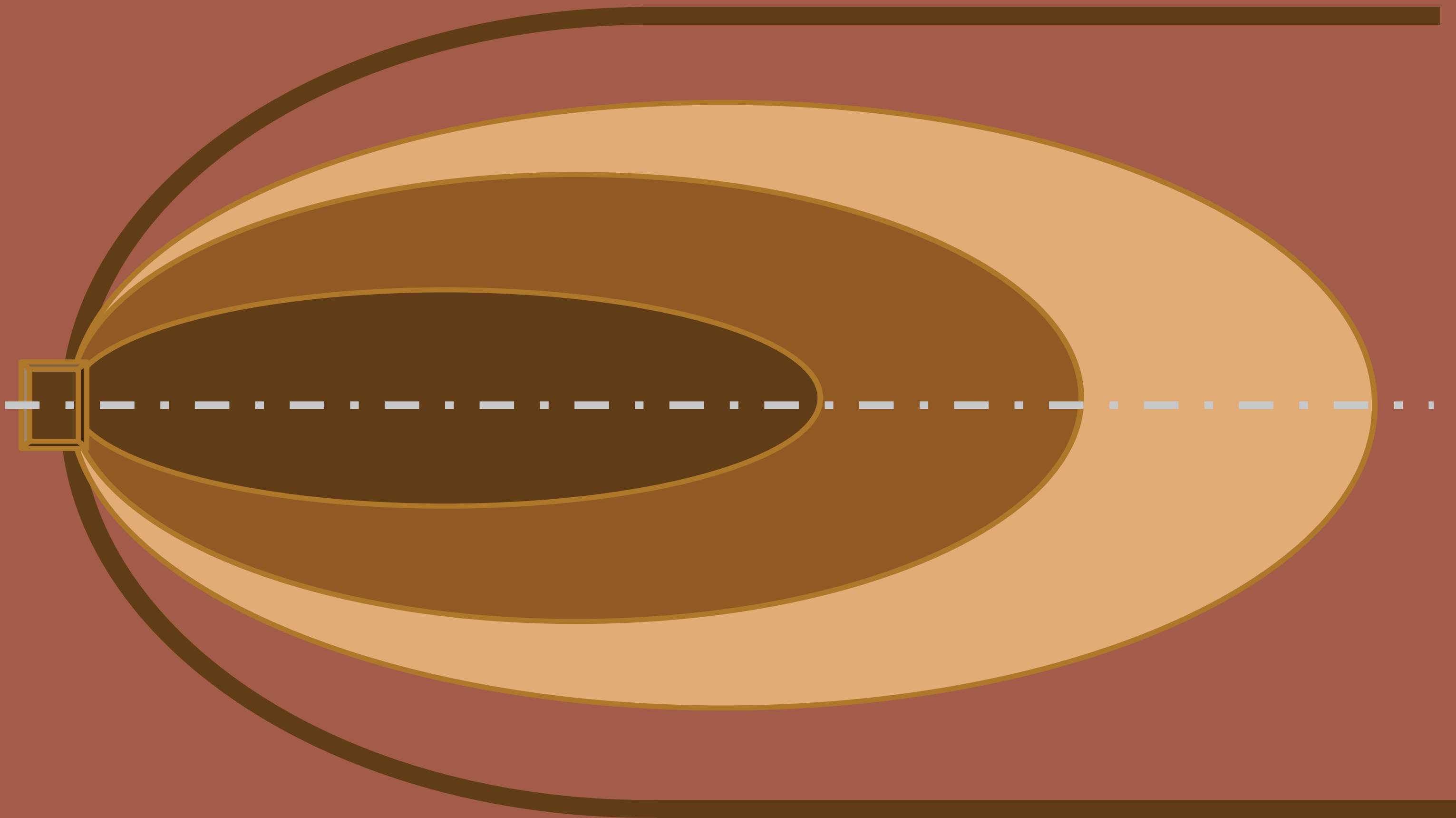
CONSIDERATION OF NATURAL ATTENUATION



IN REMEDIATING CONTAMINATED SITES

Umwelt
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Für Mensch und Umwelt

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FEDERAL / STATE WORKING GROUP ON SOIL PROTECTION – LABO

CONTAMINATED SITE COMMITTEE – ALA

AD HOC SUBCOMMITTEE "NATURAL ATTENUATION"

CONSIDERATION OF NATURAL ATTENUATION

IN REMEDIATING CONTAMINATED SITES

POSITION PAPER

OF 10/12/2009

The position paper of 01/06/2005 was revised by the Ad hoc Subcommittee "Natural Attenuation" of the Contaminated Site Committee (ALA) of the Federal/State Working Group on Soil Protection (LABO).

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Please note:

This paper is a translation by order of the Federal Environment Agency.

CONTENT

0 SUMMARY

Upon the proposal submitted by its Standing Committee 5 (Contaminated Sites Committee – ALA) the Federal / State Working Group on Soil Protection (LABO) employed an ad hoc subcommittee dealing with considering natural attenuation in remediating contaminated sites and preparing an inter-State position paper. It involves:

- a definition of the terms NA, MNA and ENA,
- a consideration of the legal problems in connection with including them in the remediation of contaminated sites,
- the prerequisites for implementing a MNA concept and
- a recommendation relating to approaches to be adopted in practice.

The position paper is restricted to a consideration of natural attenuation in the saturated zone containing information on groundwater damage caused by contaminated sites. In this paper the following terms are used and defined:

- Natural attenuation processes are biological, chemical and physical processes without human intervention resulting in a reduction of the mass, load, toxicity, mobility, volume or the concentration of a contaminant in soil or groundwater. These processes involve biological degradation, chemical transformation, sorption, dispersion, diffusion and evaporation of contaminants.

Natural attenuation (NA) is the result of natural attenuation processes.

- Monitored natural attenuation (MNA) are monitoring measures for controlling the effectiveness of natural attenuation processes.
- Enhanced natural attenuation (ENA) is considered to be an in situ remediation measure because by initiating, stimulating and supporting natural attenuation processes with the input of substances using the natural reaction space the process is actively intervened.

The short term “MNA concept” is introduced to enable the authorities to decide to not envisage remediation measures in connection with MNA with regard to natural attenuation and its appropriateness. A MNA concept contains basically the following components of a regulation:

a) fixing of verifiable targets in time and space based on prediction considered as the necessary result of the natural attenuation processes and of intermediate results for the time up to reaching the fixed terminal state,

b) fixing of monitoring measures for checking the effectiveness of natural attenuation processes (MNA) and of obligations to reporting,

c) reservation of further measures if the prediction would prove to be inapplicable up to reaching the fixed terminal state.

Such an approach requires investigations to prove the effectiveness of attenuation processes, their prediction and a verification of the site-related prerequisites and may be adopted only in connection with checking if the remediation measures technologically taken into consideration will be appropriate.

Under the soil protection law natural attenuation processes are classified as site conditions relevant to assessment. As monitored natural attenuation (MNA) does not actively affect the current process it may not be put on a level with a remediation measure in accordance with the Federal Soil Protection Act. In the view of a majority MNA may not be classified as a protection and restriction measure pursuant to Art. 2 (8) of the Federal Soil Protection Act including equally active technological or administrative measures.

It would be reasonable to enforce the regulations described above under a) to c) by an administrative ordinance, by adopting a remediation plan or concluding a contract under public law. If the authority will unilaterally give sovereign orders in the case of contaminated sites Art. 15 (2) of the Federal Soil Protection Act lends itself as legal basis for taking over monitoring measures and obligations to reporting (in particular as regards remediation measures and the additional consideration of natural attenuation).

In the case of a gradual remediation of contaminated sites special investigations of the natural attenuation processes will, as a rule, be only useful from the detailed investigation onwards. In this case natural attenuation may be only considered when assessing a hazard so that a decision on a MNA concept may be only made based on a hazard assessment. Thus, the prerequisite for implementing a MNA concept is that a sole remediation will be inappropriate.

Furthermore, it is necessary that site-related investigations will be carried out to check the prerequisites for implementing a MNA concept and to assess it subsequently in the individual case. Here, the following subjects play a decisive part:

- consideration of the contaminant source including the decision how to deal with it,
- consideration of the contaminant plume, notably the prediction of the plume behaviour,
- determination of the relevant natural attenuation process on site and
- consideration of the groundwater not yet affected and further protected objects.

Recommendations are given as a decision aid for evaluating site-related investigations and prerequisites. They imply in short that for implementing a MNA concept

- the contaminant quantity in the source or the discharge of contaminants from it should be reduced to prevent further hazards for groundwater or further protected objects and/or to reduce the period of existence of a groundwater damage,
- all load reducing processes (such as biological degradation, chemical transformation, sorption) should have an essential share in the contaminant attenuation and diluting processes should play only a subordinate part,
- results of investigations have to be available on the basis of which the development of a plume could be predicted and
- the prediction should show that the contaminant plume is “quasi stationary” or shrinking, thus allowing to exclude a contamination of the groundwater not yet affected or a hazard for further protected objects.

Carrying out MNA as sole measure will be only possible if after the assessment of hazards the site-related prerequisites will be fulfilled in the individual case and remediation measures are assessed to be inappropriate. If a remediation as sole measure will be appropriate a MNA concept will not be taken into consideration. In addition, knowing the effectiveness of attenuation processes will in the framework of a remediation investigation serve also the assessment of remediation measures (discretion in selecting) and fixing of remediation targets. Carrying out MNA may be then appropriate in connection with or after a remediation. It is to be expected that MNA concepts will take effect preferably in connection with remediation measures.

A potential approach to preparing a MNA concept in practice will be outlined in a separate Annex

(Annex 1). It involves the following steps:

- investigations to determine and assess natural attenuation processes and to predict their efficiency,
- consideration of the results in verifying the appropriateness of measures and targets of measures,
- planning and implementing of monitoring to check the effectiveness of these processes (MNA) and
- checking if these targets of the measures will be permanently fulfilled.

In the present position paper the way how to consider natural attenuation in practical remediation of contaminated sites is described. The systematic approach outlined allows an understandable decision-finding. A way is shown how the competent soil protection authorities may exercise discretion and in the framework of checking the appropriateness of measures may decide on the implementation of MNA based on a MNA concept. It is, however, also explained that when carrying out MNA a decision always made in an individual case is concerned which should be made in a close agreement between the obligated party and the authority.

Annex 2 should serve as an aid to select methods, experiences and approaches with a view to the prerequisites to be checked for implementing a MNA concept. It provides a selection of methods relevant to the problems to be dealt with and classified as being suitable for practice.

In particular, methods and instructions from the funding priority KORA “Controlled Natural Retention and Attenuation of Contaminants in Contaminated Soil and Contaminated Groundwater Remediation” of the Federal Ministry of Education and Research are mentioned. They are supplemented by further findings, developments and experiences.

1 REASON, COMMISSION AND FIELD OF APPLICATION

REASON

The assessment of contaminated sites requires to know the spatial and temporal development of contamination in soil and groundwater. The situation in contamination determined in the framework of exploratory and detailed investigations forms the basis of a hazard assessment which may then lead to remediation, protection or restriction measures.

The experiences gathered with remediating contaminated sites show in the majority of harmful soil changes and contaminated sites that only on a limited scale the "status quo ante" may be restored by carrying out remediation measures and the remediation targets as agreed may frequently not be reached. This is mostly due to the fact that it is not possible to determine sufficiently the effectiveness of the processes determining the spreading of contaminants before making the decision for a remediation. For this reason, it is in practice frequently only possible to carry out partly suitable or to a certain extent successful remediation measures.

Thus, after carrying out a remediation over many years in spite of a contaminant potential still existing further cost-intensive measures will not be considered to be appropriate and the residual contamination will have to be left to natural attenuation. Against this background the fact if natural attenuation may be considered as a supplementation or alternative to remediation measures is discussed before making a decision on a remediation.

Thus, knowing natural attenuation, its assessment and subsequent consideration in making decisions on remediation measures is attached increasing importance in remediating contaminated sites. The actual discussion on natural attenuation and the increasing number of inquiries submitted to enforcement agencies with a uniform basis suitable for enforcement and recommendations lacking show the necessity to deal with this subject on an inter-State level and to take a concerted position. For the time being, complex rules [1, 2] the subject of which is the consideration of natural attenuation processes when remediating contaminated sites exist only in a few Federal State.

COMMISSION

Upon the proposal submitted by its Standing Committee 5 (Contaminated Sites Committee – ALA) at its 24th session the Federal / State Working Group on Soil Protection (LABO) employed an ad hoc subcommittee dealing with considering natural attenuation in remediating contaminated sites and preparing an inter-State position paper on it. Here, in particular, a definition of the terms natural attenuation, monitored natural attenuation and enhanced natural attenuation and their classification in the remediation of contaminated sites was to be prepared, legal aspects had to be considered, the prerequisites for considering it in their enforcement were to be stated and a possible approach to be applied in practice was to be shown. The position paper was released for publication by the circular resolution no. 17/2005 of the Conference of Environment Ministers as per 01/6/2005 and recommended to the States for application.

Upon the proposal submitted by the Contaminated Sites Committee LABO at its 33rd session employed once more an ad hoc subcommittee "Natural attenuation" which had to check the content of the position paper "Consideration of the natural attenuation processes in remediating contaminated sites" of 01/06/2005. The subcommittee had to find out whether owing to the results prepared in the funding priority KORA "Controlled Natural Retention and Attenuation of Contaminants in Contaminated Soil and Contaminated Groundwater Remediation" of the Federal Ministry of Education and Research the position paper had to be altered or supplemented. Apart from that, the subcommittee had the task to evaluate the results of the funding priority KORA (recommendations for action/branch guides) in particular with a view to the problems relevant from the viewpoint of implementation.

FIELD OF APPLICATION

The content of this position paper is restricted to the consideration of natural attenuation in the saturated zone containing information on groundwater damages caused by contaminated sites. Thus, on the one hand, an overlapping with the ad hoc subcommittee "Leachate Prediction in the Detailed Investigation" is avoided which, a. o., deals with considering natural attenuation in the unsaturated zone in the framework of leachate prediction. On the other hand, the considerations will be only started after a groundwater damage[1] was detected, i.e. the assessment if a groundwater damage exists had been concluded. In a joint committee of LABO and LAWA [3] assessment aids were prepared (in particular for the terms from Art. 4 (7) of the Federal Soil Protection Ordinance [4] "in the long run", "locally"[2] and ""small contaminant loads"[3]).

Specific support e.g. in applying specific methods of investigation or the possibilities of MNA for various contaminant groups can be found in the funding priority KORA of the Ministry of Education and Research which reviewed these subjects comprehensively in a recommendation for action with a collection of methods [5] and branch-specific guides [6, 7, 8, 9, 10, 11].

The term remediation is used in this paper in accordance with Art. 2 (7) of the Federal Soil Protection Act [12], remediation is defined as active technical measures

- to eliminate or reduce contaminants (decontamination measures),
- that prevent or reduce spreading of contaminants in a lasting way without eliminating the contaminants themselves (securing measures) and
- that eliminate or reduce harmful changes in the soil`s physical, chemical or biological characteristics.

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1 We can only speak of a groundwater damage if the insignificance threshold in groundwater has been exceeded.

2 The term „locally" refers exclusively to contaminant concentrations in leachate or other contaminant drag-out into groundwater resulting only locally in an increased contaminant concentration in groundwater. It does not describe if the contaminant plume is locally restricted in the sense of stationary. Further comments see [3].

3 The term „small contaminant loads" refers exclusively to the contaminant concentration in leachate or other contaminant drag-out into groundwater and not to contaminant loads in groundwater. Further comments see [4].

2 DEFINITION OF TERMS

When dealing with this subject it is necessary to define the terms **N**atural **A**ttenuation (NA), **M**onitored **N**atural **A**ttenuation (MNA) and **E**nhanced **N**atural **A**ttenuation (ENA) at present spread in practice, however used in different ways, thus providing the basis for a uniform understanding of the terms. Hereby, a German nomenclature is adopted for the terms taken over from U.S.A. which is recommended for future use in practice.

Natural attenuation processes in accordance with this paper – following the OSWER directive of U.S. EPA [13] - are biological, chemical and physical processes causing, without the intervention of man, a reduction of the mass, load, toxicity, mobility or concentration of a substance in soil and groundwater. These processes involve biodegradation, chemical transformation, sorption, dispersion, diffusion and volatilization of the substances.

The result of these processes is **natural attenuation (NA).**

Monitored natural attenuation (MNA) in accordance with this paper means measures to monitor the effectiveness of natural attenuation processes. This term is hereinafter abbreviated with **MNA**.

Enhanced Natural Attenuation (ENA) is considered here as an "in situ" remediation measure because by initiating, stimulating or supporting natural attenuation processes with the input of substances using natural reaction spaces the processes are actively intervened. In the present position paper ENA is classified as a remediation measure according to the Federal Soil Protection Act. In the present position paper ENA is, as a rule, a use of water bodies subject to permission pursuant to Art. 3 (1) sentence 5 and (2) sentence 2 of the Federal Water Act (WHG).

The short term "**MNA concept**" is used hereinafter for an official decision renouncing remediation measures (preliminarily, partially or by exception completely) with regard to natural attenuation and their appropriateness in connection with MNA. A MNA concept contains basically the following components of a regulation (Chap. 3):

a) fixing of verifiable targets relating to space and time which based on the prediction are considered as the necessary result of natural attenuation processes and the intermediate results for the time up to reaching the fixed terminal state,
b) fixing of measures to monitor the effectiveness of natural attenuation processes (MNA) and of obligations to reporting,
c) reservation of further measures if the prediction has later proved to be inapplicable up to reaching the fixed terminal state.

Such an approach requires investigations to prove the effectiveness of attenuation processes, their prediction and checking of the site-related prerequisites (Chap. 4 and Annex 1) and may be adopted only in connection with checking if the remediation measures technologically taken into consideration will be appropriate (Chap. 5).

3 CONSIDERATION OF NATURAL ATTENUATION IN ADMINISTRATIVE PROCEDURES RELATING TO SOIL PROTECTION LAW

Natural attenuation processes form part of the **site conditions relevant to evaluation** (circumstances of each individual case) which are to be taken into account when carrying out exploratory and detailed investigations and evaluating their results (Art. 4, (1) and (4) of the Federal Soil Protection Ordinance). If necessary, a deepening investigation of natural attenuation processes form part of a remediation investigation.

The determination of natural attenuation processes concerns measures of investigation the suitability, requirement and appropriateness of which depends on the circumstances of the individual case at the various stages of exploratory, detailed and remediation investigations.

Natural attenuation may be included in the gradual remediation of contaminated sites and groundwater damages caused by contaminated sites in accordance with Fig. 1. Annex 1 contains recommendations for action in practice.

According to Art. 2 (3) of the Federal Soil Protection Ordinance the **exploratory investigation** aims at finding out whether the suspicion of a contaminated site or an adverse soil alteration can be ruled out or whether there is reasonable suspicion within the meaning of Art. 9 (2) of the Federal Soil Protection Act (possibly due to the reasonable suspicion of a pollution of water emanating from the area concerned).

As a rule, this task is to be accomplished by the competent authority ("official investigation"). Owing to the task to be accomplished (investigation of hazards, not yet measures to prevent hazards or to eliminate damage) the authority has to achieve a clarification at the lowest possible expenditure. That is why an investigation of attenuation processes is basically not required in an exploratory investigation.

If it is intended to include the determination of natural attenuation processes or factors relevant to them also in a subsequent arrangement of investigations the findings available should, however, allow an assessment of the importance of these processes in the respective case.

If as a result of the exploratory investigation or specific criteria determined otherwise there is reasonable suspicion of a contaminated site or a harmful soil change pursuant to Art. 9 (2) sentence 1 of the Federal Soil Protection Act the competent authority may order the obligated parties to carry out the studies necessary to assess hazards **(detailed investigation).** This includes investigations to assess the development of the effects caused by a contaminated site. If a groundwater damage caused by contaminated sites was detected the obligated party may basically be asked to carry out investigations to detect attenuation processes at this stage. Also series of investigations to detect the temporal courses of attenuation processes may be the subject of investigations ordered according to Art. 9 (2) sentence 2 of the Federal Soil Protection Act: Pursuant to Art. 3 (7) of the Federal Soil Protection Ordinance in the framework of such orders also "recurrent investigations of the contaminant spread and the relevant circumstances are another possibility."

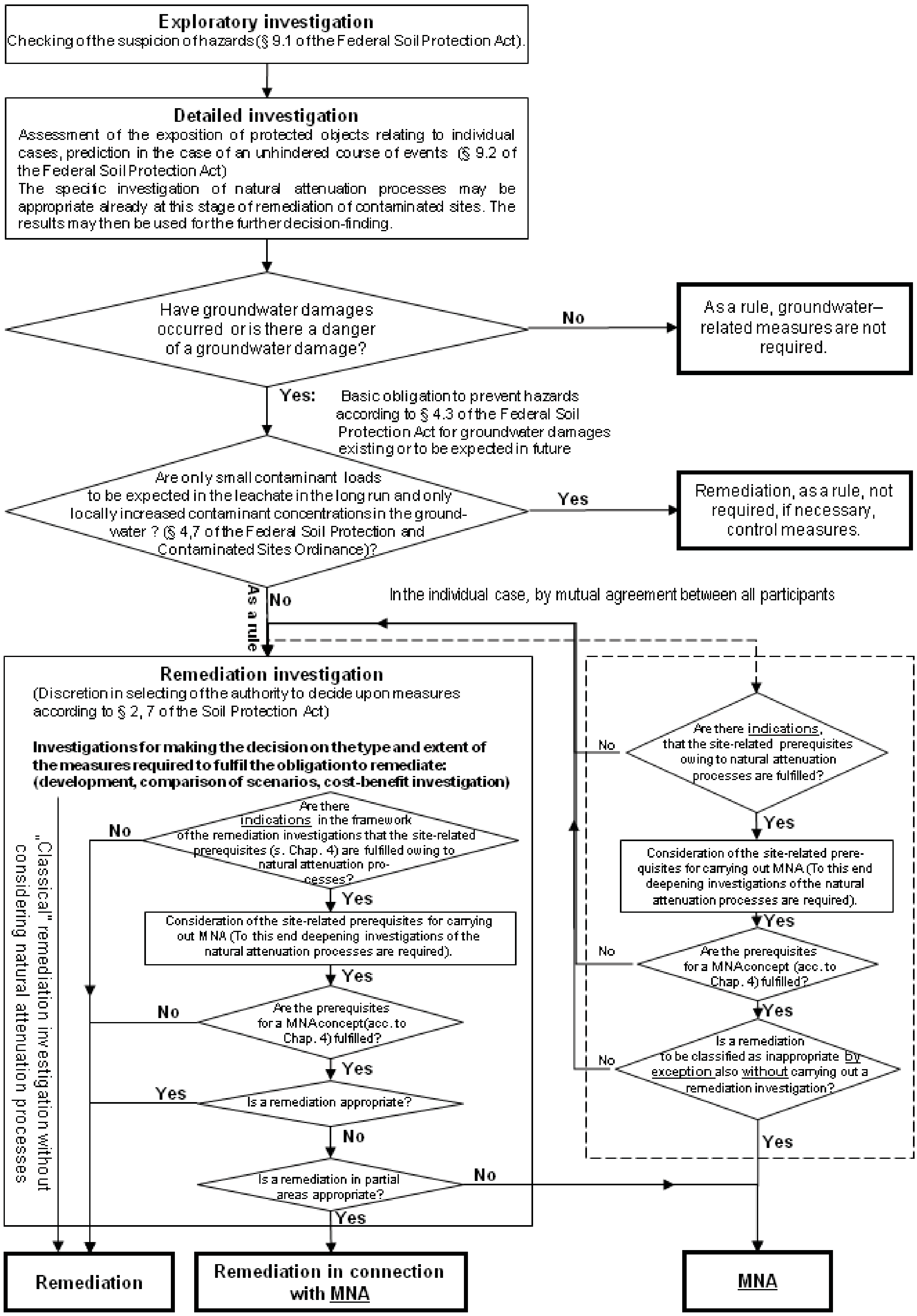

Fig. 1 Consideration of natural attenuation in remediating contaminated sites

The appropriate determination of natural attenuation processes concerns preferably expensive, specific investigations exceeding by far the usual determination of contaminant concentrations which apart from the quantitative assessment involve also a prediction of the effects of the processes. An obligation to assess the development of a contaminated site or the effects caused by a harmful soil change follows basically from Art. 9 (2) of the Federal Soil Protection Act. That is why a decision whether and at which state of detection special investigations will be required for this purpose and whether an obligated party may be charged with them may be only made in the individual case and with regard to further measures intended. For reasons of appropriateness respective orders will be a possibility rather in a minor portion of cases. An order will be excluded, in particular, if it is already foreseeable that natural attenuation does not play a remarkable part when deriving or ordering further measures.

That means that a deepening investigation of the natural attenuation processes requires possibly that the authority due to intermediate results will make respective considerations (refraining partly or completely from a remediation ordinance) and inform the obligated party on it.

Pursuant to Art. 4 (3) ff. of the Federal Soil Protection Act the obligated party, however, is free to carry out such investigations at its own initiative and to include the results in the further decision-finding.

Respective results are to be considered when deciding on further measures to prevent dangers. In addition, these results serve the risk assessment of protected objects not yet affected.

When determining suitable, required and appropriate measures to fulfil the obligations to prevent risks in the framework of a **remediation investigation** [Art. 13 (1) of the Federal Soil Protection Act] natural attenuation processes may be investigated and considered if monitoring of the effectiveness of such processes as an accompanying measure is taken into consideration. Relevant attenuation processes have to be determined and a quantitative assessment of their effectiveness which is to be considered in the decision on remediation measures by the authorities has to be made at this stage of remediation of contaminated sites. Here, in particular, variants may be considered by means of which remediation measures considering the natural attenuation processes detected may contribute to reaching the remediation target. Art. 13 (1) in the same way as Art. 9 (2) provide a legal basis for the soil protection authority to demand respective investigations.

The **decision of the soil protection authority** to refrain partly or completely from a remediation order with regard to the findings on natural attenuation [estimation according to Art. 10 (1) of the Federal Soil Protection Act] requires urgently to carry out appropriate investigations of the type and extent of the natural processes and to make a prediction of their effectiveness and the future spread of contaminants.

Natural attenuation may only be considered in connection with reviewing the site-related prerequisites (Chap. 4) and in connection with checking the appropriateness of the technologically possible remediation measures (Chap. 5).

An official decision according to which remediation measures in connection with MNA shall be (preliminarily, partly or by exception completely) dropped with regard to natural attenuation and their appropriateness contain basically the following regulations:

a) fixing of verifiable targets relating to space and time which based on the prediction are considered as the necessary result of the natural attenuation processes and the intermediate results for the time up to reaching the fixed terminal state,
b) fixing of measures to monitor the effectiveness of natural attenuation processes (MNA) and of obligations to reporting,
c) reservation of further measures if the prediction will later prove to be inapplicable up to reaching the fixed terminal state.

Monitoring of natural attenuation **(MNA)** may involve various technological steps. They reach from sampling (groundwater, if necessary soil and soil air), via analyzing risk- and process-related parameters and evaluating the analytical results up to checking the prediction process. MNA monitors basically "only" the processes determined before as being relevant with raising the question whether they will go on in future resulting in an attenuation of contaminants as it was detected at the time when the decision on a MNA concept was made, thus allowing to renounce a remediation measure partly.

It is acceptable to adopt the regulations described in items a) – c) by an official order, by the approval of a remediation plan or by concluding a contract under public law. As far as the authorities will unilaterally give sovereign instructions Art. 15 (2) of the Federal Soil Protection Act lends itself as legal basis for monitoring measures and obligations to reporting (in particular in the case of remediation measures and additional consideration of natural attenuation). The "obligated parties" pursuant to Art. 4 (3), (5) and (6) of the Federal Soil Protection Act may be interpreted as a designation of a group of people which may be requested to carry out self-monitoring measures in accordance with Art. 15 (2) of the Federal Soil Protection Act by the authority even if remediation or protection measures will not be requested at the same time. As far as monitoring measures are to be essentially justified by the fact that the success of remediation measures not eliminating all contaminants has to be observed a justification pursuant to Art. 15 (2) sentence 4 of the Federal Soil Protection Act will be possible.

After the decision was made to renounce partly or completely a remediation order owing to findings on natural attenuation the administrative procedure will further remain unsettled as it is shown by the continuous obligations to monitoring and reporting and the respective control by the authority and, if necessary, by an expert. We may proceed on the fact that natural attenuation processes take essentially longer time to reach a defined target of contaminant attenuation than remediation measures according to the Federal Soil Protection Act. Natural attenuation processes proceed also without the intervention of man and without monitoring according to MNA. The monitoring regulations of a MNA concept ensure "only" that all participants will understand as far as the natural processes go on in the same way as was determined at the time when making the decision. Owing to the possibility to check the effectiveness of the processes the authority may intervene e. g. in the case of an insufficient effectiveness and take other measures, if need be.

Pursuant to Art. 4 (3) of the Federal Soil Protection Act the obligated party itself shall consider whether it will put up with this time factor – which may negatively affect the value of its real property. Equally as the authority it shall be interested in carefully fixing the criteria according to which the total result to be achieved will be considered as having been finally reached (item a) of the regulations on a MNA concept).

Many facts seem to indicate that in most of the cases a MNA concept will involve considering and monitoring of natural attenuation supplementary to or in connection with a remediation measure, thus a separate legal classification will not be required in these cases.

As monitoring of the natural attenuation processes (MNA) does not actively intervene in the current attenuation process it may not be compared with a remediation measure pursuant to the Federal Soil Protection Act.

In the view of the majority MNA does not represent a protection and restriction measure pursuant to Art. 2 (8) of the Federal Soil Protection Act including equally active technological or administrative measures such as e. g. enclosures, warning devices or restrictions of use. Monitoring of natural attenuation is not to be compared with active measures of this type.

4 SITE-RELATED INVESTIGATIONS AND PREREQUISITES FOR IMPLEMENTING A MNA CONCEPT

4.1 INTRODUCTION

In the gradual remediation of contaminated sites special investigations to determine the natural attenuation processes are, as a rule, only appropriate from the detailed investigation onwards. Natural attenuation may then only be considered in the framework of risk assessment. That is why a decision on a MNA concept may be only made on the basis of a risk assessment. In the majority of cases carrying out of MNA is to be expected after a remediation investigation in connection with remediation measures was carried out and will be seldom carried out as a sole measure on a site.

To allow a uniform and understandable assessment site-related prerequisite for implementing a MNA concept will be made up hereinafter. Thus, it is to be checked whether MNA may be carried out in partial areas of a groundwater damage as a supplementation or alternative to remediation measures. Checking these prerequisites represents a consideration of an individual case. This means, on the one hand, that in the event of individual prerequisites being not fulfilled a MNA concept will not be automatically excluded. On the other hand, if the prerequisites will be fulfilled a MNA concept may not be demanded. The site-related investigations and the prerequisites to be checked refer to the subject's contaminant source, contaminant plume, understanding of the process, prediction and consideration of further protected objects.

4.2 HANDLING OF THE CONTAMINANT SOURCE

Handling of the contaminant source[4] - e. g. in the form of a complete or partly decontamination or securing (hydraulically or structurally engineered) – affects the conditions existing in the contaminant plume[5] and has to be considered in a MNA concept.

4 Areas of the mobile and residual saturated phases and the contaminants fixed in the soil matrix of the unsaturated and saturated zones are referred to as contaminant source.

5 The groundwater volume in the outflow of a contaminant source where the substance concentrations exceed the respective insignificance threshold is referred to as contaminant plume.

Thus, carrying out MNA requires basically to characterize the contaminant source if it is not completely decontaminated or secured.

The characterization should, in particular, contain information on the contaminant inventory (type, spread and quantity of contaminants in subsoil) and on the drag-out behaviour (mass/time).

Fig. 2 shows by an outlined groundwater damage where the drag-out behaviour from the source and the contaminant load in the plume shall be considered by means of balance levels.

The requirements for characterizing the contaminant source depend, a. o., on the planned remediation method. Whereas e.g. in planned excavation measures knowledge of the position of the source is in the foreground the existing contaminant mass plays, in addition, a major part in hydraulic securing measures as it determines the extent of the securing measures required. Characterizing the contaminant source is indispensable for implementing a MNA concept. The mass and the drag-out behaviour of the contaminants have to be estimated as they affect the temporal and spatial development of the contaminant plume.

Thus, considerations on the source have an essential influence on the prediction of the effectiveness of the attenuation processes and carrying out of MNA. If remediation measures are not to be carried out the question how the source will emit contaminants is of decisive importance.

To this end, in particular, the following information on the contaminant source is required:

- position and spread,
- existing contaminant mass,
- condition of the contaminants (dissolved, fixed, residual, mobile),
- drag-out rate / mass / time).

Limiting of the emission of contaminants by carrying out remediation measures may result in the fact that subsequently their drag-out into groundwater may be assessed as being insignificant. This applies, in particular, if there will be predicted that owing to natural attenuation the contaminant contents in the downflow will permanently remain below the hazard threshold. By a remediation of the contaminant source the period of the existence of a contaminant plume will be additionally reduced. Thus, the monitoring period for the groundwater damage left will be reduced.

For a MNA concept it is, as a rule, necessary to reduce the contaminant drag-out from the source by carrying out remediation measures (remediation of the source). Thus, the hazards for the groundwater so far not contaminated and for further protected objects are to be prevented and/or the period of existence of the groundwater damage is to be essentially reduced.

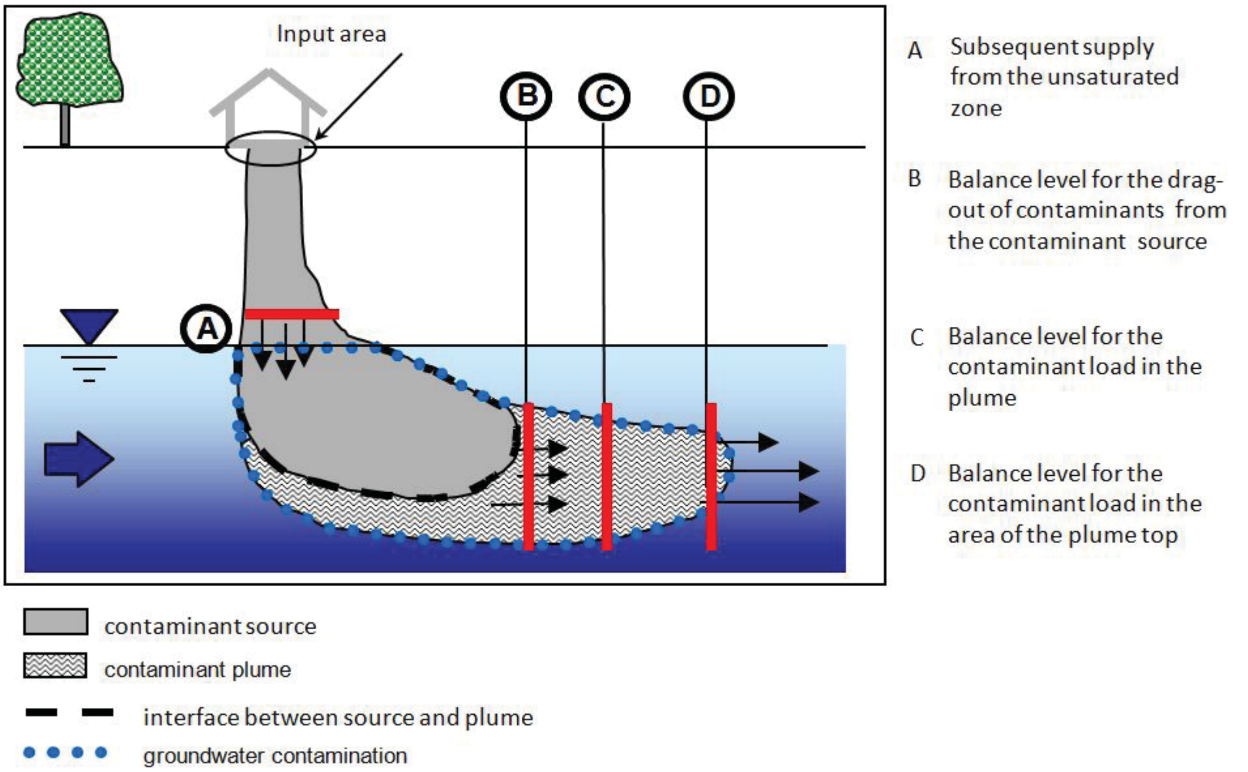

Fig. 2: Consideration of the drag-out of contaminants from the contaminant source and the load in the plume, altered according to [3]

4.3 CONSIDERATION OF THE CONTAMINANT PLUME

4.3.1 Connection between contaminant source and contaminant plume

In the case of groundwater damages with the contaminant source not yet or only partly having been eliminated or secured the emission affects immediately the contaminant plume. That is why the properties of the contaminant source which determine the development of the contaminant plume have to be investigated for assessing the contaminant plume.

In addition, the development of the contaminant plume depends decisively on the transport processes going on in the subsoil (Chap. 4.3.2) and the hydrogeological environment. Some of the various possibilities of the plume development determined solely by a variation of the hydrogeological conditions have been represented in an exemplary way.

The insignificance threshold value (= insignificance threshold - GFS[6]) of the respective contaminant or contaminant group is used to delimit the contaminant plume from the groundwater not yet contaminated [14].

Hereinafter the most important aspects to be considered in connection with characterizing and assessing a contaminant plume are mentioned:

- contaminant inventory (type, spatial spread and mass of the contaminants in subsoil) in the contaminant source as well as in the plume,
- occurrence or formation of metabolites (e. g. in LCHC: cis-DCE, VC and ethene),
- actual spatial delimitation of the plume,
- drag-out behaviour from the source, in particular, the contaminant load (mass per time unit, balance level B of Fig. 2) and
- spatial and temporal spreading behaviour of the contaminant plume, in particular the contaminant load in at least 2 flow sections arranged downstream (balance level C and D of Fig. 2).

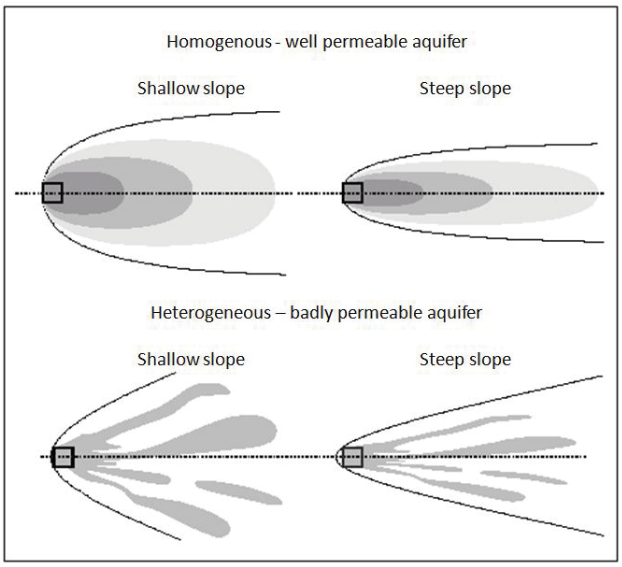

Fig. 3: Schematic representation of various plume contours as a function of the hydrogeological marginal conditions [15]

6 GFS is a substance-specific concentration in groundwater representing the boundary between an insignificantly modified chemical quality of groundwater and a harmful pollution of groundwater (groundwater damage).

4.3.2 Identification and quantification of natural attenuation processes

A prerequisite for implementing a MNA concept is the detection of natural attenuation processes on the site. Here, it is necessary to distinguish between two types of processes: processes reducing the contaminant **load** (e. g. biological degradation, chemical transformation and sorption) and processes reducing only the contaminant **concentration** (hydrodynamic dispersion). As the distinction between the individual processes may be very expensive it would be, first of all, useful to prove that the load is reduced within the contaminant plume. Thus, it is possible to delimit **load reducing processes** from **diluting processes**. A determination of the essential individual processes will be then required to give subsequently a prediction. As diluting processes do not reduce the contaminant load in groundwater they may only play a subordinate part in a MNA concept. Hereinafter the individual attenuation processes are briefly characterized. In the KORA funding priority detection methods and evaluation approaches were developed and investigated. They are documented in the respective branch guides [6, 7, 8, 9, 10 and 11] and in the collection of methods [5].

For many groundwater damages **biological degradation** is the decisive load reducing process. That is why the detection of degradation is an important criterion for a MNA concept. The distinction between degradation processes and other contaminant reducing processes is already possible at an early stage of the investigation. At present, it is advisable to detect indirect indications to a biological degradation activity via parameters of the site to be routinely determined (e. g. redox potential, temperature. concentration of hydrogen carbonate) or the occurrence of metabolites. For the time being, methods for detecting the degradability “in situ” are developed e. g. by determining functional genes.

Degradation rates (reduction of contaminant concentration by biological activity per time unit) are required to predict the degradation of contaminants (Chap. 4.3.3). At present, it is difficult to determine these rates in situ and that is why they are frequently taken from literature or obtained in laboratories for microcosm studies. Yet, as microcosms may simulate reality only insufficiently they show only a degradation potential. That is why it is the aim to determine the degradation rates for process modelling also “in situ”. For this purpose various methods are developed such as special sampling techniques (growth bodies) molecular-biological methods or determination of isotope fractioning by measuring the isotope conditions in the respective starting contaminants and/or degradation products equally.

Depending on the site conditions and the type and concentration of contaminants – given natural conditions - there has also to be expected that biodegradation would be incomplete in biological processes. Therefore, metabolites accumulating in the plume have to be also assessed.

Chemical transformation processes may have contaminant reducing effects. Chemical transformation sums up all processes altering the chemical properties of the contaminant without microorganisms directly participating in them. These processes can be predominantly observed in inorganic contaminants (e. g. precipitation). In qualitative respect chemical transformation processes may be evaluated via investigating the marginal conditions (e. g. availability of reactants, determination of the redox conditions).

Sorption leads to fixing of dissolved contaminants at the solids matrix. This type of fixing is an equilibrium process depending on the quality of the subsoil and the contaminant properties. Depending on the equilibrium (or strength of interaction) the substances are fixed weakly to nearly irreversibly. Sorption processes may be quantified by batch and column tests with site material and under conditions close to site (such as pH value, temperature). The sorption parameters for a number of contaminants may be also taken approximately from literature. To assess the sorption of organic contaminants it is necessary to determine the site-specific carbon content in the solid. If dangers do no longer emanate from sorbed contaminants sorption may be included as a process for reducing the contaminant load. Here, there has, however, to be checked whether by altering the hydrochemical and geochemical marginal conditions a desorption can take place and how it should be evaluated.

Hydrodynamic dispersion (sum of dispersion and molecular diffusion) is a process only reducing the concentration of contaminants (dilution) by spreading contaminants to a bigger volume in groundwater. In this connection, the heterogeneity in aquifers affects, to a high degree, the longitudinal and transversal dispersion, thus determining immediately the dilution of the contaminant in subsoil. The contaminant mass in groundwater is not reduced by hydrodynamic dispersion, yet load reducing processes are indirectly affected. Delimiting the dilution of processes reducing the contaminant mass in groundwater (mainly biological degradation) or retaining contaminants (mainly sorption) is frequently difficult. That is why a prediction of the contaminant reduction cannot be based solely on the detection of the reduction of the contaminant concentration in the measuring points as this detection does not allow to draw a conclusion relating to the share of dilution in the contaminant reduction.

The hydrodynamic dispersion may be assessed e. g. with the aid of tracer tests with “conservative” (not reactive) tracers.

First of all, load reducing processes are to be distinguished from diluting processes for a MNA concept; both of them should be subsequently quantified. The investigation should show that the load reduction has an essential share in the reduction of contaminants. Determining the relevant individual processes is the prerequisite for the subsequent prediction of the plume behaviour.

4.3.3 Evaluation of the contaminant plume and prediction of the plume behaviour

An evaluation of the contaminant plume requires that the horizontal and vertical spreading of the contaminant plume is known. To evaluate the plume behaviour a prediction of the temporal alteration owing to the effect of natural attenuation processes is required. The plume behaviour may be evaluated by means of two features:

- The contaminant plume recedes, is **quasi-stationary**[7] or expands further. That means for the first two cases that due to the expansion behaviour a further groundwater damage in the downflow is not to be expected if the marginal conditions for the natural attenuation processes will not change. That means, that also shifting to lower aquifers is excluded. In the third case there are risks for groundwater and further protected objects in the downflow. A first worst case assessment to find out whether a contaminant plume is stationary may be made with the aid of simple analytical calculation approaches.
- The contaminant drag-out rate from still existing contaminant sources is higher or smaller as compared to the attenuation rate caused by natural processes proceeding in the plume. If the attenuation rate is bigger or equal to the drag-out rate we may proceed on the fact that the contaminant plume has reached a "quasi-stationary" or receding state.

In this place only prerequisites for the prediction of the plume behaviour are formulated. Targets for the application of a mathematical solution are not set, software recommendations are not given. However, the consideration should be started on the basis of a conceptual, hydrogeological site model [16]. When predicting the plume behaviour the following possibilities may, in principle, be distinguished:

- The prediction is made on the basis of conceptual considerations. This may be e.g. an analysis of a time series of groundwater quality data (contaminants, metabolites and guiding parameters) and an extrapolation of these time series to the future. However, experience has so far shown that
  a) reliably interpretable time series exist only in the exceptional case and frequently the number of measuring points is not sufficient and
  b) an extrapolation is difficult and involves high insecurities.

  The exploration of concentration time series can be made only in individual measuring points taking the hydraulic conditions into account.
- The prediction is made additionally on the basis of a model. However, such an approach will be only practical if
  a) apart from modelling of the groundwater flow also the contaminant transport and the contaminant transformations will be modelled,
  b) the marginal conditions in situ (in particular hydrogeology, hydrochemistry, characteristic of the contaminant source and the contaminant plume, the processes and process space) will be known or assessable with a sufficient accuracy and
  c) the required scope of the parameter determination or identification for modelling will be known.

Hereby, mathematical models simulating occasionally complex physical, chemical and biological processes will be able to make a prediction always only on the basis of partly insufficiently available data or simplified, conceptual assumptions.

Based on the results of the investigations it should be possible to make a prediction on whether a contamination of the groundwater not yet affected or further protected objects may be excluded at present and in future.

The contaminant plume should be "quasi-stationary" or shrinking.

4.4 PROTECTION OF THE GROUNDWATER NOT YET AFFECTED AND CONSIDERATION OF FURTHER PROTECTED OBJECTS

4.4.1 Preliminary remarks

When investigating the site-related prerequisites for implementing a MNA concept, in particular, the groundwater not yet contaminated and further protected objects have to be considered. That is why there should be found out whether further protected objects have been affected or may be affected in future.

The criterion for hazard assessment in the case of groundwater damages caused by contaminated sites results from the water law. When considering the question if and to which extent measures relating to hazard prevention shall be carried out the reference to criteria pertaining to water law in Art. 4(4) of the Federal Soil Protection Act shall be taken into account.

4.4.2 Protected objects according to the soil protection and water law

Protected objects are not explicitly defined in the Federal Soil Protection Act. The protection concept of the Federal Soil Protection Act is aimed at maintaining and restoring soil functions. That is why the Federal Soil Protection Act obliges to prevent hazards in the case of harmful soil changes and contaminated sites and water pollution caused by them.

The following protected objects may be derived from Art. 1 and Art 2 (2) of the Federal Soil Protection Act not definitively and without evaluation:

a) the soil in its functions of use (raw material deposit, area for settlement and recreation, site for agricultural and forestry uses and site for economic and public uses) and
b) water bodies.

Via the definition of the pathway in Art. 2 no. 8 and the (not concluding) naming of the pathways in Annex 1 of the Federal Soil Protection Ordinance it is directly referred to the following protected objects:

a) man (soil-human health pathway, soil-plant pathway),
b) groundwater (soil-groundwater pathway) and
c) plant (soil – plant pathway).

Pursuant to Art. 1a water bodies as part of the ecosystem and as habitat for animals and plants have to be protected. Protected objects are water bodies themselves, independent of their function and use.

7 A contaminant plume is considered to be „quasi-stationary" if it does no longer permanently spatially expand. That means, that its spatial contour described by the limit between exceeding or remaining below the insignificance threshold will no longer expand or be shifted in the direction of the further downflow. Thus, it has to be stationary in the framework of the natural variation of the flow conditions (velocity, direction of flow) but also of the reaction condi-

4.4.3 *Consideration of relevant protected objects*

When checking the prerequisites for implementing a MNA concept there arises a. o. the question: Which further protected objects are so affected by the damage of groundwater already occurred or affected in their function that tolerating this load and thus implementing a MNA concept will not be possible.

In this above-mentioned check, in particular, the following protected objects are to be taken into account:

a) soil in its natural soil functions: e. g. negative effects on its function as habitat in sites with polluted groundwater
b) soil in its functions of use:
e. g. as an area for settlement and recreation or area for commercial use if highly volatile harmful compounds will be formed by degradation processes and degassing and contaminant enrichment in buildings will cause hazards.
c) surface waters and groundwater in the downflow of the polluted groundwater areas.

For implementing a MNA concept further protected objects should not be affected in future

5 EXERCISE OF DISCRETION AND APPROPRIATENESS TEST

In the framework of remediating contaminated sites the competent authority exercises its discretion[8] a. o. in making decisions on the following questions relevant, in particular, in connection with a MNA concept:

a) after carrying out and evaluating the detailed investigation and determining the hazardous situation:
Has a remediation investigation and, if required, a remediation to be started or will other measures (e. g. monitoring measures, protection and limiting measures) be sufficient?
b) In selecting the required measures (as a rule, in the framework of a remediation investigation):
Which measures for preventing hazards would be suitable, required and appropriate and therefore to be carried out?
c) In fixing the remediation or measure targets:
Which targets can be achieved with relatively simple means in the specific individual case?

Ref. to a)

If the competent authority detects a hazard to groundwater or a groundwater damage after carrying out and evaluating the detailed investigation it will decide whether in the framework of its discretion measures for preventing hazards will be required. After detecting the damage the authority is authorized, however not obliged, to intervene [Art. 10 (1) Sentence 1 of the Federal Soil Protection Act: “The competent authority may take the measures necessary in order to fulfil…”].

Thus, after detecting the hazard/damage there has to be decided in the individual case whether measures for preventing hazards will be required. As a result of this consideration the basic decision on the necessity to take further (in particular remediation) measures will be made. This regulatory discretion involves a check of the appropriateness[9] of further measures for which e. g. Art. 4 (7) of the Federal Soil Protection Ordinance mentions for example possible criteria such as “small contaminant loads” or “locally increased contaminant concentrations”.

This refers also to a MNA concept if the site-related prerequisites (Chap. 4) have been already fulfilled at this stage of the decision-making process. This, however, requires that detailed investigations of attenuation processes have been already carried out and that it may be assessed whether remediation measures would be inappropriate for this extent of damage.

Ref. to b)

Considering the remediation targets fixed, as a rule, in the framework of a remediation investigation the technologically appropriate procedures are to be determined and the variants are to be compared. At this time the authority is granted a discretion in selecting which should consider its appropriateness when exercising it. The discretion in selecting refers to measures which

- are suited to reach the fixed remediation target,
- represent the mildest means to reach the remediation target and
- are to be carried out at an expense which is in an appropriate proportion to the remediation target striven for.

8 **Discretion** means that an authority has a room for manoeuvre as several different approaches/possibilities of remediation would be permitted by law for the case to be specifically decided upon. Related to the Federal Soil Protection Act there results from Art. 10 (1) that the authority can, however, need not take the required measures.

In exercising discretion the authorities have always to make such decisions as the legislator would presumably have settled the specific case himself. That is why apart from the general legal principles (such as e. g. appropriateness of the means, necessity and reasonableness for the person concerned) also the purpose of the regulation authorizing to exercise the discretion and the limits relating to the content of this discretion have always to be taken into account. An administrative regulation may provide for typical individual cases how the discretion shall be used.

Action in conformity with the administrative law distinguishes two types of discretion: if an authority was granted a regulatory discretion under certain conditions it is obliged to decide itself whether it will become active at all. If it will become active the authority has frequently several possible alternatives of action among which it may select an alternative in the framework of the **discretion in selecting.**

9 In the framework of exercising the discretion checking of the **appropriateness** is attached special importance. The principle of appropriateness has been derived from the constitutionality principle embodied in the basic law and has therefore the status of a constitution. The legal criterion for exercising the discretion results from Section 40 of the Administrative Procedures Act: “Where an authority is empowered to act at its discretion, it shall do so in accordance with the purpose of such empowerment and shall respect the legal limits to such discretionary powers.” The check of appropriateness is classified into three steps:

Suitability: A measure is suitable if it may reach the success striven for.

Necessity: Only a measure achieving the same success as compared with other measures, which, however, is less stressing for the obligated party and the general public or requires a lower expenditure (“milder means”) is required.

Appropriateness: A measure is appropriate if the drawback or expenditure and the success striven for are in a reasonable relationship with each other (cost-benefit comparison).

The principle of appropriateness requires a gradual approach depending on the violation of law and the severity of the intervention. In the framework of remediation of contaminated sites this means that the measures fixed by authorities and their consequences for the obligated party have to be in an appropriate proportion to the extent of the hazard to be prevented.

Here, there should be taken into account that these criteria are based on each other, i. e. the measures unsuitable for reaching the respective remediation target are left out of account. This will exclude that measures suited and unsuited for reaching the remediation target will be compared from the viewpoint of costs (milder means) and the possibly lower costs will be the crucial factor for choosing an unsuited measure.

As far as a remediation measure will fulfil the three a. m. criteria a MNA concept will not be taken into consideration as sole alternative.

If the criteria will, first of all, not apply to one of the remediation measures investigated and at choice with regard to the technical feasibility the remediation target is to be newly formulated and the suitable measures have to be checked anew (this adaptation of the remediation targets to the technical feasibility is made as an iterative approach within a remediation investigation. That is why several remediation investigations have to be carried out in succession). Then a MNA concept may be only considered (in the framework of the discretion in selecting) if the newly formulated target may be reached by natural attenuation processes. If the investigations required for it were not carried out in the detailed investigation the obligated party may make up for them in the framework of the remediation investigation. At this stage important technical aspects in checking the appropriateness are, in particular, the time up to which the target may be reached, the security of the prediction based on assumptions and the security with which the groundwater damage may be monitored by the obligated party up to reaching the target. This involves also controlling if the target will be maintained in the long term.

Ref. to c)

After deciding on the site-specific measures/remediation targets (if necessary, in a remediation investigation) also the values pinned on the targets will be iteratively fixed. In this connection, the natural attenuation processes known from preceding investigations are to be considered. If the investigations required for that have not been carried out in the detailed investigation they may be demanded by the obligated party or it may be made up for them in the framework of the remediation investigation.

In the above-mentioned discretionary decisions the following principles shall be followed: From Art. 4 (3) of the Federal Soil Protection Act there follows that the Act requires basically to carry out remediation measures eliminating, in the short term, the danger caused by the harmful soil change or contaminated site. In the hazard prevention law hazards shall, in general, be eliminated. That is why refraining from fulfilling this obligation pursuant to Art. 10 (1) of the Federal Soil Protection Act is an exception requiring a justification. First of all, the soil protection authority is subject to an obligation to justification if it demanded that a remediation exceeding natural attenuation should be carried out. In discussing the alternative to decide in favour of considering natural attenuation the question is concerned "Is including natural attenuation with regard to the future use sufficiently suited, the postponement and the remaining risk sufficiently justifiable to refrain partly (by exception completely) from carrying out remediation measures?"

Thus, it will, at the same time, become evident that the remediation target which may be reached through remediation measures according to the Federal Soil Protection Act forms the legally founded guideline for that what should be reached materially, i. e. is in doubt also appropriate (subject to the specific features at the troublemaker according to legal decisions of the Federal Constitutional Court).

A MNA may be only carried out as sole measure if according to the hazard assessment the site-related prerequisites are fulfilled in the individual case and remediation measures are estimated as being inappropriate.

If a remediation as a sole measure will be appropriate a MNA concept will be out of the question.

Knowing about attenuation processes serves also to assess remediation measures and to fix remediation targets (discretion in selecting) in the framework of a remediation investigation. A MNA concept may then be appropriate in connection with a remediation or subsequent to a remediation measure. It is to be expected that MNA concepts will take effect preferably in connection with remediation measures.

6 MONITORED NATURAL ATTENUATION (MNA)

The predicted effect of the natural attenuation processes is to be proved by a groundwater monitoring program adapted to the individual case. It may be regulated by an official order, by approving a remediation plan or by a contract under public law.

6.1 MONITORING PROGRAM REQUIREMENTS

When designing the monitoring program there has to be taken into account that the reaction system "contaminant plume" may change over longer periods. That is why also changes of the hydrogeological, geochemical, microbiological and other framework conditions affecting the effectiveness of attenuation processes have to be recorded. The monitoring program has therefore the continuous task

- to ensure checking of the prediction,
- to record changes of the development of the contaminant plume and
- to allow making statements on the relevant attenuation processes.

Thus, the monitoring program exceeds the sole registration of the contaminant concentrations.

As a result of the determination of natural attenuation processes the processes themselves and, in particular, their effects have been proved. By means of these results it is possible to fix then also the relevant parameters and measuring points for monitoring this effectiveness. They determine the minimum volume for the monitoring program.

6.2 ASSESSMENT CRITERIA FOR MONITORING

The basis for considering the success is the prediction. Monitoring shall be carried out until the agreed target will have been reached and it will be ensured that the contaminant concentrations will remain permanently below the target values. If contrary to the prediction the processes will not contribute to reaching the agreed target the hazard shall be anew assessed and it shall be checked whether alternatives will be required.

In the framework of the MNA concept the obligated party should explain the further actions if the results of monitoring will indicate a deviation from the prediction and thus the attenuation processes will not proceed in the way as it was originally assumed for the MNA concept.

6.3 PERIOD FOR MNA

The period for MNA to be expected results, first of all, from the prediction. However, monitoring shall be carried out at least until the contaminant concentrations will remain permanently below the defined target values.

The period when the natural attenuation processes will lead to reaching the agreed targets shall be determined by assessing the specific framework conditions for the individual case.

A general recommendation for a maximum period when MNA may be carried out does not seem to be appropriate.

Specific times of monitoring (e. g. measurements at critical dates, sampling cycle) shall be fixed in connection with intermediate targets. To ensure that monitoring will be ensured also in the long term and that in the case of deviations from the prediction occurring, if applicable, alternative measures may be taken the requirement of a security based on Art. 16 (1) of the Federal Soil Protection Act is taken into consideration. So far judicial decisions on this problem have not been made.

ANNEX 1 RECOMMENDATIONS FOR APPROACHES IN PRACTICE

Ist step Checking of the prerequisites for preparing a MNA concept

I.1 Targets set by the authority for agreeing on framework conditions with the obligated party

I.2 Checking of the site-related prerequisites according to the present state of knowledge

IInd step Proof of the effectiveness of attenuation processes and preparation of a MNA concept

II.1 Site investigations to prove the effectiveness of attenuation processes

II.2 Prediction of the development of the contaminant plume

II.3 Evaluation and assessment of the results

II.4 Preparation of a MNA concept and explanation of its suitability

IIIrd step Administrative decision on the suitability and implementation of MNA

IVth step Carrying out of MNA

In the following the consideration of natural attenuation in the practical remediation of contaminated sites is explained by means of a gradual approach. The essential steps with the relevant content may be taken as summaries from the table hereinafter. Hereby, there shall be considered that the preparation of a MNA concept and the decision on carrying out MNA is always an individual decision which can be made only in a restricted way by means of fixed procedures.

Tab. A1-1: Recommendations for gradual approaches in preparing a MNA concept, deciding for and executing of MNA

Ist step	**Checking of the prerequisites for preparing a MNA concept.**
I.1 Targets set by the authority for agreeing on framework conditions with obligated party	• The MNA concept is the result of checking an individual case. • The type and extent of the proof of the effectiveness of attenuation processes have to be concerted. • The basic requirement for remediation is not doubted by MNA. • MNA as sole measure is only possible if the site-related prerequisites will be fulfilled and remediation measures assessed as being inappropriate. • If a remediation as a sole measure will be appropriate MNA will be unsuitable. • A concerted monitoring shall be carried out to check the effectiveness of the attenuation processes. • An alternative option for action is to be scheduled.
I.2 Checking of the site-related prerequisites according to the present state of knowledge	• Site potential • Contaminant input and reaction spaces • Presentation of the hydrogeological model
IInd step	**Proof of the effectiveness of attenuation processes and preparation of a MNA concept**
II.1 Site investigations to prove the effectiveness of attenuation processes	• Spatial position and expansion of the contaminant plume • Investigations to determine the contaminant loads at balance levels • Investigations for identifying and quantifying the essential individual processes • Investigations on the basis of a deficit analysis to prepare the prediction
II.2 Prediction of the development of the contaminant plume	• Preparation of a numerical model (flow, transport and reaction processes) • Assesment of the long-term course and the of the process • Representation of prediction uncertainties by means of scenario considerations and sensitivity analysis • Identification of the key parameters
II.3 Evaluation and assessment of the results	• Concluding evaluation and assessment of all marginal conditions and results of investigations • Site-specific assessment of remediation measures (upon completion of the remediation investigation)
II.4 Preparation of a MNA concept and explanation of its suitability	• Preparation of a MNA concept with its respective components of regulation • Monetary representation of the measures • Explanation of the suitability of the MNA concept
IIIrd step	
Administrative decision on the suitability and implementation of MNA	• Criteria for the decision: - Are the site-related prerequisites acc. to Chap. 4 of the text part fulfilled and, if yes, to which extent? - Does the MNA concept ensure the required monitoring intensity and does it provide the possibility of a punctual intervention? - For which areas of the groundwater damage will a remediation be appropriate and will have thus to be carried out? - For which areas of the groundwater damage will a remediation be inappropriate solely before the back ground of attenuation processes and a MNA will be the appropriate measure instead of a remediation? • Agreement on a binding instrument of regulation
IVth step	
Carrying out of MNA	• Execution of monitoring on the basis of a monitoring plan • Checking of the prediction (variance comparison), if necessary, adaptation of the approach • After reaching the target concluding assessment of hazards

A1-I Checking of the prerequisites for preparing a MNA concept

A1-I.1 Targets set by the authority for agreeing on framework conditions with the obligated party

Ist step	Checking of the prerequisites for preparing a MNA concept.
I.1 Targets set by the authority for agreeing on framework conditions with obligated party	• The MNA concept is the result of checking an individual case. • The type and extent of the proof of the effectiveness of attenuation processes have to be concerted. • The basic requirement for remediation is not doubted by MNA. • MNA as sole measure is only possible if the site-related prerequisites will be fulfilled and remediation measures assessed as being inappropriate. • If a remediation as a sole measure will be appropriate MNA will be unsuitable. • A concerted monitoring shall be carried out to check the effectiveness of the attenuation processes. • An alternative option for action is to be scheduled.
I.2 Checking of the site-related prerequisites according to the present state of knowledge	• Site potential • Contaminant input and reaction spaces • Presentation of the hydrogeological model
IInd step	Proof of the effectiveness of attenuation processes and preparation of a MNA concept
II.1 Site investigations to prove the effectiveness of attenuation processes	• Spatial position and expansion of the contaminant plume • Investigations to determine the contaminant loads at balance levels • Investigations for identifying and quantifying the essential individual processes • Investigations on the basis of a deficit analysis to prepare the prediction
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IIIrd step	
Administrative decision on the suitability and implementation of MNA	• Criteria for the decision: - Are the site-related prerequisites acc. to Chap. 4 of the text part fulfilled and, if yes, to which extent? - Does the MNA concept ensure the required monitoring intensity and does it provide the possibility of a punctual intervention? - For which areas of the groundwater damage will a remediation be appropriate and will have thus to be carried out? - For which areas of the groundwater damage will a remediation be inappropriate solely before the back ground of attenuation processes and a MNA will be the appropriate measure instead of a remediation? • Agreement on a binding instrument of regulation
IVth step	
Carrying out of MNA	• Execution of monitoring on the basis of a monitoring plan • Checking of the prediction (variance comparison), if necessary, adaptation of the approach • After reaching the target concluding assessment of hazards

When starting to consider if a MNA should be executed there shall be clarified whether the authority will think the implementation of a MNA concept to be basically possible. It must be realizable that the obligated party will furnish proof (II.1) according to the targets set by the authority. As a rule, this should be clarified after a detailed investigation has been and before a remediation investigation will be made. Hereby, the following aspects shall be taken into account:

- The decision to carry out MNA is the result of checking an individual case. Here, the results of the gradual approach to preparing a MNA concept will be continuously assessed, mainly with the aim to decide whether the preparation of a MNA concept shall be continued or if MNA as an alternative option for action has to be rejected.
- The type and extent of the proof that attenuation processes are effective to a relevant extent should be coordinated with the authority.
- The basic requirement for remediation is not called into question by the decision to carry out MNA. MNA means only to tolerate a temporarily and spatially limited groundwater damage on the basis of attenuation processes detected and predicted with regard to the principle of appropriateness.
- It will be only possible to carry out MNA if the site-related prerequisites (Chap. 4 of the text part) are fulfilled and remediation measures are assessed as being inappropriate.
- If a remediation will be appropriate as sole measure a MNA concept will be out of question.
- In the case of a decision for MNA a concerted monitoring adapted to checking the effectiveness of attenuation processes shall be carried out.
- An alternative option for action shall be envisaged for the case that the prediction of the effectiveness of attenuation processes will not be reached to the required extent.

In practice the obligated party should explain why it renounces completely or partly a remediation and would like to carry out MNA instead of it. Here, the obligated party should take into account the above-mentioned marginal conditions and as regards the required investigations and proofs it should be orientated towards the site-related prerequisites (Chap. 4 of the text part).

The specific gradual work aimed at preparing a MNA concept should be started after the participating parties (authority, obligated party) will have reached a consensus on the framework of action, investigation and detection.

It is recommended to present the partial results reached by the authority at the individual stages assessing, at the same time, also the actual probability of success of a MNA concept. This will ensure a decision-oriented and cost-optimized approach aiming at a solution to be reached by mutual agreement between the obligated party and the authority.

A1-I.2 Checking of the site-related prerequisites according to the present of knowledge

Ist step	Checking of the prerequisites for preparing a MNA concept.
I.1 Targets set by the authority for agreeing on framework conditions with obligated party	• The MNA concept is the result of checking an individual case. • The type and extent of the proof of the effectiveness of attenuation processes have to be concerted. • The basic requirement for remediation is not doubted by MNA. • MNA as sole measure is only possible if the site-related prerequisites will be fulfilled and remediation measures assessed as being inappropriate. • If a remediation as a sole measure will be appropriate MNA will be unsuitable. • A concerted monitoring shall be carried out to check the effectiveness of the attenuation processes. • An alternative option for action is to be scheduled.
I.2 Checking of the site-related prerequisites according to the present state of knowledge	• Site potential • Contaminant input and reaction spaces • Presentation of the hydrogeological model
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II.1 Site investigations to prove the effectiveness of attenuation processes	• Spatial position and expansion of the contaminant plume • Investigations to determine the contaminant loads at balance levels • Investigations for identifying and quantifying the essential individual processes • Investigations on the basis of a deficit analysis to prepare the prediction
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II.4 Preparation of a MNA concept and explanation of its suitability	• Preparation of a MNA concept with its respective components of regulation • Monetary representation of the measures • Explanation of the suitability of the MNA concept
IIIrd step	
Administrative decision on the suitability and implementation of MNA	• Criteria for the decision: - Are the site-related prerequisites acc. to Chap. 4 of the text part fulfilled and, if yes, to which extent? - Does the MNA concept ensure the required monitoring intensity and does it provide the possibility of a punctual intervention? - For which areas of the groundwater damage will a remediation be appropriate and will have thus to be carried out? - For which areas of the groundwater damage will a remediation be inappropriate solely before the back ground of attenuation processes and a MNA will be the appropriate measure instead of a remediation? • Agreement on a binding instrument of regulation
IVth step	
Carrying out of MNA	• Execution of monitoring on the basis of a monitoring plan • Checking of the prediction (variance comparison), if necessary, adaptation of the approach • After reaching the target concluding assessment of hazards

Based on the existing state of knowledge (as a rule, detailed investigation) and the above-mentioned aspects (I.1) there will be checked if the preparation of a MNA concept would be an option for action leading to success, i. e. if the site-related prerequisites for carrying out MNA could be fulfilled.

That is why before starting expensive investigations for detecting natural attenuation processes the data already available should be looked through and reviewed as the sites discussed with regard to implementing a MNA concept show already frequently a comprehensive investigation history up to remediation measures carried out or going on. The assessment is made, on the one hand, under scientific-technical aspects (identification of the process), however, in particular, by means of the site-related prerequisites (Chap. 4 of the text part) relevant to a MNA concept. Already at this stage the requirement to not affect further protected objects may be assessed. In addition, there should be considered if the existing groundwater damage could be tolerated as reaction space in the spatial extent known so far and would, in principle, allow the implementation of a MNA concept or if other criteria would conflict with it.

As at this time an assessment of the time frame when MNA could be carried out is still very insecure we should "for the time being" proceed from the existence of the actual groundwater damage as "worst-case" approach. The following should be taken into account:

Site potential

- Type and properties of contaminants relevant to assessment

  Here there shall be checked whether these contaminants are altogether sufficiently accessible to attenuation processes owing to their properties. References are provided among others by literature research on sorption and degradation properties of the contaminants.

- Degradation and retention potential

  The degradation potential may be assessed e.g. by means of data on the general degradability based on usually available data on the distribution of contaminants (change of the contaminant pattern and formation of metabolites), a comparing assessment of the actual plume spread, the fictive contaminant transport without considering the degradation and by means of data on the identification of the redox conditions. The retention potential may be e. g. estimated by means of the Kd approach.

- Quality of the source

  The spatial structure and the substance composition of the source and the availability of phase bodies have an essential influence on the duration of the emission and the volume of the load.

- Expansion and development of the plume

  The available data on the spatial expansion and the previous development of the plume shall be assessed with the aim to estimate the effects and the further remediation of the groundwater damage.

- Hydrogeochemical marginal conditions

  The hydrogeochemical marginal conditions may inform on whether the essential degradation processes (e.g. reductive dechlorination) can take place in the individual case.

- Groundwater flow conditions

  Varying groundwater flow conditions may affect the effectiveness of the attenuation processes.

Contaminant input and reaction spaces

It is of importance for the further consideration of the MNA option that the space of investigation will be known or delimited. This includes that all areas with contaminant input, contaminant spread as well as areas where an input of other relevant substances (e.g. electron acceptors) takes place will be considered.

Presentation of the hydrogeological model

Based on the available (hydro-)geological and (hydro-)chemical data a concept model is to be prepared showing the marginal site conditions relevant for the assessment of attenuation processes. The concept model will serve specifically to visualize and describe the predominant flow and transport and hydrochemical conditions.

At this stage of consideration there may be, as a rule, assessed if and for which areas of the groundwater damage a MNA concept will be a possibility and which areas have to be remediated. It is, however, decisive for the implementation of a MNA concept if and to which extent the site-related prerequisites according to Chap. 4 of the text part are fulfilled.

As a result of checking the above-mentioned site-related marginal conditions the next stage of treatment may be agreed upon between the authority and the obligated party.

A1-II Proof of the effectiveness of attenuation processes and preparation of a MNA concept

A1-II.1 Site investigations to prove the effectiveness of attenuation processes

Ist step	Checking of the prerequisites for preparing a MNA concept.
I.1 Targets set by the authority for agreeing on framework conditions with obligated party	• The MNA concept is the result of checking an individual case. • The type and extent of the proof of the effectiveness of attenuation processes have to be concerted. • The basic requirement for remediation is not doubted by MNA. • MNA as sole measure is only possible if the site-related prerequisites will be fulfilled and remediation measures assessed as being inappropriate. • If a remediation as a sole measure will be appropriate MNA will be unsuitable. • A concerted monitoring shall be carried out to check the effectiveness of the attenuation processes. • An alternative option for action is to be scheduled.
I.2 Checking of the site-related prerequisites according to the present state of knowledge	• Site potential • Contaminant input and reaction spaces • Presentation of the hydrogeological model
IInd step	Proof of the effectiveness of attenuation processes and preparation of a MNA concept
II.1 Site investigations to prove the effectiveness of attenuation processes	• Spatial position and expansion of the contaminant plume • Investigations to determine the contaminant loads at balance levels • Investigations for identifying and quantifying the essential individual processes • Investigations on the basis of a deficit analysis to prepare the prediction
II.2 Prediction of the development of the contaminant plume	• Preparation of a numerical model (flow, transport and reaction processes) • Assesment of the long-term course and the of the process • Representation of prediction uncertainties by means of scenario considerations and sensitivity analysis • Identification of the key parameters
II.3 Evaluation and assessment of the results	• Concluding evaluation and assessment of all marginal conditions and results of investigations • Site-specific assessment of remediation measures (upon completion of the remediation investigation)
II.4 Preparation of a MNA concept and explanation of its suitability	• Preparation of a MNA concept with its respective components of regulation • Monetary representation of the measures • Explanation of the suitability of the MNA concept
IIIrd step	
Administrative decision on the suitability and implementation of MNA	• Criteria for the decision: - Are the site-related prerequisites acc. to Chap. 4 of the text part fulfilled and, if yes, to which extent? - Does the MNA concept ensure the required monitoring intensity and does it provide the possibility of a punctual intervention? - For which areas of the groundwater damage will a remediation be appropriate and will have thus to be carried out? - For which areas of the groundwater damage will a remediation be inappropriate solely before the back ground of attenuation processes and a MNA will be the appropriate measure instead of a remediation? • Agreement on a binding instrument of regulation
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Carrying out of MNA	• Execution of monitoring on the basis of a monitoring plan • Checking of the prediction (variance comparison), if necessary, adaptation of the approach • After reaching the target concluding assessment of hazards

At this partial stage the scientific-technical data for proving the suitability of the MNA concept shall be prepared for a specific site. Thus, this stage is of decisive importance. It is oriented to the processes on which the development of the contaminant plume is based. As a result there shall be clarified which processes are of essential importance and to which extent they contribute to attenuating contaminants. The type and extent of the proof have to be agreed upon by the obligated party and the authority.

Specific site investigations require, if appropriate, the support by special experts e.g. in connection with specific methods or modelling instruments.

Basically the following priorities may be distinguished in the investigations:

- Spatial position and spread of the contaminant plume,
- Determination of the contaminant loads at the balance levels,
- Identification and quantification of the essential individual processes (in particular degradation and retention),
- Deficit analysis to clarify/check if the previous investigations have been sufficient to predict the development of the contaminant plume (partial stage II.2). If the occasion arises, supplementary investigations are required.

When considering the site-related prerequisites, first of all, the development of the contaminant plume is of top priority ("quasi-stationary state" and distinction between load reducing and diluting processes). If the balance levels required for assessment do not exist in the immediate downflow from the source, in the course of the plume and in the area of the plume top they have to be established and considered in the framework of this partial stage.

The determination of the load at balance levels aims at a summary consideration of the natural attenuation processes. Thus, it is possible to recognize load reducing processes (in principle the sum of sorption and degradation) and to distinguish them from the diluting processes. If several individual processes are responsible for the reduction of the load and a summary balance will not be sufficient for the assessment a quantification of these individual processes will be required in a next stage. For this purpose further process-specific investigations (e. g. investigations of isotope, sorption, tracer, microbiological degradation etc.) will, as a rule, be required.

The available methods of investigation are to be distinguished, in particular, as regards the expenditure and informative value (qualitatively or quantitatively). To optimize the costs, first of all, less expensive methods with "qualitative information" should be applied. The appearance of degradation products and the consumption of electron acceptors furnish e.g. qualitative indications to attenuation processes. The processes should be only quantified if there will be sufficient indications to relevant attenuation processes. In addition, there should be considered that it is not always possible to quantify individual processes. A quantification is not always relevant to a decision.

At this stage of consideration it is with regard to a model-based prediction, as a rule, necessary to carry out a deficit analysis of the available knowledge. That is why if knowledge relevant to the assessment, e. g. sufficient knowledge on the geological, hydrogeological and hydrochemical conditions, the contaminant potential, identification and quantification of the individual processes (if required), process spaces and, in particular, knowledge for predicting the development of contaminants, is lacking for preparing a MNA concept additional investigations will be required. These might be e.g. the completion of the chemical analyses, detailed investigations of the hydrogeological site conditions, mapping of the contaminant plume with detecting the essential process spaces, investigations of time series or further considerations at balance levels.

Apart from that, as a rule, a reactive substance transport model will be required for balancing with quantifying the individual processes. The data basis necessary for that will have to be completed, if required, in the framework of the investigations to be carried out at this stage of treatment. In this connection, there should be assessed whether instead of determining site-related data literature data might be applied.

If remediation measures have been already carried out or planned at the source or at the plume this should be taken into account as a marginal condition in the investigation to prove the effectiveness of the attenuation processes with a view of the equilibrium state to be re-established.

Apart from the information on the contaminant plume additional information on the contaminant source will be required to predict the period when a groundwater damage to be monitored exists and MNA is to be carried out, in particular, if the remediation of the contaminant source may not or only incompletely carried out. This may be e.g. reached by investigations in the area of the source and in the immediate downflow. These investigations are aimed at estimating the drag-out rate and the period of release and its development.

As a result of this partial stage the basis should be provided for predicting the development of the contaminant plume reliably. This involves clarifying which processes are of essential importance and to which extent they contribute to reducing contaminants and/or the contaminant load. Depending on the site conditions and the extent of the additional investigations this partial stage may take a longer period of time, in particular, if investigations of further or longer time series will be required.

A1-II.2 Prediction of the development of the contaminant plume

At this partial stage subsequent to the determination of the attenuation processes and other site-specific marginal conditions the long-term course and the sustainability of the process shall be assessed. Here, especially the site-related prerequisite shall be checked if the contaminant plume is "quasi-stationary" or shrinking and thus no further protected objected will be endangered. The prediction of the development of the contaminant plume forms thus an essential basis for deciding whether MNA will be suited and executed.

As a rule, a numerical model showing flow, transport and reaction processes will be required. By means of sensitivity analyses and, if required, scenario considerations

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critical parameters and marginal conditions and prediction insecurities shall be shown and assessed.

The basis for drawing up the numerical model is a hydrogeological-hydrogeochemical model representation based on site-specific conditions. The requirements imposed on it are mentioned i. a. in FH-DGG (Hydrogeological Section in the Association of Geoscience) 2002 [16] and in the recommendations for action [5] and the guides [6, 7, 8, 9, 10, 11, 17] of the KORA funding priority of the Federal Ministry of Education and Research.

In the course of modelling the essential marginal conditions, processes and parameters of the authority shall be explained, in particular, if literature data were used and remarkable abstractions of the local conditions shall be made. The individual stages of the development of the model (e.g. fixing of the marginal conditions and parameters, data basis, abstractions, calibration, validation, sensitivity analyses applied) shall be documented in a reconstructable way. As a rule, scenario considerations shall be made for the prediction. The cases to be considered in this connection should be coordinated in advance.

In simple and/or clear site conditions the use of a numerical model for proving "quasi-stationarity" will not be always required if e.g. evaluations of time series of the plume show "quasi-stationarity", the processes are known and the basic conditions have to be assumed as being constant.

The evidential security of prediction should be later reflected in the scope of monitoring: the less reliable prediction will be the more intensive monitoring should be. Monitoring is aimed at confirming the prediction made by means of a model or the prediction made otherwise with the aid of the data collected in the field.

The investigation (guiding) parameters relevant to the later monitoring for checking the effectiveness of natural attenuation processes should be worked out in the course of making the prediction. In addition, the measuring points for monitoring and the monitoring intervals should be fixed with the aid of prediction.

A1-II.3 Evaluation and assessment of the results

Ist step Checking of the prerequisites for preparing a MNA concept.	
I.1 Targets set by the authority for agreeing on framework conditions with obligated party	• The MNA concept is the result of checking an individual case. • The type and extent of the proof of the effectiveness of attenuation processes have to be concerted. • The basic requirement for remediation is not doubted by MNA. • MNA as sole measure is only possible if the site-related prerequisites will be fulfilled and remediation measures assessed as being inappropriate. • If a remediation as a sole measure will be appropriate MNA will be unsuitable. • A concerted monitoring shall be carried out to check the effectiveness of the attenuation processes. • An alternative option for action is to be scheduled.
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Administrative decision on the suitability and implementation of MNA	• Criteria for the decision: - Are the site-related prerequisites acc. to Chap. 4 of the text part fulfilled and, if yes, to which extent? - Does the MNA concept ensure the required monitoring intensity and does it provide the possibility of a punctual intervention? - For which areas of the groundwater damage will a remediation be appropriate and will have thus to be carried out? - For which areas of the groundwater damage will a remediation be inappropriate solely before the back ground of attenuation processes and a MNA will be the appropriate measure instead of a remediation? • Agreement on a binding instrument of regulation
IVth step	
Carrying out of MNA	• Execution of monitoring on the basis of a monitoring plan • Checking of the prediction (variance comparison), if necessary, adaptation of the approach • After reaching the target concluding assessment of hazards

After concluding the partial stages II.1 and II.2 the obligated party or its expert shall finally evaluate and assess all marginal conditions and results of investigation. Thereby, there should be found out if or to which extent the site-related prerequisites according to Chap. 4 of the text part for carrying out MNA are fulfilled and if a MNA concept would help the obligated party to reach the target. This refers also to the question whether a remediation or partial remediation of the source shall be carried out.

A further prerequisite for carrying out MNA is that remediation measures are inappropriate for the area of the groundwater damage for which the obligated party intends to carry out MNA. That is why with regard to the appropriateness test in stage III made by the authority all investigations required for a site-specific test of the appropriateness of remediation measures shall be made and evaluated. Thus, with a view to the "classical" stages of remediation of contaminated sites the stage of a remediation investigation has been reached. The extent of the remediation investigation should be coordinated in advance with the authority, in particular, with regard to the reliability of the appropriateness test. Investigations required for that should, as a rule, be carried out already parallel to the investigations made to prove the suitability of a MNA concept.

A1-II.4 Preparation of a MNA concept and explanation of its suitability

Ist step	Checking of the prerequisites for preparing a MNA concept.
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IInd step	Proof of the effectiveness of attenuation processes and preparation of a MNA concept
II.1 Site investigations to prove the effectiveness of attenuation processes	• Spatial position and expansion of the contaminant plume • Investigations to determine the contaminant loads at balance levels • Investigations for identifying and quantifying the essential individual processes • Investigations on the basis of a deficit analysis to prepare the prediction
II.2 Prediction of the development of the contaminant plume	• Preparation of a numerical model (flow, transport and reaction processes) • Assesment of the long-term course and the of the process • Representation of prediction uncertainties by means of scenario considerations and sensitivity analysis • Identification of the key parameters
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Administrative decision on the suitability and implementation of MNA	• Criteria for the decision: - Are the site-related prerequisites acc. to Chap. 4 of the text part fulfilled and, if yes, to which extent? - Does the MNA concept ensure the required monitoring intensity and does it provide the possibility of a punctual intervention? - For which areas of the groundwater damage will a remediation be appropriate and will have thus to be carried out? - For which areas of the groundwater damage will a remediation be inappropriate solely before the back ground of attenuation processes and a MNA will be the appropriate measure instead of a remediation? • Agreement on a binding instrument of regulation
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The ideas of the obligated party of how to further deal with the groundwater damage should be presented to the authority at this time and for the case that the authority will also consider a MNA concept to be promising they shall be included in the MNA concept with its respective components of regulations. This involves proposals referring to intermediate and final targets as regards space and time, a monitoring draft plan adapted to it, a. o. including proposals on guiding parameters and alternative measures if it will appear that the targets will not be reached when carrying out MNA. To this end, it will be necessary to indicate criteria showing a deviation from the prediction.

In a combination of MNA and remediation the MNA concept should be made up as an independent component of a remediation concept, otherwise as an independent concept. This will ensure a goal-directed approach oriented to a decision based on the early coordination of the content with the authority before making up the expensive and already very specific remediation plan.

The envisaged monitoring program shall be described as a component of the MNA concept allowing to check the efficiency and sustainability of the natural attenuation processes in the MNA monitoring plan. In addition, the respective obligations to reporting shall be fixed. Here, the monitoring program cannot be restricted solely to measurements of the contaminant concentration but shall also contain parameters (guiding parameters) for process control and adjustment of the prediction made up with the aid of calculation models. Apart from that repeated load considerations at balance levels may be required as components of the monitoring program.

As also a monetary consideration of appropriate measures will have to be carried out by the authority in the course of the appropriateness test it is necessary to indicate the costs to be planned for MNA in the framework of a MNA concept.

Finally, the suitability of the MNA concept shall be explained in a way to enable the authority to make a decision on the further approach based on the documents presented in the framework of the discretion in selecting.

A1-III Administrative decision on the suitability and implementation of MNA

Ist step	Checking of the prerequisites for preparing a MNA concept.
I.1 Targets set by the authority for agreeing on framework conditions with obligated party	• The MNA concept is the result of checking an individual case. • The type and extent of the proof of the effectiveness of attenuation processes have to be concerted. • The basic requirement for remediation is not doubted by MNA. • MNA as sole measure is only possible if the site-related prerequisites will be fulfilled and remediation measures assessed as being inappropriate. • If a remediation as a sole measure will be appropriate MNA will be unsuitable. • A concerted monitoring shall be carried out to check the effectiveness of the attenuation processes. • An alternative option for action is to be scheduled.
I.2 Checking of the site-related prerequisites according to the present state of knowledge	• Site potential • Contaminant input and reaction spaces • Presentation of the hydrogeological model
IInd step	Proof of the effectiveness of attenuation processes and preparation of a MNA concept
II.1 Site investigations to prove the effectiveness of attenuation processes	• Spatial position and expansion of the contaminant plume • Investigations to determine the contaminant loads at balance levels • Investigations for identifying and quantifying the essential individual processes • Investigations on the basis of a deficit analysis to prepare the prediction
II.2 Prediction of the development of the contaminant plume	• Preparation of a numerical model (flow, transport and reaction processes) • Assesment of the long-term course and the of the process • Representation of prediction uncertainties by means of scenario considerations and sensitivity analysis • Identification of the key parameters
II.3 Evaluation and assessment of the results	• Concluding evaluation and assessment of all marginal conditions and results of investigations • Site-specific assessment of remediation measures (upon completion of the remediation investigation)
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Administrative decision on the suitability and implementation of MNA	• Criteria for the decision: - Are the site-related prerequisites acc. to Chap. 4 of the text part fulfilled and, if yes, to which extent? - Does the MNA concept ensure the required monitoring intensity and does it provide the possibility of a punctual intervention? - For which areas of the groundwater damage will a remediation be appropriate and will have thus to be carried out? - For which areas of the groundwater damage will a remediation be inappropriate solely before the back ground of attenuation processes and a MNA will be the appropriate measure instead of a remediation? • Agreement on a binding instrument of regulation
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The decision of the authority to carry out MNA is based on

- an appropriateness test of suitable remediation variants which are, as a rule, the result of a remediation investigation (Chap. 5)
- the concluding assessment of the site-related prerequisites according to Chap. 4 of the text part and
- the MNA concept submitted.

It is important for the decision

- for which areas of the groundwater damage a remediation is appropriate and has thus to be carried out,
- if or to which extent the site-related prerequisites are fulfilled according to Chap. 4,
- for which areas of the groundwater damage a sole remediation would be inappropriate before the background of attenuation processes detected and MNA would be an appropriate measure and
- if the MNA concept ensures the necessary intensity of monitoring and, if required, will provide the possibility of intervening in time.

The decision to carry out MNA will be made after carrying out the appropriateness test. Here, the measures shall be always regarded with a view to the target of the measures having, on the other hand, also effect on the appropriateness of measures in an iterative process and, if need be, has to be adapted. At this time, the decision on how to handle the contaminant source should have been made as this will be also of importance to the MNA concept.

After the decision to carry out MNA was made by the authority the obligated party and the authority should find a regulation on carrying out MNA binding to both parties. It should contain the monitoring plan, the targets, the measures with the necessary adaptations and an alternative option of action.

As it is to be expected that the decision to carry out MNA is mostly made in connection with the decision to carry out remediation measures such a regulation may be made e.g. by declaring a remediation plan to be binding or by concluding a contract under public law.

A1-IV Carrying out of MNA

Ist step	Checking of the prerequisites for preparing a MNA concept.
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Administrative decision on the suitability and implementation of MNA	• Criteria for the decision: - Are the site-related prerequisites acc. to Chap. 4 of the text part fulfilled and, if yes, to which extent? - Does the MNA concept ensure the required monitoring intensity and does it provide the possibility of a punctual intervention? - For which areas of the groundwater damage will a remediation be appropriate and will have thus to be carried out? - For which areas of the groundwater damage will a remediation be inappropriate solely before the back ground of attenuation processes and a MNA will be the appropriate measure instead of a remediation? • Agreement on a binding instrument of regulation
IVth step	
Carrying out of MNA	• Execution of monitoring on the basis of a monitoring plan • Checking of the prediction (variance comparison), if necessary, adaptation of the approach • After reaching the target concluding assessment of hazards

In this phase of the procedure monitoring is carried out on the basis of the MNA monitoring plan. It serves to check the prediction (variance comparison) and control if the attenuation processes function permanently. It should be underlined that, as a rule, for this purpose not only contaminant and process-related concentration measurements are made according to guiding parameters but also repeated load considerations forming part of the control may be required. Here, measurement and prediction insecurities shall be taken into account.

At regular intervals (e. g. every 5 years) the type and extent of the monitoring program may be checked and adapted upon request or the suggestion of the obligated party.

Due to the obligations for reporting – as agreed – a continuous assessment and evaluation of the monitoring results is made while carrying out MNA.

If the attenuation processes do not develop or take place in the prognosticated way a decision is to be made on the measures shown in the framework of the MNA concept up to taking up alternative options of action such as e. g. remediation measures.

In this case it might be useful to, first of all, carry out a process-related assessment and repeated evaluation, in particular, if MNA was carried out over a longer period as it is to be expected that the data basis for assessing the attenuation processes has become more extensive. If appropriate, supplementary investigations should be agreed upon if the cause for the deviating development is not clear. MNA can be only continued if the check shows that the attenuation processes will be sufficiently effective also in future. If the reliability of the prediction model will no longer be sufficient for making a new prediction on the basis of the supplemented data the model shall be revised, if applicable. In addition, if need be, also modified targets and a modified monitoring program may be arranged.

If the targets will not be reached also after carrying out measures of adaptation the alternative option of action envisaged when agreeing on MNA according to III should be applied for this case.

Upon reaching the concerted targets the authority will subsequently check whether there exist still hazards, in particular, to groundwater and groundwater uses. This check does not basically differ from the investigations related to the pathways in the framework of aftercare which are carried out after the final acceptance of a remediation measure. If there will be proved that hazards may be permanently excluded the authority will agree to terminate MNA on application filed by the obligated party.

ANNEX 2 METHODICAL INSTRUCTIONS FOR CHECKING THE PREREQUISITES FOR CARRYING OUT MNA

A2-0 INTRODUCTION

In the position paper (Chap. 4) site-specific prerequisites for implementing a MNA concept are mentioned. To decide whether the site-related prerequisites are fulfilled in the individual case suitable and practicable methods of investigation and approaches are required.

The present Annex 2 is to serve as aid for selecting methods, experiences and approaches in view of the prerequisites for checking the implementation of a MNA concept. It provides a selection of methods relevant to the problems to be dealt with and classified as being practicable to a high degree.

In particular, methods and instructions from the KORA funding priority are mentioned which have been published in the recommendations for action, collection of methods, guidelines and research reports. They are supplemented by further knowledge, developments and experiences. The individual methods and instructions are not described here in detail. That is why references to KORA or respective literature have been made (reference in brackets in the text, e. g. M 2.1.1 means KORA – recommendations for action, collection of methods, Chap. 2.1.1).

In Chap. 4 of the position paper the site-related prerequisites for implementing a MNA concept relating to the subjects contaminant source (Chap. 4.2), contaminant plume (Chap. 4.3) and protection of the groundwater not yet affected and consideration of further protected objects (Chap. 4.4) are formulated. This classification is taken over in the present Annex. Methods for estimating the contaminant mass and contaminant release rate are dealt with in Chap. A2-1 "Contaminant source". Chap. A2-2 "Contaminant plume" contains methods for determining the load, detecting and predicting "quasi-stationarity" and developing an understanding of the process/system. In addition, methodical approaches to consider further protected objects are described.

The flow chart hereinafter shows ways of decision for the final assessment of the site-related investigations with regard to making up a MNA concept. It indicates the suitable methods and approaches for checking the prerequisites for MNA which may be applied to the respective problem in the individual case.

A2-1 Contaminant source

As one of the prerequisites for carrying out MNA there is required in Chap. 4 that the contaminant quantity in the source and/or the drag-out of the contaminants from the source is to be reduced by carrying out remediation measures.

If for reasons of appropriateness or technical feasibility a comprehensive remediation of the source is not possible alternatively a partial remediation of the source, in the exceptional case also no remediation of the source, will be carried out. If contaminants will remain in the source the duration of emission (release) may be estimated when knowing the contaminant mass and the release rate. This is, in particular, relevant to cases when the duration of the groundwater damage – and thus the period for carrying out MNA – is a decisive criterion. The more important the temporal perspective of a damage is when making the decision on MNA the higher are the demands for estimating the contaminant mass and rate of release from the source.

In the case that it will not be possible to remediate the source, first of all, the results of the detailed investigation have to be checked as to whether the estimates of contaminant mass and release rate made are sufficient for making the decision to implement a MNA concept.

A determination of the contaminant mass in the source and of the rate of release from the source is required in the case when the prediction of the development of the contaminant plume is decisively based on stoichiometric considerations, i.e. on quantitative calculations of the chemical reaction. Here, the released contaminants are compared with the reactants required for the reduction of contaminants to assess whether e.g. sufficient electron acceptors will be available for the biological degradation.

A2-1.1 Methods and approaches to assess the contaminant mass

The starting point for assessing the contaminant mass in the source is the determination of contaminant contents in the unsaturated and saturated soil zones, on the one hand, and the assessment of the spatial expansion of the contaminated soil and groundwater, on the other hand. The key elements of this approach have been already described in the working aid of the LABO Prediction of Leachate in Detailed Investigations [18].

The determination of the spatial expansion of the contaminants is based on known methods of investigation such as soil/groundwater sampling during ramming core sounding or core drilling and their analyses in the laboratory. Direct push sounding (M1.1) provides the possibility of a semi-quantitative investigation of the contaminant content in subsoil without taking material samples:

- Sounding by means of a MIP (Membrane Interface Probe) (M1.1.1) is suited for the semi-quantitative determination of highly volatile contaminants such as BTEX, CHC and short-chain MHC.
- It is possible to determine the PAC content occurring in traces also in fuel (petrol, diesel, kerosene), crude oils or in phenol sludges directly semi-quantitatively for difficultly volatile contaminants through LIF (laser induced fluorescence) probes (M1.1.2).

Making statements on the type and volume of phase areas is possible on a limited scale.

The advantage of direct sounding consists i. a. in a higher working speed and in a clearly better differentiation of the contamination allowing a detailed picture of the contaminant distribution in soil. On the other hand, direct push sounding is, as a rule, restricted to a drilling depth of 30 – 50 m, to loose rock without coarse gravel components and to surface weathered solid rock. When passing highly loaded areas MIP sounding (in contrast to LIF technology) may carry off contaminants (memory effect) so that the determination of the lower limit of contamination is connected with a higher insecurity than the determination of the upper limit of contamination:

Direct push sounding offers, in addition, the possibility to develop the sounding hole into a 1" measuring point with a most varied development of the filter or sampling area subsequent to the measurements (M1.1.4). These measuring points allow thus a deep differentiated sampling of groundwater and soil air. Owing to the low groundwater sampling rate and thus the drainage area pumping samples from 1"measuring points are not

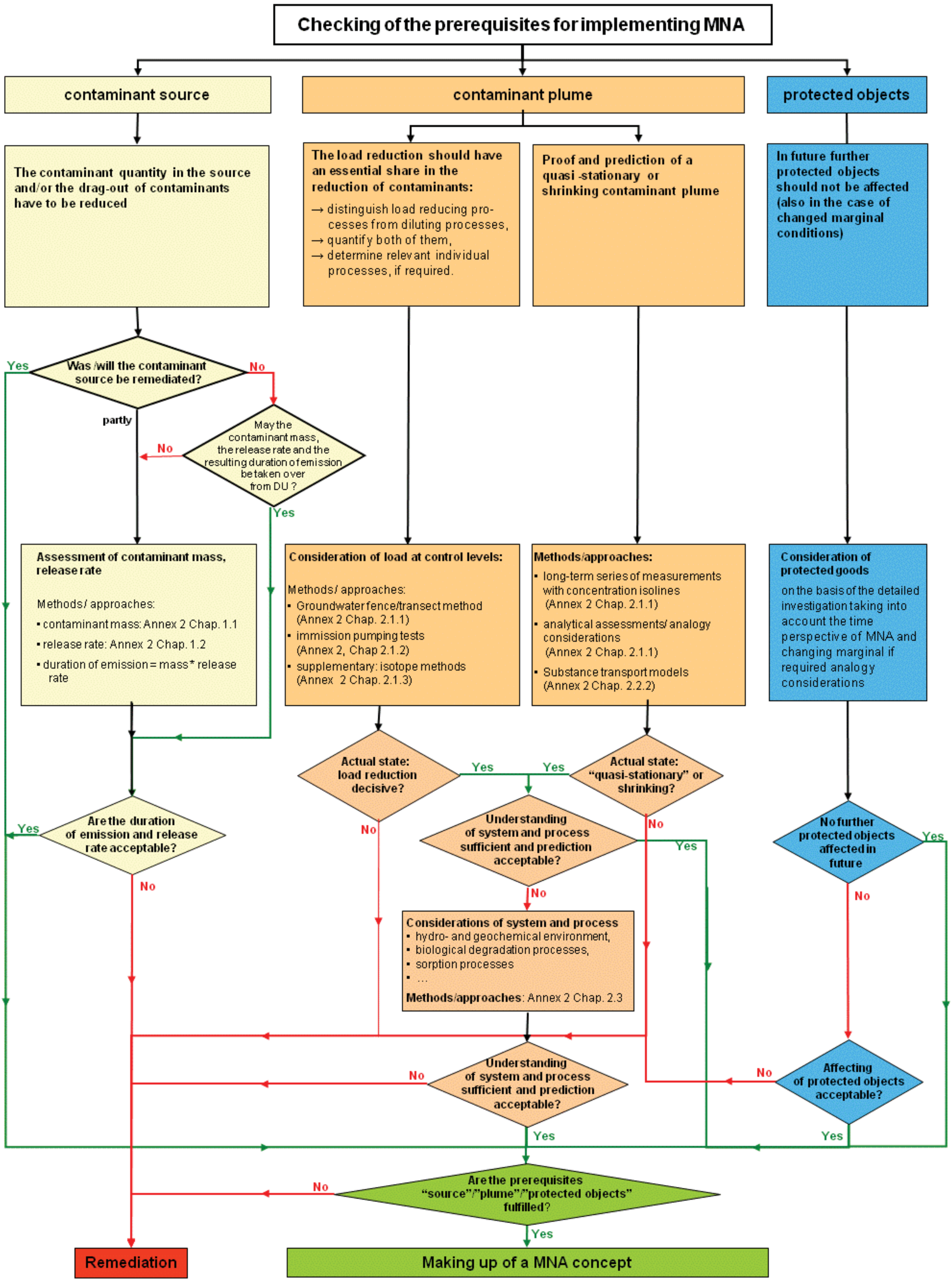

Fig. A2-1 Flow chart for checking the prerequisites for implementing MNA comparable with pumping samples from conventional measuring points.

The expansion of the contaminant source as well as of the contaminant plume may be determined in this way with a clearly higher degree of detailization and at lower costs than by means of conventional methods. In this way also the location of conventional groundwater measuring points may be optimized.

In highly volatile contaminants contaminant sources may be delimited also through measurements in soil air. In insignificantly permeable soils the diffusion may, however, be strongly reduced.

In the case of a phase (LNAPL) swimming on groundwater there may be checked whether measurements of radon (M1.1.7) in soil air may be used to identify and horizontally delimit a phase body. The strong limitations as regards the applicability of this method have to be taken into consideration,

To find out whether a measuring point is in hydraulic contact with a free phase pumping tests may be carried out to determine the phase mobility (M1.1.6). In addition to the conclusions relating to the mobility of the phase it may be assessed from the results of them whether the measuring point is located in the phase carrying area. Apart from that information can be obtained whether a phase sampling will be successful.

When determining the thickness of the phases by sampling in groundwater measuring points several sources of errors shall be taken into consideration.

- The filter layers of the measuring points have to be adapted to DNAPL or LNAPL.
- Varying groundwater levels may affect the inflow of LNAPL into the measuring points. Before this background it is important to take up time series of groundwater and phase levels to reliably interpret the vertical expansion of the areas contaminated by NAPL.
- A difference should be made between the phase thickness in the measuring point (apparent phase thickness) and the phase thickness in the adjacent sediment which, as a rule, is smaller.

That is why the phase thickness determined in the measuring point should be verified by respective checks (e. g. soil sampling) before being transferred to the adjacent sediment.

After determining the contaminant contents and the spatial distribution of the substances in the source the contaminant mass may be assessed as follows:

- by interpolating the contaminant contents and multiplying them with the respective volume (s. working aid of LABO leachate prediction in detailed investigations [18]) or
- if required, by analytical calculation of the contaminant mass from the geometry of the phase body through the spatial integration of saturation profiles (TV1 Chap. B3.1.2).

When interpolating the contaminant contents the information security of the data depends essentially on the representativeness of the data base. Statistical parameters (TV3 Chap. B2.2.2.2.1 and KORA recommendations for action Chap. 7.6 "Virtual aquifer") relating to the heterogeneity of the data stock – if their limits of use are taken into account – may indicate whether the number of samples and sampling points is sufficient for assessing the contaminant mass.

When calculating the contaminant mass of phase bodies through the spatial integration of saturation profiles a multitude of site-specific parameters has to be determined, e.g. grading curve, water tension curves and porosity. In particular, due to the possibly high sensitivity of the van Genuchten parameters depending on the soil type this calculation allows only an estimation of the contaminant mass.

The identification and mapping of contaminants in phase is an important basis for evaluation. If the contaminants as phase are located in the unsaturated or saturated zones their total content in soil samples allow to estimate if the contaminants exist as residual or even mobile phases. Equally there is to be determined if and to which extent the contaminants are bound to the soil matrix and if the sorption is reversible [19]. This information on the type and spatial distribution of the contaminants in the source is decisive for the determination or assessment of the release rate.

A2-1.2 Methods for assessing the release rate

The determination of the contaminant release has been equally dealt with in the working aid of the LABO "Leachate Prediction in Detailed Investigations" [18]. Some extracts from it:

"The actual contaminant concentration in leachate or contact groundwater of the source is to be determined and their future development is to be estimated to determine the release of contaminants. These investigations deliver the source strength of the contaminated material, i.e. the contaminant mass coming from the respective contaminant source per time and area unit (mass flow density). By multiplying the source strength with the area size of the contaminant source the load coming out of the source (mass per time unit)..." is calculated.

"The water solubility of the individual substances may be used approximately as source concentration for contaminants in phase. The solubility of organic substance mixtures (MHC, creosotes) is reduced as against the individual substance in conformity with the mole portion of the respective substance and may be calculated by means of the Raoult's law". Column experiments may be carried out to assess the release of organic contaminants from contaminated soils pursuant to the Federal Soil Protection and Contaminated Sites Ordinance [19]. If column experiments may not be applied primarily chemical-physical data for assessing the leachate concentrations of organic contaminants will be appropriate." "The duration of emission from a contaminant source depends directly on the leachate concentration and the mobilizable mass of contaminants in the source). "A mobilizable mass of 100 % of the total content (aqua regia extraction) is not rarely assumed as worst case scenario in practice for inorganic contaminants. However, an assessment with the aid of less strong extractants is more realistic for the "foreseeable future".

This appears, in particular, during the release of organic contaminants with a limited quantity of solvents.

The prediction instrument ALTEX-1D [18] which is a component of the above-mentioned working aid allows to put these considerations into practice and to specifically estimate the individual operands. Though ALTEX-1D was originally developed only for the unsaturated zone the calculation approaches may be applied to the saturated zone.

The actual release rate from the source may be determined also by a load consideration at the first control level in the immediate downflow from the source (s. Chap. A2.2.1). The biological degradation of well-degradable substances such as e.g. many mineral oil containing contaminants is so high in the source that already a significantly lower load is determined a few meters in the flow from the source than the release rate from the source. In addition, the temporal development of the release rate may not be predicted by determining the load.

A2-2 CONTAMINANT PLUME

The considerations hereinafter relating to the contaminant plume assume that knowledge of the spatial (3D) distribution of the contaminants is available. As a rule, these investigations have been already the subject of detailed investigations. If such knowledge is not available basically the same methods which were mentioned also to explore the contaminant source, however focussed to dissolved and sorbed contaminants suggest themselves. As compared with conventional bore holes direct push sounding provides detailed findings at low costs. And the location of conventional groundwater measuring points may be optimized in this way.

Load considerations at control levels situated in the downflow (Fig. 2 Chap. 4.2), the proof and the prediction of the "quasi-stationarity and the development of an understanding of the system and the process are the essence of the MNA specific considerations relating to the contaminant plume. Based on it further protected objects should be considered with regard to a potential future adverse effect on them.

A2-2.1 Load consideration at control levels

In Chap. 4 of the position paper there is mentioned as one of the prerequisites for implementing MNA that a "distinction shall be made between load reducing and diluting processes, both of them should be subsequently quantified. The investigation should prove that the load reduction has an essential share in the attenuation of contaminants." As the distinction between the individual processes may be very expensive, first of all, the proof would be appropriate that the load is reduced along the contaminant plume. Thus, **load reducing processes** may be delimited from **diluting processes.**

The decline of concentration to be frequently observed in contaminant plumes (areas near the source show high concentrations, with the distance from the source increasing the concentration goes down) is based also on diluting processes apart from the proper degradation and retention processes. Thus, the proof of a decline of the concentration along the contaminant plume is solely not sufficient for implementing a MNA concept. In each case there shall be determined whether a clear reduction of the load takes place.

In a first step the control levels situated vertically to the downflow direction shall be defined along the contaminant plume. The groundwater volume flows (Q) and the medium contaminant concentration are to be determined at these control levels. The load (E) will be determined from the product of the medium concentration and the volume flow at the respective control level ($E = C^*Q$). The "groundwater fence/transect" approach (Chap. A2-2.1.1) or the immission pumping test (Chap. A2-2.1.2) are suitable methods. The load reduction along the contaminant plume will be determined from the differences between the loads at the respective control levels. The load reducing factor may be determined from the ratio between the loads.

The location of the control levels is here essential: The 1st control level should be located in the direct downflow of the contaminant source to determine the reference load released from the contaminant source where the loads of the control levels in the downflow are related to. The position and the number of further control levels result from the individual case. The last control level should be in the area of the plume top which may be analytically reliably determined (Fig. 2 Chap. 4.2).

The proof that the load at the last control level amounts only to 20 % of the load at the 1st control level is, as a rule, sufficient to assess if the load is **essentially** reduced as against the dilution.

In the case of insecurities there should be proved that the load reducing factor (E1/E2) between the control levels 1 and 2 is bigger than the respective dilution factor (Q_2/Q_1).

A first impression of the ratio between load reduction and dilution may be obtained at individual measuring points by comparing degradable or sorbable contaminants with "conservatively" behaving substances which are neither subject to degradation nor to sorption processes (TV1 Chap. B3.3.1.2.1).

If the attenuation of contaminants detected is essentially based on sorption (retardation) the extent of a potential desorption should be considered e.g. by means of modelling.

A2-2.1.1 Groundwater fence / transect method

A method for determining the load at control levels is the "groundwater fence method" (BOCKELMANN et al. 2003, KING et al. 1999, BORDEN et al. 1997). Relating to this the guide of KORA-TV1 Chap. B3.3.2.1.1 contains the following:

"...along a control level contaminant concentrations and specific groundwater flows are measured vertically as well as horizontally in a dense raster which are subsequently interpolated to the control level areas by means of a polygon network. Owing to the mostly very heterogeneous contaminant distribution a dense raster of sampling points (e.g. by direct push sounding and measuring points) is required to obtain reliable data relating to the contaminant load. Information and recommendations:

- *The advantage of this spatially interpolating method is balancing of loads over bigger cross-sectional areas considering the various concentration gradients occurring.*
- *This method will then result in reliable values if the distance between the interpolation points of the heterogeneously distributed parameters is small as compared to the length of correlation. Sampling in deep horizons should be made, if possible the Kf values should be determined (e.g. injection logging with DP technique, slug tests, sieve*

analyses etc.). As a rule, hydraulic gradients may be only indicated as average values over the control level."

- *Owing to the typical degradation the gradient of the contaminant concentrations is sometimes very steep in the near downflow of the contaminant source in sites contaminated by mineral oil which may complicate" the establishment of a control level near the contaminant source and the determination of the contaminant load corresponding to the substances drag-out from the contaminant source".*
- *"In heterogeneous sites a very high density of measuring points is required for a reliable determination of the contaminant loads."*

If short-term variations of the concentration have to be expected on a site e.g. by strong variations of the groundwater level which may be only recorded by frequent sampling at critical dates passive collector units may be used in addition to the determination of the average concentrations or loads (M1.2.2).

A2-2.1.2 Immission pumping tests

The basic concept of the immission pumping tests or the integral groundwater exploration methods are based on the fact that the contaminated downflow along the control level is recorded by pumping measures at appropriate wells (M1.2.1, s. a. Peter et al. 2004, Bauer et al. 2004, Teutsch et al. 2000). During the pumping measure the concentration curves for the relevant contaminants are determined. The extracted groundwater flows from the well to an ever bigger catchment area, thus integrating an increasing groundwater volume. The contaminant load may be determined from the temporal concentration course and the quantity of the water pumped off [25]. The prerequisite for applying this method is sufficient hydraulic knowledge on the subsoil. It is basically suited for all contaminant groups of typical contaminated sites. However, establishing a control level near the source is difficult if a mobile or mobilizable phase exists in the contaminant source which could be displaced by long pumping.

Depending on the processing and discharge costs immission pumping tests could become very expensive, in particular if it will be necessary to build for this, first of all, special wells with the required yields. That is why recording of the whole contaminated downflow will not be possible in each case. The method is less appropriate for aquifers with small permeabilities and/or a high thickness owing to the small catchment area of the wells in connection with long pumping test periods.

A2.-2.1.3 Isotope methods

Isotope methods can be applied to clarify whether the load reductions detected or recession of the concentrations with the transport way increasing between two control levels may be caused by biological degradation processes. Supplementary to or in combination with the a. m. approaches to investigation the determination of isotope signatures (TV1 Chap. B3.3.2.2.3) of an element ($^{13}C/^{12}C$, $^{2}H/^{1}H$) being a component of the contaminant molecule may furnish the clear proof of a biological degradation.

The biological degradation of a contaminant is frequently connected with a relative enrichment of heavy isotopes (^{13}C, ^{2}H) in the contaminant not degraded as microorganisms mostly utilize preferably molecules built up of light isotopes. As a result the isotope ratio (isotope fractionation) is changed. Other processes where contaminants are exposed to e.g. hydrodynamic dispersion, sorption or volatilization do not significantly result in a fractionation so that we can proceed on the fact that an enrichment of heavy isotopes observed was caused solely by biological degradation.

The isotope signatures should be determined at various control levels. Using process-specific fractionation factors determined in the laboratory the biological degradation may be quantified. However, the prerequisite for that is that the degradation mechanisms and environmental conditions in the field are known and fractionation factors representative for that are available.

On the other hand, it is, however, not applicable that lacking of an isotope fractionation is a negative result for the biological degradation (s. a. Guide of KORA-TV1 Chap. C4.3.1 and TV3 Chap. E4.II.7.1). For the time being, fractionation or enrichment factors (for $^{13}C/^{12}C$) for about 20 organic contaminants, i. a. for all BTEX components, some PAC, various chlorinated hydrocarbons and MTBE are available (summarized in MECKENSTOCK et al. 2004 [26], SCHMIDT et al. 2004b [27]).

Apart from that isotope ratios may be only used to distinguish various contaminant sources from each other if the starting materials have different signatures. Before applying isotope methods the marginal conditions relevant to the problems have to be checked (s. a. M2.2.4 and M2.2.5).

A2-2.2 *Proof and prediction of "quasi-stationarity"*

In Chapter 4 of the position paper it is required as one prerequisite for carrying out MNA that on the basis of the results of investigations relating to the contaminant plume it shall be possible to make a prediction if at present or in future negative effects on further protected objects may be excluded. This demand requires to detect a quasi-stationary or shrinking contaminant plume.

In practice frequently essential variations of the concentrations over the time have been, in particular, observed at the plume top. That is why the following potential causes have to be considered in predicting the development of the plume or proving the "quasi-stationarity":

- a changing groundwater recharge (e. g. by seasonal variations or due to surface sealing), temporary groundwater extraction (e. g. owing to building measures) and influences of surface waters may cause natural changes of the hydraulic conditions such as fluctuations of the groundwater level or changes of the flow direction. This may result in the fact that the contaminant plume will be possibly only incompletely recorded by the existing measuring points.
- various sampling conditions, sampling techniques and analytical methods,
- complex contaminant sources with various or temporarily changing contaminant loads /source power and
- superposition of several contaminant plumes.

A2-2.2.1 Proof and prediction by means of series of measurements and analogy considerations

By means of geostatistically verifiable series of measurements over many years carried out at a sufficient number of appropriately positioned groundwater measuring points in the contaminant plume as well as in its environment the stationarity of a contaminant plume may be most convincingly detected. If the contaminant concentrations detected over a longer period will not or only insignificantly change in the individual measuring points this may be interpreted as stationarity of the contaminant plume. It is to be recommended to represent its temporal development as concentration curves as well as concentration isolines showing especially the spatial development of the contaminant plume. In this connection the measuring points at the plume top are especially relevant as they are of great importance to the assessment whether the groundwater damage is spreading.

In investigations of contaminated sites not carried out under the aspect of implementing a MNA concept we have to expect that time series statistically evaluable are not available to the required extent in appropriate measuring points as the position and the extension of the measuring points are only rarely suited for that. In these cases, first of all, the technical prerequisites should be provided and implemented in the necessary period. Here, it is disadvantageous that a decision on a MNA concept may not be made in this period which may comprise several years. On the basis of site investigations directed at attenuation processes (load considerations at control levels, qualitative and quantitative proof of degradation processes and actual delimitation of the contaminant plume) the probability of stationarity of a contaminant plume may, however, be plausibly assessed in most of the cases. Calculations of analytical models based on simplified site conditions may be used for an assessment. Both approaches require invariable site conditions, a. o. sustainable natural attenuation processes.

In simple cases / hydrogeological and hydraulic site conditions the prediction can be made analogously to stationary plumes known without measurement series over many years being available (< 5 years). However, this refers, in general, only to cases of damage caused by specific contaminant groups with a short plume length (such as MHC) and a comparatively insignificant source strength and sites where protected objects in the groundwater downflow cannot be endangered.

A2.-2.2.2 Proof and prediction by means of substance transport models

The application of a substance transport model (KORA TV7) is to be recommended in more complex cases. It allows to assess the spatial and temporal development of the contaminant plume and its stationarity for the essential contaminants under the given hydrogeological and hydrochemical marginal conditions and based on the degradation and sorption processes detected. The scale of the best and worst-cast predictions may be considered by means of sensitivity analyses and considerations of scenarios for varying marginal conditions in future (e.g. change of the groundwater recharge and thus of the input of electron acceptors by sealing or changing the groundwater flow direction owing to construction measures). A survey of the model software applied in KORA for specific sites is contained in Tab. 7.1 of the KORA recommendations for action.

Each time before making up a model the problems to be clarified have to be coordinated among the participants. In substance transport models these may be in connection with MNA, in particular:

- confirmation/assessment of the processes relevant to spreading and of the parameters determining them,
- assessment of the release rate,
- prediction of the future expansion of the plume,
- prediction of the development of concentration within the contaminant plume,
- delimitation of contaminant plumes with comparable contaminant spectra and various contaminant sources,
- checking, comparing and optimization of the remediation variants,
- optimization of groundwater monitoring (e.g. position and extension of the measuring points, sampling interval).

A conceptual understanding of the system/process with all important features **(conceptual site model)** is the prerequisite for a prediction by means of a substance transport model. Table A2-2 gives a survey of the respective conceptualities and model types which are of importance with regard to the prediction of the development of the plume and are described hereinafter.

Based on the **model of the geological structure a model of the hydrogeological structure** is made up by means of determining the basis, data acquisition and explorations [16], [20], [21], and [22]. This model of the hydrogeological structure forms the basis for building up a **numerical groundwater flow model**. The problems to be clarified are to be considered already when choosing the model approach. In addition, the connections between balance, model and data space have to be considered in making up the model. There has a. o. to be decided whether a stationary or non-stationary modelling or a 2D or 3D modelling will be required. The last-mentioned requires that sufficient data of a different depth will be available. After calibration by means of the measured data sets the validation is made by means of a data set independent of the calibration. By a sensitivity analysis the influence of important model parameters on the model result should be shown.

Parallel to building the flow model the substance transport processes can be parameterized. In lack of field data for many substances literature data have to be used. Choosing of suitable values requires a high interdisciplinary expertise.

For the subsequent **numerical substance transport modelling**, in particular, data relating to the type, number and source strength of the contaminant sources or data on the inclusion of the source in the model are of importance. Apart from that the marginal concentration conditions at the inflow margins and the substance transport parameters (effective porosity, dispersivity, hydrodynamic dispersion, retardation factors and reaction parameters) have to be explained.

When choosing degradation parameters from literature attention should be paid to the fact that the hydro-chemical conditions should correspond to the conditions under which the coefficients described in literature have been determined. As a rule, plausible ranges are determined from field, literature and laboratory data which will be calibrated in the framework of substance transport modelling, i.e. determined by comparing measured and simulated contaminant concentrations. This assumes that it was possible to make an exacter assessment of the remaining substance transport parameters, i.e. that the ranges of the remaining parameters defined, first of all, if need be, also to be calibrated will be smaller. It is to be explained why the chosen degradation term is used and which value will be assumed.

If appropriate, it will be possibly necessary to carry out specific investigations (tracer tests, sorption tests) to determine the remaining transport parameters.

When calibrating the substance transport model, as a rule, the parameters of the groundwater flow model are no longer changed. The results of the substance transport model are to be compared with the requirements made and the questions formulated. When representing the results of the prediction calculations the hydrochemical and hydraulic marginal conditions chosen have to be documented and the uncertainties of the results of prediction resulting a. o. from a sensitivity analysis have to be discussed. In particular, scenario considerations suggest themselves in the case of these marginal conditions changing or high prediction insecurities not exactly foreseeable arising to represent the scope of potential developments.

Numerical substance transport models may be extended to **multi-species models**. Unlike one-component models multi-species models allow a process-related reproduction of the reactions as they consider also the reactants, i.e. the biological degradation is only possible in the presence of reactants. The essential processes are to be determined in process exploration. Thus, at the margins of MHC, PAC, CHC and BTEX plumes mostly aerobic processes are important whereas frequently anaerobic conditions with a reduction of nitrates, sulphates or iron predominate within the plume.

Only if the input data are of a sufficient quality and density it may be expected that all models will be sufficiently convincing and able to make predictions. This aspect is to be considered when drawing up and developing the model. If need arises, additional data have to be collected. In particular, there should be taken into consideration that mostly short monitoring periods of a few years are taken as basis to calibrate transport models for predictions of frequently several decades up to hundreds of years. That means, that a monitoring measure in the framework of carrying out a MNA concept should not only serve to monitor the site or the sustainability of the NA processes but also be used to continuously to keep up the model, if necessary to recalibrate and update the prediction.

Tab. A2-2: Survey of conceptuality in models

Conceptual site model	System, process and effect describing model: Representation of a conceptual idea of the system with all important features of the site (e.g. geological conditions/structure of layers, groundwater stockworks, groundwater damage, direction of groundwater flow, substance sources, concentrations, protected objects, known and/or assumed effect of natural attenuation processes), uses, requirements to model results. The conceptual site model is not a mathematical model but the preliminary intellectual stage of a numerical, in simple cases also analytical modeL:
Geological structure model	Geological structure Description and representation of the geological Model conditions: lithology, stratigraphy and genesis. These elements are represented in their spatial position to each other as lines, areas and/or bodies
Hydrogeological structure model	Hydrogeological properties (e.g. porosity, storage model coefficient, hydraulic permeability) are assigned to the geological structures / units. If necessary, geological units are united with identical hydrogeological structures or conversely also further differentiated. Here, the geohydraulic and geochemical transfer and storage properties are described. The hydrogeological structure model forms the basis for the process-related models mentioned hereinafter
Numerical groundwater flow model	The numerical groundwater flow model converts the flow model flow processes into mathematical relations. Indicating starting and marginal conditions either a stationary flow field (i.e. groundwater levels and flow speeds calculated from them) or in the case of transient (non-stationary) model simulations groundwater levels and flow speeds and directions varying temporarily are calculated.
Numerical substance transport model	Based on the flow speed field calculated the numerical transport model substance transport model calculates the transport of substances in subsoil determined by processes such as advection, hydrodynamic dispersion, diffusion, substance storage (sorption/desorption, precipitation/ dissolution), if necessary, volatilization and by reaction processes (e. g. biological degradation).
Multi-species model for reaction systems	Multi-species model for The multi-species model considers the reaction processes reaction systems with their reaction parameters showing the transport and reaction behaviour of a system of interacting substances

A2-2.3 Methods to assess the processes or to develop an understanding of the process / system

In Chap. 4 of the position paper *"The determination of the relevant individual processes is the prerequisite for the subsequent prediction of the plume behaviour."* is mentioned as one of the prerequisites for MNA.

Whereas the methodical instructions in the preceding chapters were largely contaminant-unspecific the methods for investigating the processes are, as a rule, contaminant-specific.

Independent of the type of contaminants it is, however, necessary to determine the hydrochemical and geochemical media in the inflow to the site and along the contaminant plume.

Determination of the hydrochemical and geochemical media

This includes, in particular, the determination of the redox-sensitive parameters and the actual and future availability of electron acceptors and donators as they are, as a rule, controlling or indicating values for the degradation of all organic substances. That is why they are indispensable for understanding the process/system.

According to standard there have to be determined:

- physical-chemical parameters (conductivity, pH, Eh-value, temperature), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), acid capacity and hydrogen carbonate, phosphate,
- indicator of redox ratios/zones (electron acceptors and donators): dissolved oxygen, nitrate, sulphate, iron(II), manganese (II), methane, and ammonium.

In addition it can become necessary to consider the redox system more comprehensively and to determine iron(III), manganese(IV), sulphide, nitrite, hydrogen.

As a supplementary method to determine and observe redox zones in the long term redox bands (M1.2.10) can be used. This method is, however, not to be recommended in the case of strong vertical flows in an aquifer.

To develop an understanding of the process/system apart from main contaminants also accompanying contaminants have to be considered as they can remarkably affect the degradation and transformation of the main contaminants. The same refers to the hydrogeological marginal conditions, in particular the fluctuations of the groundwater level and the direction of groundwater flow.

In the individual case there has to be fixed how complete and detailed the site-specific understanding of the processes should be. It is possible to reduce expensive process investigations if the load reduction and the "quasi-stationarity" may be assessed with a sufficient security and predicted.

Not all contaminant reducing processes are of the same importance for the various substance groups. The table hereinafter reveals in a strongly simplified way the substance group-specific relevance of degradation, sorption and volatilization processes in the contaminant plume. Here, the relevance of the processes may not be mixed up with the effectiveness of the processes in the individual case. Further information on the individual substances may be taken from substance data bases [23].

Methods and concepts for determining biological degradation processes

The methods applied in KORA for characterizing the biological degradation processes are summed up in the KORA recommendations for action, notably in the collection of methods Chap. M2. In the individual case depending on the way of putting the question and target the appropriate methods may be chosen. In particular, the methods mentioned hereinafter seem to be appropriately usable in practice:

- Isotope methods (s. a. M2.2.4 and M2.2.5)
- Microbiological methods:
  - Determination of metabolism-specific bacterial counts to detect microorganisms supplementary to hydrochemical investigations difficult to interpret. By the MPN method for the determination of bacterial counts (M2.1.1) specific metabolic physiological groups of microorganisms may be detected. Soil eluates or groundwater samples are distributed on special nutrient media containing various contaminants and incubated. Their growth is observed and (qualitatively and quantitatively) evaluated; Findings on the general substance degradation potential are obtained for hydrocarbons and the utilization of various electron acceptors.

Tab. A2-3: Substance group specific relevance of degradation, sorption and volatilization in the contaminant plume

Substance group	Degradation		Sorption*	Volatilization
	Aerobic	Anaerobic		
MHC (C5 –C9)	●●●●	●●●	●●	●●●
MHC (C10 –C40)	●●●●	●●●	●●	●
BTEX	●●●●	●●●	●●	●●
MTBE	●●	●	●	●●
HVCHC	● (except VC)	●●●● (except VC)	●	●●
PAC	●●●	●●●	●●●●	●
Heterocyclic NSO-compounds	●●●	no data	●●●	●

●●●● very relevant ●●● relevant ●● less relevant ● as a rule, not relevant

*) The relevance increases if the subsoil shows carbon particles, peat or high Corg contents.

- Degradation experiments and microcosm studies (M2.2.1, M2.2.9, TV2 Chap. E5.3) are to provide findings relevant to degradation processes on site. In microcosm studies (M2.2.1) laboratory experiments are described where the degradation of HVCHC in laboratory reactions with site material (soil/sediment or groundwater) are observed, if possible, maintaining the natural marginal conditions. However, a direct transfer of the results, in particular the degradation rates, to field conditions is not given. Bactraps (M2.2.9) preferably used for BTEX by means of which the conditions in situ are directly explored provide another procedure. Hereby, the degradation of 13C marked substrates immobilized on carrier material is observed with in-situ microcosms. Instructions for use are to be found in the Chap. "Methods of microbiological NA investigations" (M2). Both methods are comparatively expensive providing apart from qualitative data quantitative data only to a restricted extent.
- Investigation of the microbiological activity and detection of specific degradation organisms: If in the case of CHC loads ethene or ethane cannot be detected the detection of dehalococcoides, in particular by means of molecular-biological methods, is useful [PCR detection of specific genes (M2.1.6); in-situ fluorescence probes (fish) for specific organisms, a. o. MTBE degrading agents (M2.2.10)].

Methods and concepts for determining sorption processes

The detection and quantification of sorption is described in detail in Annex 2.4 of the LABO working aid "Leachate Prediction in Detailed Investigations" [18]. The expenditure on the determination of the site-specific sorption isotherms is only justified if special site conditions are present which do not allow a transfer of sorption data known from literature or if the spread of the literature values does not allow a reliable transfer to the site.

Methods and concepts for determining volatilization processes

The potential extent of volatilization may be calculated in the framework of simplifying 1D analytical model calculations (Fick laws for describing diffusion) or in the framework of the numerical transport modelling with regard to the unsaturated zone. The physical regularities of volatilization are largely known so that apart from parameters for characterizing the unsaturated zone (porosity, water contents) further special investigations will not be required and the extent of volatilization may be calculated sufficiently exact [TV1 Chap. A3.5 and TV3 Chap. B3.5.2].

A2-2.3.1 Mineral hydrocarbons (MHC), benzene, toluene, ethyl benzene and xylene (BTEX)

Mineral hydrocarbons (MHC) and benzene, toluene, ethyl benzene and xylene (BTEX) are compounds consisting exclusively of carbon and hydrogen without special functional groups. Their similar physical-chemical behaviour in groundwater, comparable degradation processes and the frequent occurrence of mixed contaminations recommend the joint consideration of these substance groups. Owing to their smaller density than water MHC and BTEX form swimming phase bodies (LNAPL).

MHC (aliphatic hydrocarbons) may be straight-chain and branched or cyclic hydrocarbons. In most of the damages saturated hydrocarbons (without multiple bonds) dominate.

BTEX and styrene and cumene show an aromatic ring structure and are summed up as highly volatile aromatic hydrocarbons.

MHC contaminations are preferably due to damages with kerosene, diesel and light fuel. BTEX are used notably as fuel components and solvents (damages by tar oil are specially considered in Chap. A2-2.3.3).

Most of the damages caused by MHC are mixtures of numerous individual components of a specific boiling range. MHC and BTEX may occur as mixed contaminations, in particular in damages caused by carburetting fuels.

The mobility of MHC depends strongly on the length of their chains and their molecular weight. With the chain length increasing their mobility is reduced as their water solubility goes down, their viscosity and sorption, however increase. MHC with a chain length of more than 17 carbon atoms (lubricating oils and heavy fuel oil) are viscous up to solid at room temperature and insignificantly water-soluble and scarcely relevant in the groundwater downflow because of these properties.

MHC and BTEX may be oxidized by microorganisms and used as carbon and energy sources. Depending on the redox conditions in groundwater they may be degraded aerobically or anaerobically with the availability of electron acceptors being the limiting factor in many cases. Volatilization may bring about an additional reduction of contaminants for short-chain aliphatic hydrocarbons (C5-C9).

The aerobic degradation is distinctively more effective than the anaerobic degradation. In the case of bigger damage the demand for oxygen exceeds its additional supply. Then the anaerobic degradation dominates, in particular, in the plume centre.

Owing to the substance properties and the processes mentioned the length of the contaminant plumes of MHC and BTEX is, as a rule, limited to a few 100 m [TV1 A2.5 – p. 13 and TV1 C1 – p. 111].

The gas chromatographic determination according to DIN EN ISO 9377 covering compounds with a chain length of C10 to C40 is available for the summary determination of MHC. As far as MHC with shorter chains (C5-C9) have to be considered an additional analysis of the easily volatile compounds has to be carried out, if necessary, by analogy to BTEX analyses. Standard analyses by means of gas chromatography are also available for BTEX.

In the case of MHC damages considering the contaminant pattern with regard to the chain length, branching and possibly the share of multiple bonds is relevant. A first survey may be given by evaluating the "finger prints" of gas chromatograms. The lack of peaks of n-alkanes in the gas chromatogram of diesel and heating fuel damages caused by degradation is e.g. characteristic. The optimum of the degradability of MHC lies in compounds with 10-16 carbon atoms. Owing to their high affinity to the microbial cell membranes short-chain hydrocarbons are toxic and may be degraded only by special microorganisms. Saturated aliphatics (containing only simple bonds) are more easily degradable than unsaturated aliphatics with multiple bonds. Branched aliphatics (e.g. isooctanes) are essentially worse degradable than unbranched aliphatics.

MHC damages age by degradation and volatilization of the respective components. With the age increasing the mobility of the remaining compounds and their degradability go down.

If the age of a damage is known also conclusions relating to the plume behaviour may be drawn (TV1 p. 13 ff.). By comparing gas chromatograms (MHC) or substance concentrations (BTEX) the decrease of well degradable individual components as against less degradable components is proved. Here, however, attention should be paid to the fact that this decrease can be also caused by the varied mobility of the individual components.

The degradation of BTEX can be proved by measuring the changes of isotope signatures ($^{13}C/^{12}C$) (M2.2.5).

The redox processes associated with the degradation are in the centre of the process-related considerations of MHC and BTEX damages. A semi-quantitative assessment of the contaminant degradation is possible by detecting the decline of electron acceptors at balance levels. To this end, the consumption of redox equivalents of the decline of MHC and BTEX is compared taking sorption and volatilization into account.

As the degradation of individual substances is not always clear microcosm studies (analogously to M2.2.2.1a-c) may be additionally used for assessment (e. g. in the case of isooctanes).

As far as specific process steps may not be verified in another way a microbiological potential may be proved, if necessary by means of the MPN method (M2.1.1) (e. g. if a sulphate reduction through sulphide contents in groundwater is not detectable due to FeS being precipitated).

Guiding parameters as regards carrying out MNA are loads of the relevant hydrocarbons (MHC / BTEX) and substance loads resulting from the consumption of redox equivalents.

A2-2.3.2 Methyl tertiary butyl ether (MTBE)

Apart from ETBE (ethyl tertiary butyl ether) or TAME (tertiary amyl methyl ether) MTBE (methyl tertiary butyl ether) is used as fuel additive to increase the knock resistance. So-called oxygenates persist in the environment owing to their molecule structure (ether bonds, steric arrangement of the substituents) and the substance properties resulting from it.

Massive soil and groundwater contamination by MTBE occurs e. g. in petrol dumps or in “classical” cases of filling stations if MTBE containing fuel (primarily premium and premium-plus gasoline) caused the damage.

Physical-chemical substance properties [water solubility 42,000 mg/l (20°C), log Kow 1.06 (20°C), boiling point 55°C] are relevant for assessing the natural attenuation. Thus, MTBE is more water-soluble than BTEX, sorbes less to the soil matrix and shows an insignificant tendency to volatilization.

Owing to the comparatively stable ether bond and the steric obstacle by tertiary butyl groups MTBE is microbiologically difficult to degrade. It was, however, possible to degrade MTBE in the laboratory aerobically and in some cases also under anaerobic conditions. All ways of aerobic degradation go via TBA (tertiary butanol) the detection of which in groundwater may thus indicate a microbial degradation of MTBE. However, TBA may also be contained in fuel also in insignificant portions (as pollution by MTBE) or have been added purposefully as antiknock additive.

When making up MNA concepts there should be determined, at any rate, whether MTBE, TDA or TBF (tert. butyl formiate) are contained in this contaminant group. In the case of uncertainties there should be additionally considered that the microbial degradation of MTBE may result in forming further intermediate products, by-products and final products which are less persistent under environmental conditions with the exception of TBA and TBF and occur accordingly only in low concentrations [TV1 A3.3.4 p. 26 ff].

Altogether the degradability of MTBE is to be classified as being distinctly lower than that of BTEX or MHC. Given aerobic conditions it is essentially more favourable than given anaerobic conditions.

Insignificant growth rates and a delayed adaptation of the MTBE utilizing bacterial communities and the above-mentioned substance properties result frequently in far-reaching contaminant plumes.

For considering the natural attenuation processes KORA has used as a qualitative method (including limits of application) the determination of cell populations in soil and aquifer material by means of MPN methods/ determination of the number of nuclei (M2.1.1) for several substance groups. In addition, also in-situ fluorescence probes (fish) (M2.2.10) were used to detect the degradation specialists. As, however, only a few MTBE degraders were characterized the use of in-situ fluorescence probes has to be decided in the individual case.

For the time being, standardized methods suitable for practice are not available for quantifying the individual processes. The degradation rate could be assessed through quantifying specific metabolites of the MTBE degradation (M2.2.12). TBA accumulated in the plume in a characteristic way and subsequently also degraded is an example for that. If kinetic parameters will be available from laboratory investigations the accumulation of TBA could be used for quantifying the MTBE degradation.

A2-2.3.3 Polycyclic aromatic hydrocarbons (PAC) and NSO-heterocyclic compounds

Typical damages with PAC developed in wood impregnating sites and former gasworks /coking plants. Apart from PAC NSO-heterocyclic compounds occur as further relevant contaminants. In addition, co-contaminations with BTEX and phenols are of importance. The contaminant distribution in groundwater (extension of the contaminant plume) has to be investigated for all contaminants mentioned to decide if MNA shall be carried out.

PAC and NSO-heterocyclic compounds differ as to their water solubility, sorption capacity and degradability. PAC with a log K_{ow} value below 4.5 or a water solubility above 1 mg/l are relevant to the groundwater pathway. These are naphthalene, acenaphthene, acenaphthylene, fluorine, anthracene and phenantrene from the 16 PAC according to U.S. EPA. In addition, methyl naphthalene, indane and indene (TV2 Chap. A3 Tab. 7 p. 13/14) are relevant. NSO-heterocyclic compounds are contained in tar oils by 3 to 5 %, however reach a portion up to 40 % of the tar oil bearing contaminants in the contaminant plume owing to their high water solubility. TV2 A3 Tab. 8 p. 16/17 contains a first list of priorities for NSO-heterocyclic compounds/metabolites. With the distance from the contaminant source increasing the well degradable and the well sorbing contaminants decline distinctly. That is why the more mobile and badly degradable substances (e. g. 3-ring PAC such as acenaphthene and single NSO-heterocyclic compounds) dominate at the plume top.

In the case of PAC damages a long lasting contaminant drag-out (frequently > 100 years) is to be expected owing to the low solubility and high sorption capacity if the contaminant source will not be rehabilitated. "Long-lived" contaminant plumes are the result. At the same time, these physical-chemical properties of PAC result in the fact that, as a rule, spreading proceeds only slowly. This extremely long-term spreading behaviour is to be especially considered when making a decision on a MNA concept.

The aerobic degradation is distinctly more effective than the anaerobic degradation. In the case of greater damage the demand for oxygen exceeds its additional supply. Then the anaerobic degradation dominates, in particular, in the plume centre.

Degradation processes and the high sorption capacity bring about a load reduction for PAC and NSO-heterocyclic compounds. A distinction between degradation and sorption and their quantification is required to assess the share which the respective processes have in the attenuation of contaminants.

To make a first assessment of the degradation and sorption processes investigations of the hydro-chemical and geochemical media are required (Chap. A2-2.3).

A semi-quantitative assessment of the contaminant degradation is possible by determining the decline of the electron acceptors at the balance levels. For this purpose the consumption of redox equivalents is compared with the decline of PAC or NSO-heterocyclic compounds. The influence of sorption should be taken into account in the interpretation.

It is not certain whether under the existing media conditions a biological degradation takes place if metabolism-specific bacterial counts (MPN) may be determined in the aquifer material (M2.1.1). Furthermore it is, as a rule, appropriate to investigate more exact the degradation behaviour of the relevant components in multiple-substance mixtures typical to PAC damages. Microorganisms (analogously to M2.2.1) are, in principle, suited to assess the degradation rates. Attention should be paid to the fact that the degradation rates determined in the laboratory may not be directly transferred to field conditions. However, a comparison of the general degradability of various substances is possible. The share of the biodegradation which took place in field may be determined by means of isotope methods (13C/12C) if the substance-specific fractionating factors are known. For the time being, the applicability of this method is restricted to naphthalene (M2.2.5).

The sorption is determined on the basis of the KOC values of the individual contaminants and the carbon content of the subsoil. By means of analytical calculation models it may be assessed how the individual contaminants would spread if a degradation would not take place (by comparing the effective plume length with the theoretical plume length to be expected without a degradation). The "balance gap" between the total reduction of load and the sorption determined may be approximately attributed to the degradation (further processes such as volatilization are only relevant in the case of co-contaminations with BTEX).

Guiding parameters as regards carrying out MNA are, as a rule, the 16 PAC according to U.S. EPA, relevant heterocyclic NSO-compounds, BTEX, phenols and electron acceptors and redox-sensitive parameters.

A2-2.3.4 Highly volatile chlorinated hydrocarbons (HVCHC)

Most of the groundwater damages with highly volatile chlorinated hydrocarbons (HVCHC) result from the input of tetrachloroethene and trichloroethene and chlorinated ethanes.

In aquifers with an aerobic environment, as a rule, essential processes of HVCHC degradation do not take place in the starting substance so that HVCHC plumes with a length of a few kilometres consisting preferably of starting products may develop. In aquifers with an anaerobic environment a degradation of HVCHC may be caused by reductive dechlorination up to vinyl chloride (VC). The further degradation of VC to ethene proceeds in the anaerobic environment remarkably slowlier as compared with the aerobic environment. This leads a. o. to the fact that notably mobile and toxic VC may be enriched in the anaerobic aquifers. Before this background considerations relating to MNA require a critical assessment in the individual case.

Co-contaminations e.g. with BTEX and MHC may have beneficial effects on the reductive degradation of HVCHC as they may serve as electron donators for the anaerobic degradation of HVCHC.

To develop an understanding of the process always the starting substances and all metabolites up to ethane / ethane and potential electron donators such as MHC / BTEX or DOC have to be determined. Indicators of a natural contaminant degradation are changes of the concentration of the starting substances which may not result from dilution or volatilization and the occurrence of metabolites. If ethane /ethane are not detectable the occurrence of specific degradation organisms (e. g. dehalococcoides sp.) (M2.1.6) should be checked. In special cases the application of isotope methods is to be recommended.

A differentiation between degradation and retention and a quantification of retention processes may, as a rule, be renounced for HVCHC owing to an insignificant retardation in aquifers with small Corg-contents. However, if the aquifer contains coal-like components or peat or brown-coal layers the retardation is to be quantified.

The following methods can be applied for the qualitative detection of biological degradation processes:

- isotope methods (Chap. 2.1.3, M2.2.4)
- molecular biological investigations: detection of dehalococcoides sp. (M2.1.6).

Microcosm studies (M2.2.1) may be applied for identifying processes. Their restricted applicability should be taken into consideration.

The following methods suggest themselves as quantitative methods of detection:

- consideration of the stoichiometric conditions of starting substances and metabolites
- isotope methods (Chap. 2.1.3 and M2.2.4)

The determination of the starting substances and all metabolites up to ethene/ethane is required for a subsequent monitoring. Apart from this, all relevant indicators (Chap. A2-2.3 Introduction) and additionally possible electron donators such as BTEX / MHC or DOC have to be investigated for the biological degradation.

A2-2.4 Consideration of further protected objects

No further protected objects shall be affected by the groundwater damage in future is mentioned as a further prerequisite for carrying out MNA in Chap. 4 of the position paper.

The consideration of the soil-man, soil-useful plant and soil-groundwater pathways forms part of the detailed investigation/assessment of hazards. Considering the conditions given in the individual case and related to the dominating or permissible use of the areas suspected of being contaminated or suspected areas based on planning law the results shall be assessed as to which extent measures according to § 2 (7) (Remediation measures) or § 2 (8) (Protection and restriction measures) of the Federal Soil Protection Act will be required. At this time it is thus basically known which protected objects in the sphere of activity of the contaminant plume are actually affected or might be affected in future.

If the "quasi-stationarity" of the contaminant plume reached or prognosticated will not be maintained or the site conditions affecting the development of the contaminant plume (such as e. g. hydrochemical and hydraulic conditions, groundwater recharge, input of / ceasing to apply electron acceptors or donators) will change this may affect also protected objects and their exposition.

When considering the individual case as to a MNA concept therefore protected objects affected or potentially affected in the sphere of activity of the contaminant plume should be considered such as:

- human health,
- the soil in its natural functions (in particular as basis for livelihood and living space),
- the soil in its functions of use (e.g. as a site for forest and agricultural use, as area for settlement and recreation or for economic and public use in the case of degassing or enrichment of highly volatile contaminants in buildings),
- groundwater and surface waters in the downflow of the contaminant plume,
- useful plants,
- buildings, structures, plants (e.g. as regards corrosion).

As the time perspective plays a decisive part in carrying out MNA and an alternative option for actions has to be implementable, if necessary in the long term, there should be considered if within this period the effects on the protected objects are "acceptable" or, if applicable, restrictions in connection with the use of areas have to be accepted such as e. g.:

- changes or restrictions of use of the site or its environment,
- restriction referring to planning law (e. g. as regards a development or interference in the subsoil),
- restrictions in the development of sites (e. g. as a result of restrictions referring to planning law or in the case of implementing specific alternative options for actions).

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