (definition of reaction time)

With correct use, most analytical and numerical models on contaminant structure and transport can answer the first question with suitable site data. To answer the second question, there are only a limited number of complex models which are able to realistically predict the temporal development of the contaminant source (transfer conditions, multiphase flow). The active processes of contaminant release from the source (source intensity) decisively determine the “lifespan” of the contaminant plume. This mainly involves subsequent delivery processes from the saturated and unsaturated soil zones (capillary forces) and complex solution processes from residual and NAPL phases of contaminants which have entered the groundwater.

The use of complex models that are able to provide a sufficiently clear image of the contaminant source generally places high demands on data and on processing personnel. Therefore, with the current state of the art and technology, it is only usable for an economically oriented damage case, and can therefore not be realized within the framework of the other processing parameters. Also, the costs for this are very high. Therefore, in present engineering practice, such model creation should be regarded critically, and attention increasingly directed to analysis data from monitoring as well as other site conditions.

If, however, the contaminant source is removed, as required by various stakeholders for acceptance of an MNA concept, prognosis is possible for degressive plume development with less modeling costs, and can provide a much clearer prediction of its temporal development.

The precision of NA process models is largely dependent on onsite factors and the data situation, as well as the recording, and implementation of the conceptual subsurface model into the mathematical model. Improving the quality of prognoses by using complex model systems is only possible if there is a suitable database. It is quite possible to obtain comparatively precise and cost effective results with simple analytical approaches.
Note that NA process models are less precise than flow models. While flow models can achieve absolute high precision, models for material transport and degradation tend to have an estimating character. A proper onsite monitoring programme is required for validation, with model recalibration if necessary. This improves the quality of the prognosis.

B-7 Summary

It is the processing personnel's responsibility to make the model selection with a view to abstraction possibilities. The respective inquiry status (available data density), model prognosis requirements and goal setting (needs) significantly determine the options for the use of a model. In the simplest case, an analytical approach to the remediation investigation can be enough with an adequate database to provide a reliable prognosis of the onsite developments. In the worst case, even a costly numerical model (FE or FD) will not provide the precision required to support acceptance of an MNA concept unless the transport parameters, the degradation rate variance and the source intensity (transfer conditions) are sufficiently quantified.

Models can be used at all processing stages to

- create the conceptual subsurface model and model the subsurface processes (system and process comprehension),
- calculate the concentrations or loads at a site where there is either no measurement data (space interpretation) or for which there is no measurement data for the relevant time (future prognosis).
- record and assess the interventions into the natural regime, e.g. by active remediation.

Regardless of which model was used for what purpose, model results must be validated in subsequent project phases, and must always be subjected to critical verification.

B-7.1 Model systems and authors

B-7.1.1 Analytical models

- Bioscreen (Version 1.4, 1997) - Natural Attenuation Decision Support System - Air Force Center for Environmental Excellence
  http://www.epa.gov/ ada/csmos/models/bioscrn.html.
- Biochlor (Version 1.0, 2000) - Natural Attenuation Decision Support System - Air Force Center for Environmental Excellence
- http://www.epa.gov/ada/csmos/models/biochlor.html#Installation
- Bioplume (Version 1.0, 1997) - US Geological Survey
  http://www.epa.gov/ ada/csmos/models/bioplume3.html
- NAPLANAL (Version 1.0, 1997)
  http://www.dukeengineering.com/ htdocs/services/environ_remedi_1d.shtml, Shareware
- NAS (Version 1.3.0) - US Geological Survey, Naval Facilities Engineering Command, Virginia Tech
  http://www.cee.vt.edu/NAS
- LNAST (Version 1.5) – American Petroleum Institute
  http://www.aquiver.com/1987b1.htm (also see: http://api-ep.api.org)

B-7.1.2 Numerical models

- Modflow family incl. MT3D or RT3D - (U.S. Geological Survey, U.S.EPA, Papdopoulos etc.)
- Visual Modflow, Waterloo Hydrogeologic
  http://www.flowpath.com, ca. € 2.500.
- Processing Modflow (PMWin) - Wen-Hsing Chiang,
  http://www.pmwin.net/pmwin/index.htm, ca. € 1.000.
- Groundwater Vistas - Environmental Simulations International
  http://www.groundwater-vistas.com, ca. € 1.000.
- GMS - US Army (DOD) & Brigham Young University
  http://www.gms.watermodeling.org, ca. € 1.000 to € 6.000
- Spring
  http://www.gkw-gmbh.de,

- FeFlow - WASY GmbH Berlin

  http://www.wasy.de, €990 to € 6.990

- AQUA3D

  http://www.scisoftware.com, ca. € 1.000.

- UTCHEM – University of Texas

  http://www.pe.utexas.edu/CPGE/UTCHEM, MSDOS-Freeware

- MS-VMS (Modflow-Surfact) - HydroGeoLogic

  http://www.hgl.com, ca. € 4.000.

- Richy – Uni-Erlangen

  http://www.am.uni-erlangen.de/am1/software/RichyDocumentation/Main.html

Appendix C Monitoring

C-1 Goal of monitoring

Monitoring NA processes has the goal of verifying the prediction of contaminant reduction resulting from natural degradation and retention.

Depending on the particular nature of the task, suitable investigation strategies must be developed, and investigation methods applied. After extensive parameter studies were done in the preceding steps during investigation of processes (step 2 of phase 1 of the MNA concept, see Chapter 5.3.3), leading to proof of principle for the effectiveness of NA processes, key parameters are selected as part of the monitoring process (see Table 5-1) to enable the NA processes to be monitored and quantified.

Prediction is normally based on measurement data obtained during phase 1 (see Chapter 5.3.3). The reaction system “down gradient plume” can, however, undergo changes over long time periods. This must be taken into account in the development of the monitoring programme. In this context, it is necessary to record changes in hydro geological, geochemical, microbiological and other general conditions which can influence the efficiency of NA processes. Monitoring procedures including costs must be specified in a monitoring programme.

C-1.1 Site monitoring network, monitoring intervals and monitoring programme

The customized geological and hydro geological site investigation is the basis for the assessment of NA processes and subsequent further investigation in the field using monitoring wells. Monitoring wells are installed in compliance with current standards, regulations and expert recommendations.

When installing an observation well network suitable for monitoring, knowledge of the plume geometry as well as precise familiarity with the groundwater flow direction (hydraulic gradient, groundwater flow velocity) as well as the hydro geological subsurface conditions (stratigraphy, hydraulic permeability, transmissivities and storage coefficients, vertical permeability profiles, dispersivity, porosity) are needed. If the location of the contaminant source is also known, it is also possible to estimate the likely position of the down gradient plume without initially sampling observation wells. Helpful recommendations for developing an MNA monitoring network are provided by Martus and Püttmann in [25] (cf. [26]).

In the following, two cases are differentiated. If the plume is relatively small, it is often difficult to find a suitable ratio of observation wells to plume size. In these cases, sampling the observation wells with the aid of pumping tests can be useful. This involves calculating the total contaminant mass flux in the investigated area from the concentration-time series (immission pumping test). Pumping tests are carried out at a defined control plane within the contaminant plume. The positions of one or more pumping wells as well as the pumping rates and times are selected so that the contaminant plume is completely included across its full width (emission). The concentration-time series are measured for one or more substances in the pumping wells during pumping. Analytical or numerical evaluation programs are used to determine the average concentrations in the well capture zone from the concentration-time series, and the total contaminant mass flux at the investigated control planes can be determined on the basis of the flow and transport model. The contaminant degradation at a site can be quantified by comparing the contaminant mass fluxes across several control planes located at varying distances from the contaminant source.

In large plumes, it is often necessary to install numerous groundwater observation wells to obtain a suitable ratio of observation wells to plume size [20]. Standard sampling methods can be used.

In addition, it must be noted that observation wells should be present both within the plume and in upstream direction (to assess background values), within the contaminant source (to assess source strength) as well as downstream of the contaminant plume (assessing the water quality in “unaffected” areas; compliance monitoring wells).

Regarding the construction of groundwater observation wells, the standard contaminated site management practice is to screen observation wells across the entire aquifer in which the contaminant plume resides. However, because the spread of contaminants is greatly influenced by subsurface heterogeneities (in some cases, formation of flow channels) and contaminant plumes also move into deeper sections of the aquifer along the direction of spreading – caused by groundwater recharge due to precipitation – sampling of fully screened observation wells may underestimate the actual contaminant concentrations due to dilution resulting from inflow of unaffected groundwater while obtaining samples, and misinterpretation of the position of the contaminated strata. Furthermore, when installing fully screened observation wells, hydraulic short circuits are often created which change the hydraulic regime with lasting and qualitatively significant displacement of contaminants. This is another aspect which demands careful planning and control after installation.

The observation well design described above is not suitable for a more detailed assessment of the spatial position of NA relevant substances. This requires the installation of multilevel observation wells along the direction of the contaminant plume spreading. They are used to determine the vertical distribution of contaminant concentrations. This involves the installation of observation well networks to investigate different aquifers or horizons according to DVWK Technical Bulletin No. 245/1997 [21] and LABO [22]. Observation well networks consist of separate observation wells set at specific depths. The installation of observation well bundles, i.e. observation wells screened at varying depths and installed as a bundle in one borehole, is not recommended. The length and position of the screen must be adapted to the depth range required. Here, it is absolutely vital to limit the screen length to max. 3 m, because with longer screens there is a risk of creating hydraulically mixed potentials, which cause mixed concentrations at the observation well.

The screen must not be near boundaries between different geological layers or heterogeneities. One should aim for the largest possible screen surface. Therefore, additional geophysical measurements should be conducted at the respective observation wells after well construction in unconsolidated sediments and prior to well construction in bedrock.

The borehole diameter must be adapted to the casing diameter, whereby the distance between the borehole wall and the observation well pipe must be at least 80 mm in every direction according to DVGW Technical Bulletin W 121 [23]. The annulus in the screened area is filled with washed quartz gravel or quartz sand according to DIN 4924 [24]. The filter grain size must be at least twice as large as the slot width of the screen. To avoid hydraulic short circuits, the various sampling horizons must be separated by suitable clay seals. Further considerations for observation well construction are given in [22].

Observation wells are often already present from earlier investigation phases. If it is planned to use such observation wells in the investigation programme, a suitability test according to DVWK Technical Bulletin no. 245/1997 [21] should be conducted. Continuously screened observation wells do not permit depth oriented sampling using standard sampling methods. In such cases, packer sampling with simultaneous protective pumping or "simultaneous pump rate method “facilitates the collection of depth oriented samples. The same processes must also be used when using multiple-screened observation wells because the risk of induced exchange flow close to the observation well may produce erroneous results.

C-2 Monitoring programme

A minimum monitoring programme includes the standard parameters obtained by sampling (groundwater level, field parameters: O_2, pH, E_h, temperature, electrical conductivity), as well as the contaminant concentrations. This allows for a monitoring and detection of changes in the spread of the contaminant plume. Additionally, general information on the biogeochemical environment is obtained. Detailed groundwater monitoring programmes with checklists are available for specific contaminant groups (including CHCs, BTEX, TPH and PAHs) in [28].

The minimal monitoring programme does not reveal whether there is still a sufficient supply of electron acceptors or electron donors. To minimize costs, concentrations – at least in larger contaminant plumes – should be measured at larger intervals, but not less than every three years.

The frequency of observations depends on the individual case. In general, resampling is needed every 6 to 12 months. The sampling frequency can be extended when very low groundwater velocities are involved. The sampling frequency can be correspondingly reduced at a later date. Overall, monitoring needs have to be flexible.

After the objectives have been reached, monitoring should continue for at least three years to ensure that residual contaminant concentrations remain below target values in the long term (follow-up monitoring).

C-3 Success criteria

The basis for the determination of success is the prediction for the temporal spread of the contaminant plume. Acceptance by the authorities also requires defined compliance criteria for evaluating performance. Reflecting the prediction, it is therefore possible to determine what residual concentrations should be attained at what time for each individual observation well. An agreement might therefore read as follows: After n years, x % of all observation wells must show concentrations less than or equal to the value predicted for them. After 2 x n years, the criterion must apply to y % of all observation wells. After m years, it must apply to all observation wells.

Alternatively, mass flux assessments can be conducted according to the administrative regulations of LfU Baden-Württemberg [28]. It is helpful to specify the precise course of action in a public-law contract, including a schedule (see Chapter 5.1.5). If remediation performance is below target, BBodSchG permits making provisions as a security for a contingency plan (e.g. equivalent to the costs for implementing active remediation measures).

C-4 Costs

Actual monitoring costs can be estimated even for long time periods with the help of the net present value method, which is commonly used today. This process takes fictional capital gains into account for expenditures to be provided at a later date, and thus enables monetary comparison of investment and O&M (monitoring) costs. A time period is estimated for the duration of monitoring. The longer the duration, the smaller the influence on costs. Costs are calculated as follows:

$$\mathrm{PCCV} \quad = \quad I_0 + \sum_{t=0}^{n} A_t \cdot (1+i)^{-t}$$

where PCCV = project net present value, I_0 = investment spending, A_t = payout at time t, i = adequate target rate, t = period index (t0 to t_n = investment period and $(1 + i)^{-t}$ discount factor for period t

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