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A tiered procedure to assess risk due to contaminant migration in groundwater

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Rapport in het kort

Een trapsgewijze procedure voor het beoordelen van risico's ten gevolge van verspreiding van verontreinigd grondwater

Het RIVM stelt in dit rapport een nieuwe methode voor om risico's van verspreiding van verontreinigd grondwater beter te beoordelen. Op basis hiervan kunnen gemeenten en provincies beter beslissen over de noodzaak om de verontreiniging aan te pakken.

Verontreinigd grondwater kan via verspreiding de kwaliteit aantasten van drinkwater, oppervlaktewater, en de bodem in natuur- en woongebieden. Hierdoor ontstaan risico's voor mens en milieu. Om te bepalen of en hoe snel een grondwaterverontreiniging moet worden opgeruimd (gesaneerd), is het belangrijk om de risico's van verspreiding in kaart te brengen. Door het herziene bodembeleid en andere wetenschappelijke inzichten is vernieuwing van de bestaande beoordelingsmethodieken nodig. In dit rapport stelt het RIVM een nieuwe methode voor waarmee de risico's van verspreiding beter kunnen worden beoordeeld.

De nieuwe methode is trapsgewijs opgebouwd volgens het principe 'eenvoudig als het kan, moeilijk als het moet'. De methode onderscheidt vier niveaus, zogenaamde 'treden'. In elke trede wordt beoordeeld of het risico acceptabel is. Is het risico niet acceptabel dan moeten maatregelen worden genomen om de verontreiniging te beheren of te saneren. Ook kan worden gekozen om met specifieker onderzoek (de volgende trede) de risico's beter in kaart te brengen. Door de gestructureerde opbouw biedt de methode gemeenten en provincies betere ondersteuning bij beslissingen over maatregelen voor sanering of vervolgonderzoek.

Naast de verbeterde methode zijn ook de beoordelingsinstrumenten die per trede nodig zijn om de risico's te bepalen grotendeels uitgewerkt in dit rapport.

Trefwoorden: risicobeoordeling; verspreiding; grondwater; verontreiniging; pluim; beoordelingsinstrumenten.

Abstract

A tiered procedure to assess risk due to contaminant migration in groundwater

RIVM presents a new procedure for better assessment of risks due to migration of contaminants in groundwater. Local authorities can use this procedure to decide if remediation is necessary. Migration causes a contaminant in groundwater to have a negative effect on the quality of surface water, on groundwater meant for drinking water, and on nature and urban areas. This effect brings with it potential risks for humans and the environment. Determining risks due to migration allows us to assess if remediation of a contaminant in groundwater is necessary, and if so, how urgent it is. Both the revised Dutch soil policy and the introduction of new scientific insights will make it possible and necessary to replace the existing methods for assessing risks due to contaminants in groundwater.

The proposed procedure for assessment of risks due to the migration of contaminants in groundwater consists of four tiers, with as underlying principle – a simple risk assessment when possible and a comprehensive risk assessment when necessary. Per tier, information is processed and decisions are taken on the measure of acceptance of the risk. If the risk is not acceptable, measures have to be taken; alternatively, the user can choose a more specific risk assessment (the next tier) to obtain better insight into the actual risks. The structured procedure provides ample support to the user (local authorities) in deciding on remediation measures or on pursuing further research on the risks.

The report also focuses on assessment tools that may be useful in the application of the tier procedure.

Key words: risk assessment; migration; groundwater; contamination; plume; assessment tools.

Preface

This investigation has been performed by order and for the account of the Ministry of Housing, Spatial Planning and the Environment, Directorate of Soil, Water and Rural Areas, within the framework of the project: Risks in relation to soil quality (M/711701).

One of its goals is to strengthen the technical basis of the *Saneringscriterium* (remediation criteria), which recently replaced the remediation urgency method.

We would like to take this opportunity to especially thank those who participated in the feedback group (Dutch, *klankbordgroep)*. The fruitfull discussions and their remarks were important in producing this report. We would also like to thank A. van de Haar, K. Janssen-Roelofs and H. Slenders for their contributions to this report.

Outline

After the brief introduction in chapter 1, chapter 2 of this report puts the assessment of risk due to migration of contaminated groundwater in the perspective of Dutch soil policy and the European Water Framework Directive. The proposed tiered procedure for the assessment of risk due to contaminant migration in groundwater is described in chapter 3. Tools used in the different tiers of the procedure are discussed in chapters 4 to 7, starting with initial characterization, followed by generic risk assessment, site-specific risk assessment and the last tier, monitoring and specific modelling. The five appendices give more specific information on various subjects discussed in this report.

Contents

Abbreviations

DNAPL	Dense Non Aqueous Phase Liquid
GWDD	GroundWater Daugther Directive
EPA	Environmetal Protection Agency
EU	European Union
IV	Intervention Value
LGM	*Dutch:* Landelijk Grondwater Model (national groundwater model)
LNAPL	Light Non Aqueous Phase Liquid
MNA	Monitored Natural Attenuation
NA	Natural Attenuation
NAPL	Non Aqueous Phase Liquid
ROSA	*Dutch:* RObuust Saneringsvarianten Afwegen (instrument to support the process of putting the mobile contamination remediation policy into practice.)
RUM	Remediation Urgency Method
SRC	Serious Risk Concentration for soil and groundwater
TPH	Total Petroleum Hydrocarbons
TPHCWG	Total Petroleum Hydrocarbons Criteria Working Group
TU	Toxic Unit
VROM	Dutch Ministry of Housing, Spatial Planning and the Environment
WFD	Water Framework Directive

Summary

When a case of soil or groundwater contamination is discovered, the human risks, the risks to ecosystems and the risks due to contaminant migration in groundwater have to be assessed. Based on the presence and the nature of the risks, the need for remediation can be determined, followed by a decision on remediation measures (VROM, 2006).

This report proposes a tiered procedure to assess the risks due to migration of contaminated groundwater.

The proposed risk assessment procedure consists of four tiers, i.e. four levels, in which the information is processed and decisions are taken with regard to the existence of an unacceptable risk.

The procedure corresponds well with the new Dutch soil policy. In each successive tier of the procedure, site specification increases, while the degree of conservatism decreases. As a consequence the complexity (and hence required effort and cost) increases with each tier. The underlying principle is this: simple risk assessment where possible and a comprehensive risk assessment where necessary.

The tiers of the procedure are:

- Tier 0: Initial characterization
- Tier 1: Generic risk assessment
- Tier 2: Site-specific risk assessment
- Tier 3: Monitoring and specific modelling

The existence of an unacceptable risk is, according tier 0, based on three criteria: the presence of Non Aqueous Phase Liquids (NAPLs), the presence of vulnerable objects and/or the presence of contaminated groundwater above the Intervention Value with a size of 6000 m^3 or more.

The generic risk assessment (tier 1) provides:

- A simple methodology for calculating the increase in volume of the contaminated subsurface
- A procedure for deciding whether a risk due to contaminant migration exists

Furthermore, the generic values for groundwater velocity are considered and the process of sorption and its effect on the migration of contaminants is discussed.

The concepts from tier 1 are used in the site-specific assessment (tier 2), but instead of generic data, site-specific (i.e. measured) data should be used.

Alternative options are also possible to assess contaminant migration, based on the availability of site-specific data:

- Contaminant migration can be assessed based on historical data.
- The possibility of natural attenuation (NA) can be considered. When trustworthy indicators for natural degradation are present, a remediation decision can be postponed, together with monitoring of natural attenuation processes. Monitoring activities can be performed as part of a tier 3 assessment.

Furthermore, leaching is taken into account in this tier, and special attention is given to Total Petroleum Hydrocarbons (TPH), a frequently occurring contaminant in groundwater.

Complex sites, complex groundwater systems and/or complex contamination require a tier 3 assessment. General groundwater modelling requirements are described, but the specific procedure in tier 3 is left open to allow for a tailored approach.

Samenvatting

In geval van een grondwaterverontreiniging dienen eventuele risico's voor de mens, het ecosysteem en het risico ten gevolge van verspreiding te worden vastgesteld. Op basis van deze risicobeoordeling kan de noodzaak voor sanering worden vastgesteld en een programma met maatregelen worden samengesteld.

In dit rapport wordt een nieuwe systematiek voorgesteld voor de beoordeling van de risico's ten gevolge van verspreiding van verontreinigd grondwater.

Deze systematiek onderscheidt vier niveaus (treden) waarop informatie wordt vergaard en de beslissing wordt genomen of het aanwezige risico wel of niet acceptabel is.

De voorgestelde aanpak past naar onze mening in het nieuwe bodembeleid. De risicobeoordeling wordt namelijk getrapt uitgevoerd volgens het principe 'eenvoudig als het kan, moeilijk als het moet'.

De vier treden in de procedure zijn:
- Trede 0: Eerste karakterisering
- Trede 1: Standaard risicobeoordeling
- Trede 2: Locatiespecifieke risicobeoordeling
- Trede 3: Monitoren en modelleren

De trede 'eerste karakterisering' is gebaseerd op drie criteria. Dit zijn de aan/afwezigheid van drijf- of zinklagen, de aan/afwezigheid van kwetsbare objecten en/of het volume van de verontreiniging boven de interventiewaarde groter of gelijk is aan 6000 m^3.

Bij de standaardrisicobeoordeling, trede 1, worden de volgende onderwerpen behandeld:
- Hoe is op eenvoudig wijze de verspreidingssnelheid van de verontreiniging te beoordelen?
- Wanneer spreek je van een onacceptabel risico?

Ook worden generieke tabellen voor grondwatersnelheid gegeven en het effect van sorptie op verspreiding van verontreiniging bediscussieerd.

De tweede beoordelingstrede wordt de 'locatiespecifieke beoordeling' genoemd en wordt gekarakteriseerd zich door een combinatie van metingen en simpele berekeningen. Deze beoordeling gebruikt vaak dezelfde concepten als de beoordeling in trede 1, alleen worden in

plaats van generieke data, locatiespecifieke data gebruikt. Daarnaast zijn er alternatieve manieren om het risico door verspreiding te beoordelen:

- Beoordelen van verspreidingsgedrag op basis van gegevens van voorgaande jaren.
- Een methode om bij de beoordeling van het risico ook natuurlijke afbraak als risicobepalende factor mee te nemen.

Ook is er op dit niveau speciaal aandacht voor vervuiling met minerale olie, een veel voorkomende vorm van grondwaterverontreiniging.

Tenslotte is een ‘state of the art’ of ‘expert’ risicobeoordeling mogelijk. Een dergelijke beoordeling is in principe voorbehouden aan complexe en omvangrijke gevallen waar de consequenties van sanering groot zijn. Dit rapport geeft een algemene omschrijving van deze ‘state of the art’ beoordeling, maar gaat er niet tot in detail op in, omdat dit maatwerk betreft.

1. General introduction

When a case of groundwater contamination is discovered, the human risks, the risks to ecosystems and the risks due to migration of contaminants have to be assessed. Based on the presence and the nature of the risks, the need for remediation can be determined, followed by a decision on remediation measures (Figure 1.1).

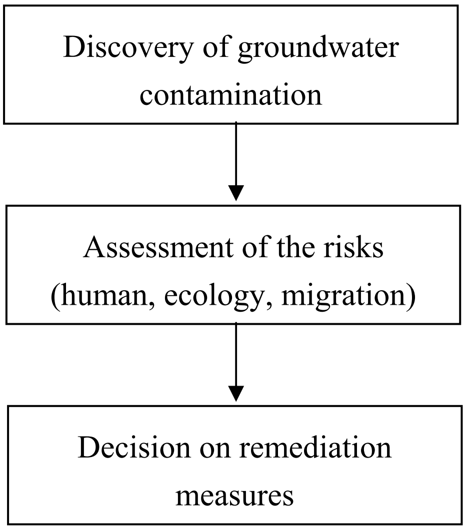

Figure 1.1 General and simplified approach to soil and groundwater contamination.

Since 1995, decisions about the need for remediation measures have taken place in accordance with a defined and statutory methodology (VROM, 1995; Swartjes, 1999). The remediation urgency method (RUM) (*SaneringsUrgentie Systematiek,* in Dutch*)* is based on actual risk assessment, which means it focuses on site-specific risks and takes current, intended and/or possible land use in consideration. This approach includes risks to humans, risks to the ecosystem and risks due to contaminant migration.

The methodology was evaluated in 2003 (see section 2.4). At the same time, an extended political evaluation of the soil quality assessment framework came to an end. This resulted in a revised policy on soil protection and soil management (Van Geel, 2003).

In 2006 a new Circular on soil remediation (VROM**,** 2006) was published. With the publication of this Circular the remediation urgency method was replaced by the Remediation criteria (In Dutch: *Saneringscriterium (Sanscrit)*), more on Sanscrit in section 2.2).

Parallel to changing national policy, EU policy on water, groundwater and soil is also evolving. More on this in relation to the risk assessment of contaminant migration can be found in section 2.3.

The objective of this report is to provide a tiered based procedure for the assessment of risks due to migration of contaminants in groundwater. Local authorities can use this procedure to decide if remediation measures are necessary. The report also focuses on assessment tools that may be useful in the application of the procedure.
The proposed procedure can be seen as a practical interpretation of the Circular on soil remediation concerning the risk due to migration of contaminated groundwater. In this report reference to the Circular is made when relevant.

The procedure is described in chapter 3. First, the next chapter goes into more detail on the backgrounds of the proposed procedure.

2. Backgrounds of the proposed procedure

2.1 Conceptual model

To understand what is meant by ‘risk due to migration of contaminated groundwater’, Figure 2.1 shows a conceptual model, which visualizes the important elements of the risk assessment. These elements are:

- Contamination plume, more in sections 5.2 and A4.5
- Vulnerable object (in Figure 2.1 the well), more in section 4.3
- Direction of groundwater flow

Figure 2.1 shows a plume (in red) of contaminated groundwater which moves in the direction of a vulnerable object, a well. Other examples of vulnerable objects are nature reserves, humans or the groundwater body itself (section 4.3). The blue arrows in Figure 2.1 indicate the direction of groundwater flow. In order to determine whether or not a vulnerable object is endangered by the plume and whether remediation measures are necessary, migration and toxicity of the plume should be assessed.

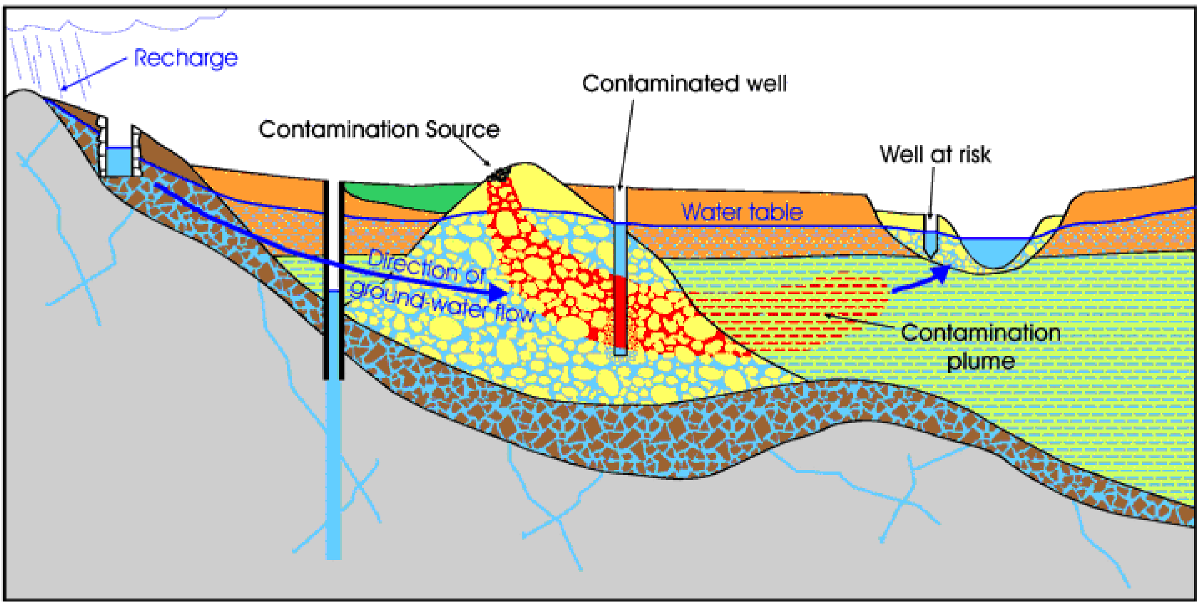

Figure 2.1 Conceptual model of the migration of contamination in a groundwater body. The blue arrows indicate the direction of groundwater flow. Due to the migrating plume (red) the well near the river is at risk.[1]

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[1] Source: http://www.maine.gov/doc/nrimc/mgs/explore/water/facts/aq-04.gif; 23-04-2007

2.2 Risk assessment within the framework of Dutch soil policy

This section places the risk assessment of contaminant migration in the context of the Dutch soil policy (section 2.2.1.), the Ministerial Circular on soil remediation (section 2.2.2) and decisions about the nature of remediation measures in the case of unacceptable risks (Doorstart A5, ROSA, section 2.2.3).

2.2.1 The Dutch soil policy

Dutch soil policy has recently been subject to many changes. In the 1980s, the policy objective was to restore all soil and groundwater contamination to multifunctional quality. The Dutch soil quality problem was expected to be solved within a single generation. But the problem was bigger than anticipated, and the goal of remediating every contaminated site to multifunctional soil quality within a few years could not be achieved. Dutch soil policy therefore changed at the end of the 1990s. Instead of multifunctional remediation, the functional approach became the goal. Thus, the remedial objectives depended on the use or function of the site. Another change was that local government gained more influence in the soil quality issue, whereas all the responsibility and work had previously been in the hands of central government.

A new era in Dutch soil policy began with a letter from Secretary of State Van Geel to the Dutch Government (Van Geel**,** 2003). The highlights of this letter were:

- an increasing shift towards regional responsibility (decentralization),
- a broader approach to soil quality,
- more focus on sustainability,
- improved coherence with spatial development
- a more rational approach to risk and risk perception
- development of simple and consistent framework for risk assessment

One of the impacts of these later renewals on the risk assessment of contaminant migration is the change in objective. The objective used to be, '*Determination of remediation urgency and moment of remediation'*, but is now, '*Distinguishing between situations with low risk, more chance of risk, and situations where the risk is such that measures should be taken'*.

2.2.2 The Circular on soil remediation

As one of the consequences of the Dutch policy renewal on soil quality, a new regulation on soil remediation came into force (VROM, 2006). The Circular describes the legal framework and the decision process for remediation measures. The Circular serves as a guide for the application of the remediation criteria. Remediation decisions are based on human and ecological risk assessment and the risk of contaminant migration in groundwater. The risks should be assessed using the decision support system Sanscrit. Sanscrit replaces the former remediation urgency method.

According the Circular, risks for human, ecology and groundwater are assessed in a three tier procedure (see Figure 2.2). In the first tier it is determined wether soil or groundwater is seriously contaminated.
The second tier (standard risk assessment) tests the presence of unacceptable risk against relatively simple criteria. For contaminated groundwater these criteria are:

- The use of the soil and the presence of vulnerable objects
- The presence of non aqueous phase liquids (NAPLs)
- The presence of an unacceptable situation due to the migration of contaminated groundwater

When the standard risk assessment results in the presence of unacceptable risks, it is possible to carry out a site-specific risk assessment (tier 3) to avoid overestimation of risks.

If at least one of the criteria for remediation (unacceptable risks) is exceeded, remediation measures must be taken. These measures do not need to be automatically and uniformly applied to the entire case. A customized approach is possible, providing that it deals with that part of the polluted zone for which unacceptable risks have been identified. When the soil quality exceeds the Intervention Value but not the criteria for remediation (i.e. the risk is acceptable), the competent authority for soil remediation should determine which management measures and restrictions on use are required (Van Geel**,** 2003).

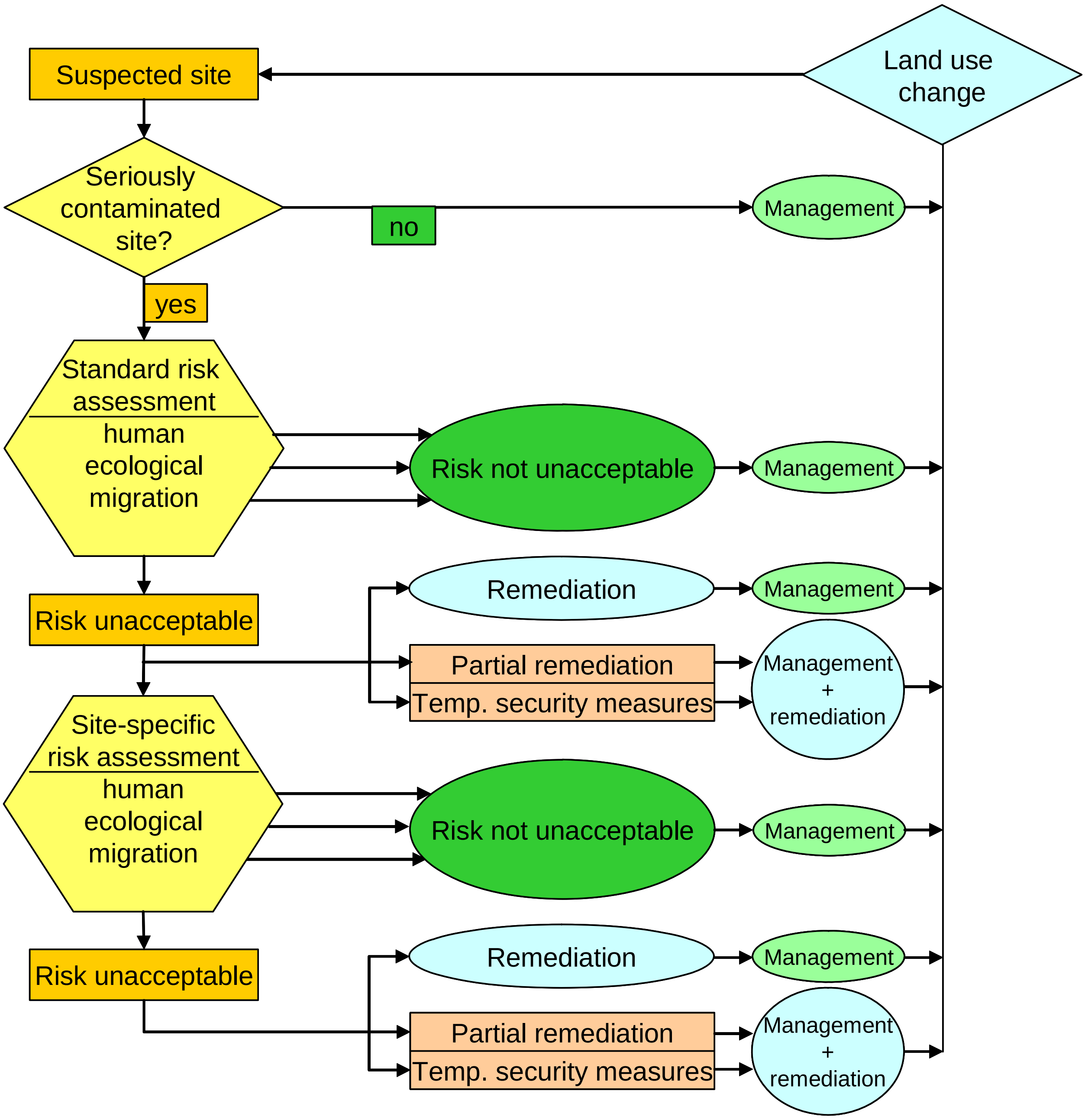

Figure 2.2 Procedure to assess risks to human, ecology and due to migration of contamination in groundwater according the Circular on soil remediation (VROM, 2006).

In the appendix of the Circular general guidelines for risk assessment are given. The test criteria are explained for the standard risk assessment (tier 2). Procedures to assess the site-specific risk due to contaminant migration in groundwater are not given.

2.2.3 Deciding between remediation options (Doorstart A5 and ROSA)

When a remediation decision is made, the question ‘which remediation option best fits the case’ arises. For decisions concerning the improvement of the quality of contaminated groundwater (the remediation decision, or *de saneringsafweging*, in Dutch) the ‘Doorstart A5’ (VROM/IPO/VNG**,** 2001) approach is recommended. ‘Doorstart A5’ describes the process of making cost-effective remediation decisions. The accompanying ROSA report (in Dutch, *Robuust Saneringsvarianten Afwegen*) gives practical assistance in solving bottlenecks which may occur during that process (Slenders et al., 2005).

More on Doorstart A5

Doorstart A5 is more than a procedure. It describes how to remediate mobile contamination of soil and groundwater in a cost-effective way. The report describes the four strategic goals for cost-effective remediation of the sub-soil:

- Design of remediation measures is to be based on an integral approach (in coherence with the top-soil and with the planned physical developments).
- Following remediation a soil should meet the requirements of the land use. Exposure should be avoided and migration minimized.
- A calibration moment should be implemented to follow the remediation process and adjust it.
- Remediation should result in minimal aftercare.

Thus, from a policy point of view, complete removal of the source and plume is preferred, as long as it can be done in a cost-effective manner. Where this is financially or technically not possible, remediation should result in a permanent and stable final situation (*stabiele eindsituatie* in Dutch). This stable final situation is defined as the situation in which, within 30 years, the concentration of contaminant in the groundwater surrounding the source, the so-called reactor chamber, reaches its original level (at target or background values), with a minimum of active aftercare. However, impermissible human and ecological risk must not take place either now or in the future.

ROSA

The ROSA document provides an instrument to support the process of putting the mobile contamination remediation policy as described above into practice. It supports the decision on the most cost-effective way to remediate mobile contamination in soil. The instrument is applied in several steps, starting from the decision that remediation is required to a complete remediation plan. The most important steps are the development of different remediation options and presenting and balancing benefits and costs for each remediation option. Table 2.1 shows the benefits and costs taken into account in the ROSA process.

Table 2.1 Costs and benefits taken into account in the ROSA process.

Benefits	Costs
• risk reduction • cost reduction • recovery of land use • stabilized final situation (after 30 years) • removal of contamination load • *optional:* reduction of liability, improvement of image, increase in value of the estate and other benefits	• financial costs • remediation time • risk of failure • aftercare • reduction of land use • *optional*: adverse effects on nature, adverse effects on cultural-historical values, adverse effects on archaeological and geological values, burdening of other environmental compartments, damage during the remediation progress, nuisance (noise, dust), other costs

'Risk reduction' is one of the important benefits of remediation activities. Risk reduction is often related to the presence of vulnerable objects. Table 2.2 shows which vulnerable objects are concerned in risk reduction under ROSA.

Table 2.2 Vulnerable objects and triggers for a remediation decision under ROSA.

	Vulnerable object	Trigger	Instrument
Human risks	- Humans	- Exposure > maximum allowable risk to humans - C-indoor air > TCA	- Assessing exposure, CSOIL
Ecological risks	- (sub) Soil ecology - Influence on surface water quality	- Unacceptable ecological effects	- TRIADE
Risk due to migration	- Clean groundwater - Drinking water - Industrial process water - Ecological quality of relevant upper groundwater - Surface water quality	- No standstill - Possible negative impact on user possibilities - Possible threat to vulnerable objects	- Assessing risk of migration

ROSA II

The ROSA II project was completed in September 2006. This project resulted in a renewed ROSA document, which helps in making robust agreements based on technical, organizational, financial and juridical aspects prior to and during remediation.

2.3 Analysis of the EU Groundwater Daughter Directive concerning the Dutch policy on contaminated groundwater

The EU Groundwater Daughter Directive (EC**,** 2006) considers that (ground)water and soil are both part of one system. Therefore, regulation on one compartment impacts the other. This section discusses the requirements of the Groundwater Daughter Directive (GWDD) and its possible effects on the Dutch approach to dealing with contaminated groundwater and contaminant migration in groundwater.

The GWDD is an extension of the European Water Framework Directive (EC, 2000) which came into force in December 2000. The purpose of the WFD is to establish a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater which, among other things:

- prevents further deterioration and protects and enhances the status of aquatic and terrestrial ecosystems (WFD Article 1);
- promotes sustainable water use based on the long term protection of available water resources (WFD Article 1).

The WFD focuses on surface water and is only brief with respect to groundwater. In Article 17 of the WFD, specific measures for the prevention and control of groundwater pollution are given. These measures are further distinguised in the GWDD. The aim of the GWDD can be defined in three goals:

1. Provision of criteria for the assessment of good groundwater chemical status.
2. Provision of criteria for the identification and reversal of significant and sustained upward trends and for the definition of starting points for trend reversals.
3. Provision of measures in order to prevent or limit inputs of pollutants into groundwater (GWDD, Article 1).

The GWDD came into force in November 2006. To find out whether the GWDD has had an impact on Dutch policy regarding contaminant migration in groundwater, the three provisions of the GWDD have been analysed.

The first goal: criteria for the assessment of good groundwater chemical status
Article 4(2) of the GWDD states that a groundwater body is in good chemical status when:

I. communitarian quality standards or relevant threshold values are not exceeded, or
II. when the communitarian quality standards or relevant threshold values (see I) *are* exceeded, this have no negative influence on:
    (a) goals for ecological or chemical quality of surface waters,

(b) terrestric ecosystems dependent on the groundwater body,
(c) possible human use of the groundwater.

If the threshold value is exceeded at one monitoring point, further research must be carried out into the effect on the WFD goals.

Communitarian quality standards are listed in Annex 1 of the GWDD for nitrates and active substances in pesticides, but are equal to existing standards.

Threshold values are quality standards set by Member States for pollutants that contribute to the characterization of a groundwater body or group of bodies as being at risk. They can be established at national level, river basement district level or groundwater body level and are not intended to be used directly on local scale (GWDD Article 3(2)). However, in the case of local defilement near a WFD monitoring point, the communitarian standard or threshold value may be exceeded at that point and further research into the effect of that contamination becomes necessary (GWDD Article 4). This further research should include a risk assessment for migration. Other relations between the GWDD and Dutch policy on contaminant migration in groundwater have not been discovered.

The second goal: criteria for the assessment of the chemical status of groundwater

Article 5 of the GWDD states that Member States are obliged to identify significant and sustained upward trends in concentrations of pollutants found in groundwater bodies identified as being at risk, and is to define the starting point for reversing those trends. This subject does not have much impact on this report because of the difference in scale (risk assessment of migration on local scale, versus trends on groundwater body scale).

However, Article 5(5) (GWDD) states that when plumes of contamination threaten the goals of the WFD, Member States have to verify that (1) the plumes are not growing, (2) the plumes do not threaten the chemical status of groundwater bodies and (3) the plumes form no risk to human and/or environmental health. These items are in theory part of the Dutch soil policy. But, when ‘growth of plumes’ and ‘no risk’ are defined absolutely, this can influence the Dutch policy on contaminated groundwater. Diffusion and advection always show some plume growth, resulting in some kind of risk. The definition of these words should be carefully considered. Thus, the last part of Article 5 is possibly contrary to current Dutch soil policy practice.

The third goal: to provide measures to prevent or limit inputs of pollutants into groundwater

Article 6 of the GWDD states that all necessary measures should be taken to prevent the emission of hazardous substances into groundwater. For other substances, emission to groundwater should be limited such that (1) the status of the groundwater body stays good, (2) there is no upward trend of concentrations in the groundwater body and (3) there is no other deterioration at the cost of the emission. Point 1 seems to suggest a standstill on a groundwater body scale, while point 3 is relatively absolute in its formulation on this subject.

Conceptual models

Conceptual models can be used for implementation of the WFD and GWDD. A conceptual model is an abstract representation of reality. For example, to provide a better understanding of the interaction between soil and water, a conceptual model of an area's geohydrology can be made (Figure 2.4). However, a procedure for carrying out WFD goals can be put into a conceptual model (Figure 2.3). In fact, the proposed procedure in this report can also be regarded as a conceptual model.

For a better understanding of the risk due to contaminant migration in groundwater, it can be useful to visualize the real situation in the form of a conceptual model.

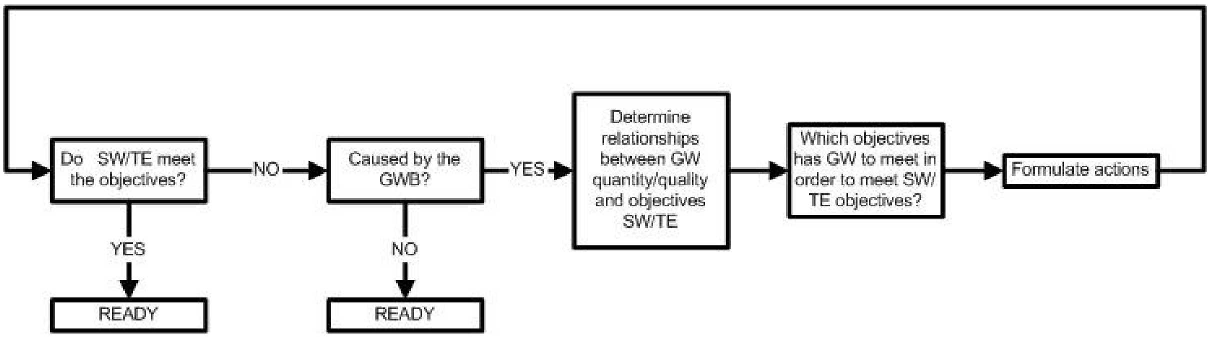

Figure 2.3 Example of a conceptual model that can be helpful during the implementation of the WFD goals. It describes how to determine the influence of groundwater quality and quantity on surface water objectives (SW) and objectives for terrestrial ecosystems (TE) (GWB = groundwater body).

Conclusions

It is important to consider WFD and GWDD requirements when making decisions concerning contaminated groundwater. Important developments that should be carefully considered are the determination of threshold values and the definitions of 'plume growth' and 'human and environmental risk'.

'Further research' for the WFD or GWDD can possibly be combined with research on a local scale, using procedures such as the one described in this report. For a better understanding of the risk due to contaminant migration in groundwater, it can be useful to visualize the real situation in the form of a conceptual model.

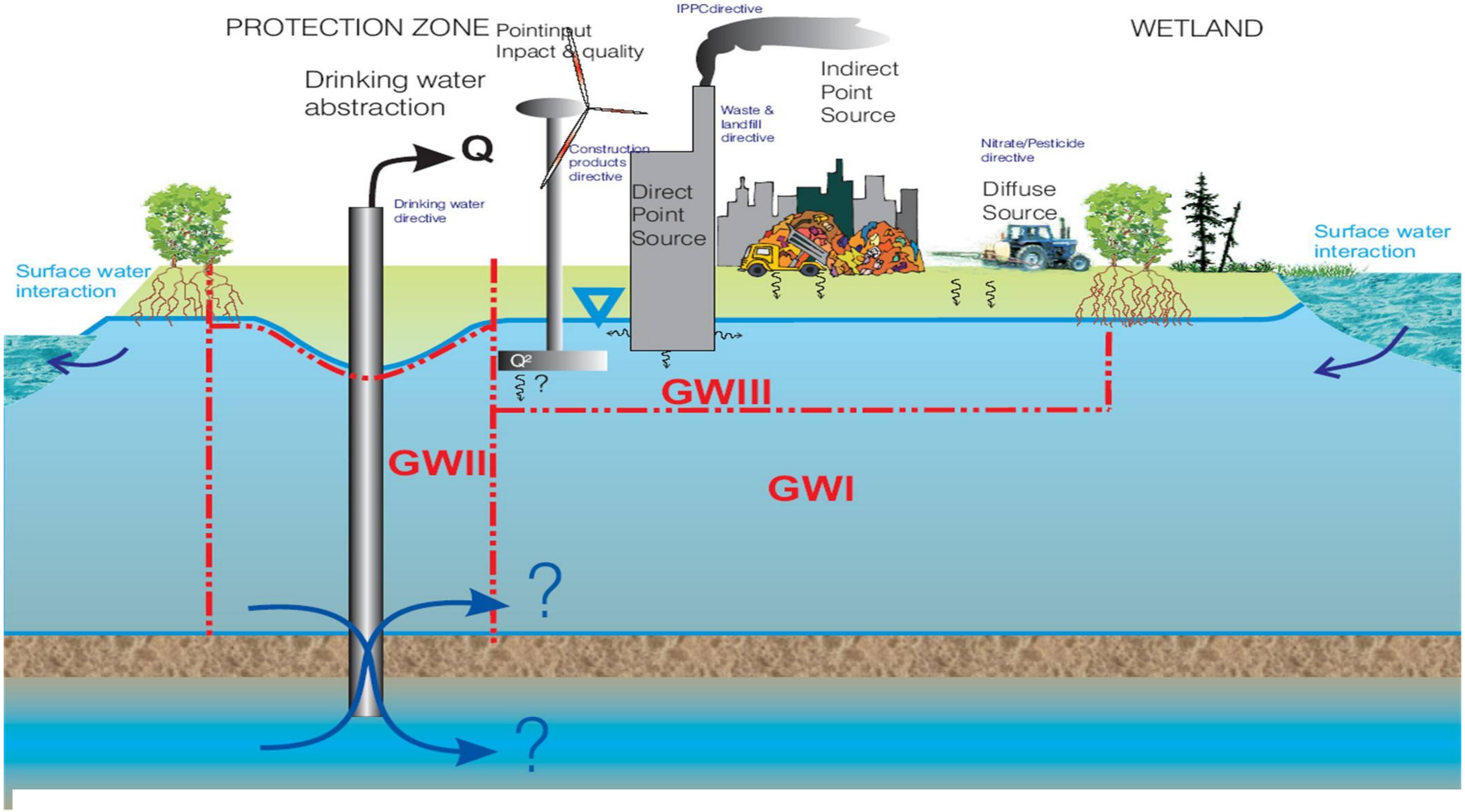

Figure 2.4 Conceptual model of the geohydrology in an area (source: Draft Guidance Document Direct and Indirect Inputs, Version 6.0, 04-05-2007, Common Implementation Strategy Groundwater).

2.4 The remediation urgency method evaluated

From 1995 onwards, the need for and urgency of remediation measures was determined using a prescribed method in the Netherlands, the ‘remediation urgency method’. In 2003 the remediation urgency method (RUM) was evaluated (Lijzen et al., 2003). Discussions with users focused on practicability, adequacy or inadequacy, statistical uncertainty, alternative approaches and techniques, decision making based on the risk assessment results and the political and social basis.

Broadly speaking, the consulted users had the opinion that the procedure was applicable to seriously contaminated and relatively small sites. However, in the case of specific situations or contaminants, several shortcomings and drawbacks were mentioned:

- A general remark was that the methodology is based on an oversimplification of the geohydrological reality.
- The method permits the easy and unquestioning use of standard model parameter values (e.g. a groundwater velocity of 30 m/year at any sandy site). The use of site-specific information for the location in question is not encouraged. Though the procedure does not exclude the use of site-specific hydrological models, it is concluded that the available standard risk-evaluation option is too easily used, also in situations where modelling would have resulted in a better risk evaluation.
- The assessment of the risk due to migration of mineral oil was felt to be unsatisfactory and too conservative. This is, amongst other things, caused by the fact that a risk approach assumes that mineral oil is a single compound, whereas mineral oil is a complex mixture.
- There is a need for an additional procedure to assess the presence of Light and Dense Non Aqueous Phase Liquids (LNAPL and DNAPL) pools. Also, the basic principle that the presence of a NAPL immediately leads to the conclusion that remediation is urgent should be discussed.
- There is a need to take into account processes such as degradation, diffusion and dispersion and preferential flow, amongst others. It is mentioned that assessors use more sophisticated models to assess the risk due to contaminant migration in practice, often in combination with additional monitoring.

The findings of this evaluation were, amongst the reviewed policy considerations, of guidance in developing the proposed new method.

3. Proposed tiered risk assessment procedure

3.1 Introduction

The human and ecological risk assessment and the assessment of contaminant migration in groundwater as defined in the Circular on soil remediation (section 2.2.2.) contain three tiers. Tier 1 and tier 2 (the generic risk assessment) are defined. For the site-specific risk assessment (tier 3) of risks due to the migration of contaminated groundwater, only the characteristics are mentioned.

Due to the complexity of risk assessment in cases of serious groundwater contamination a risk assessment procedure with four tiers is proposed to asses risks due to the migration of contaminated groundwater. According to this approach, in each successive tier site-specification increases, while the degree of conservatism decreases (see Figure 3.1). The consequence is that complexity (and hence effort and cost) increases with each tier.
When, in a lower tier, the presence of an unacceptable risk can not be rejected the risk assessor can go on to use a higher tier or, when the result of the lower tier risk assessment seems plausible, start remedial action.
The underlying principle is: simple risk assessment where possible and a comprehensive risk assessment where necessary.

The proposed risk assessment procedure consists of four tiers, i.e. four levels, in which the information is processed and decisions are taken with regard to the existence of an unacceptable risk.

- Tier 0: Initial characterization
- Tier 1: Generic risk assessment
- Tier 2: Site-specific risk assessment
- Tier 3: Monitoring and specific modelling

Tier 0, initial characterization, corresponds with the standard risk assessment of the Circular on soil remediation, standard risk assessment.
Tier 1, 2 and 3 of the proposed procedure (see Figure 3.1) corresponds with the site-specific risk assessment of the Circular on soil remediation.

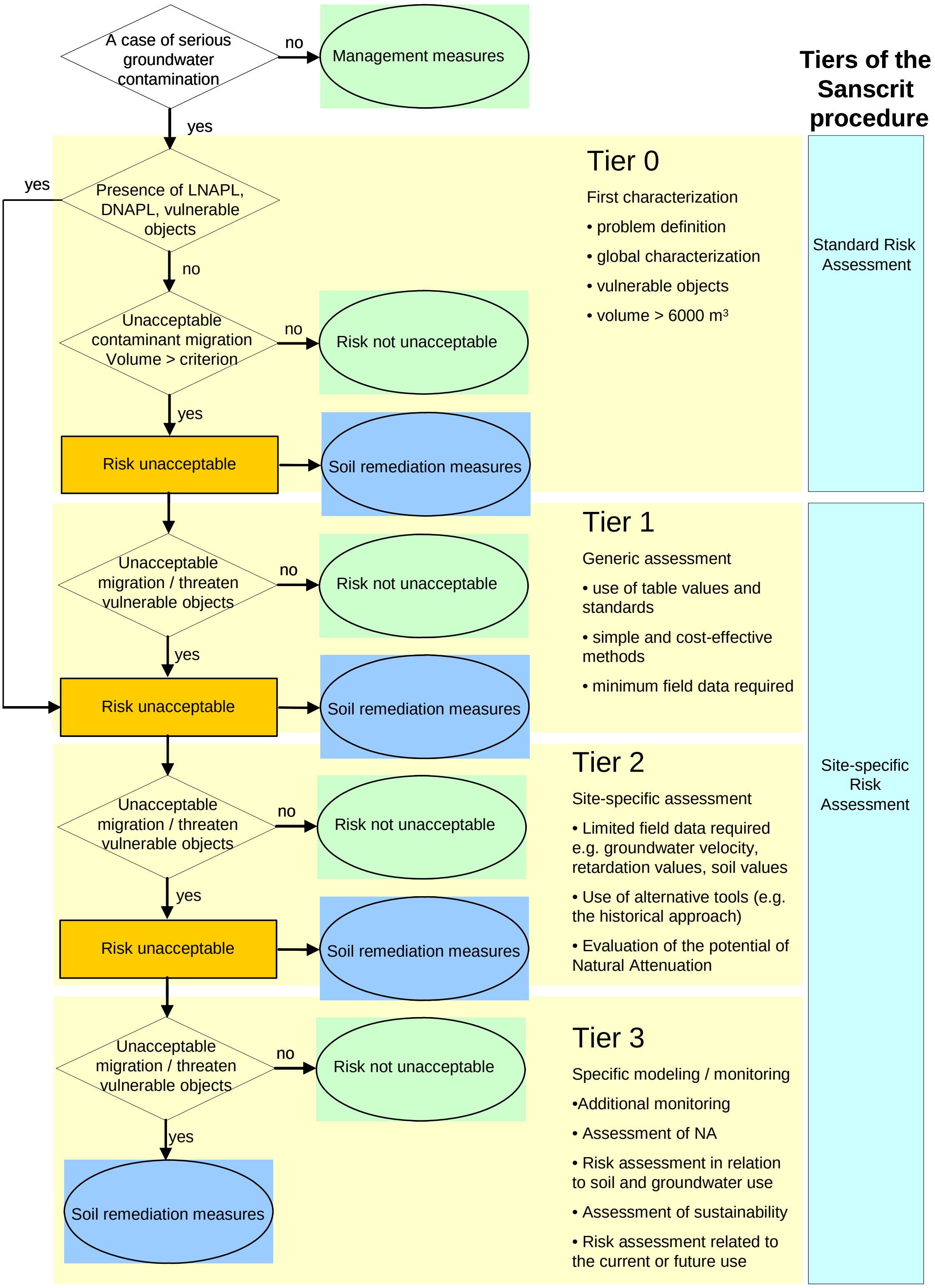

Figure 3.1 Flowchart of the proposed procedure to assess risk due to contaminant migration in groundwater.

3.2 The procedure explained

The triggers for possible unacceptable risks due to the presence of serious contaminated groundwater are:

- Human or ecological soil functions are threatened by contaminated groundwater.
- An uncontrolled situation occurs due to the presence of DNAPLs, LNAPLs or migration of contaminated groundwater.

The risk assessment has two possible results:

1) The risk is not unacceptable
2) An unacceptable risk cannot be excluded

In the case of 1, the contaminated location is registered in cadastral records and possible improvement of soil and groundwater quality can be accomplished in conjunction with future, spatial developments. When 2 is the case, a remediation decision has to be made (ROSA, section 2.2.3.) to reach the necessary quality improvement.

Figure 3.1 shows the different tiers of the procedure in detail. The procedure starts with characterization of the case; the presence of NAPLs, the volume of the contaminated groundwater and the presence of vulnerable objects (e.g. drinking water abstraction wells).

Tier 0: Initial characterization

Initial characterization of the situation is based on the following simple criteria:

1) The first criterion is the presence of a LNAPL or a DNAPL. Potentially, a NAPL leads to a remediation decision. In the case of uncertainties regarding the actual risks and/or financial and social constraints, a site-specific risk assessment (tier 2) is recommended.
2) The second criterion is whether vulnerable objects are present in the vicinity of contaminated groundwater (in or near the plume).
3) The third criterion is the volume of the contaminated groundwater. A relatively small volume indicates a standstill situation. The maximal acceptable size mentioned in the Circular is 6000 m^3. If the volume of the plume is less than 6000 m^3 urgent remediation measures are not compulsory.

When no vulnerable object is present, the risk of a NAPL on clean groundwater resources can be assessed in a higher tier (tier 2), which considers the nature and behaviour of NAPLs. In other case a remediation decision can be made.

When a vulnerable object is present, the risk assessment for contaminant migration may not be required, because action will be taken which aims to minimize the human or ecological risk.

See for details:

- Assessment of LNAPL and DNAPL, section 4.2
- Vulnerable objects, section 4.3
- Acceptable volume of contaminated groundwater, section 4.4

Tier 1: Generic risk assessment

The generic risk assessment concerns the assessment of the migration of contaminated groundwater. The assessment is based on the calculated increase in contaminated groundwater volume per unit time. The methodology is simple and has already been put into practice in the remediation urgency method. Test criteria used in this tier are conservative to prevent underestimation of the risk.

See for details:

- Concept, sections 5.2 and 5.3
- Groundwater velocity, section 5.4
- Sorption, section 5.5

Tier 2: Site-specific risk assessment

For site-specific risk assessments the same concept is used as for the generic risk assessment, but input data should be collected on-site (site-specific data rather than generic data, for example, as taken from tables). Also, in tier 2 some alternative options are possible, based on the availability of site-specific data, or contaminant migration can be assessed based on historical data. Moreover, the possibility of natural attenuation should be considered. Should trustworthy data on natural degradation be present, a remediation decision may be postponed, together with the monitoring of natural attenuation processes. Monitoring activities can be performed as part of a tier 3 assessment.

See for details:

- Assessing migration based on historical data, see section 6.6
- Considering natural attenuation, see section 6.4

Tier 3: Monitoring and specific modelling

Complex sites, complex groundwater systems and/or complex contamination require a tier 3 assessment. Should estimated remediation costs and social consequences be high, extensive risk assessment and additional monitoring are valid. Instruments for this tier are not specifically described in this report, but recommendations and conditions are given. Processes to take into account are natural attenuation, sorption, vulnerable objects, NAPLs, leaching and the function of groundwater in the area. This report does provide a general introduction to groundwater modelling and the monitoring of natural attenuation.

4. Tier 0: Initial characterization

4.1 Introduction

When a case of serious groundwater contamination is determined the initial risk assessment is based on three criteria. These criteria are the presence of NAPL, vulnerable objects and the volume of contaminated groundwater (plume). This chapter explains these criteria.

4.2 Non Aqueous Phase Liquids

4.2.1 Dense Non Aqueous Phase Liquids[2]

In this section an approach has been described for the assessment of the risks due to the presence of Dense Non Aqueous Phase Liquids (DNAPL) in groundwater. This approach combines a DNAPL-stepwise-approach with the tiered approach as described in the Circular on soil remediation (section 2.2.2).

The background to this approach and information on the monitoring of a DNAPL pool contamination is described in Appendix A1.

Step 1 – assess the likelihood that a DNAPL pool contamination is present

This element is not included in the approach as defined in the Circular (VROM, 2006). It can be based on the results of an exploratory soil investigation (*‘verkennend bodemonderzoek’* in Dutch). Such an investigation provides both historical site information, and soil and groundwater quality data. The assessment could be as follows:

- If, based on historical site information, a DNAPL pool contamination is unlikely and if no DNAPL substances are encountered in either soil or groundwater in significant concentrations, it is assumed that a DNAPL pool contamination is not present.
- If, based on historical site information, a DNAPL pool contamination is not unlikely and/or if DNAPL substances are encountered in soil and/or groundwater in significant concentrations, it is assumed that a DNAPL pool contamination may be present.

In the first case, further action is not necessary. In the latter case, step 2 should be initiated.
For the assessment of the historical site information, the approach described in
Appendix A1.1.3 could be used.

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[2] By: A. van de Haar (Elementair Utrecht)

Step 2 – assess the likelihood that a DNAPL pool contamination is present in the zone under human influence (usage zone, '*gebruikszone*' in Dutch*)*.

Following the procedure as described in the Circular on soil remediation (VROM, 2006), this step focuses on the presence of a DNAPL pool contamination in the zone under human influence. As explained in section A1.1.2 this assessment is normally based on indirect proof. Such proof of DNAPL pool contamination absence could include:

- no indication of the presence of dissolved DNAPL substances in the zone under human influence in high concentrations (typically concentrations greater than 1% of solubility, not taking into account correction for mixtures of DNAPL substances);
- no indication of the presence of a strong vertical variation in dissolved DNAPL concentrations (due to the presence of DNAPL pool layers) in the zone under human influence;
- no indication of the presence of dissolved DNAPL substances in a position in the zone under human influence which is difficult to explain as a result of migration of dissolved DNAPL substances from the source zone only (for example, in an upstream position).

If one or more indicators for the presence of a DNAPL pool contamination are found, step 3 should be initiated. If not, it is assumed that there is no significant DNAPL pool contamination present in the zone under human influence. It should be stressed that this assessment is highly dependent on the quality of the assessment of the horizontal and vertical variation in dissolved DNAPL concentrations in the groundwater in the zone under human influence.

Step 3 – assess the likelihood that a DNAPL pool contamination present in the zone under human influence poses unacceptable migration risks

Following the tiered approach as described in the Circular on soil remediation, this assessment step focuses on the potential of a DNAPL pool contamination in the zone under human influence to substantially migrate. For the assessment of this potential, the latter three of the four approaches as given in the Circular and described in section A1.2.2 are used:

1) *Make plausible that the amount of DNAPL in the usage zone is too small to pose an unacceptable migration risk*

   It is probably very difficult to discern between absent or very small DNAPL pools, based on indirect evidence. This approach is therefore likely to be less applicable.

2) *Make plausible that on the basis of properties (e.g. viscosity) of the DNAPL present in the usage zone combined with the permeability of the soil, contamination is unlikely.*

This method could be applied by comparison with standard scenarios with variable migration potential. Some examples of such scenarios are given below:

- A DNAPL pool contamination with viscous DNAPL, e.g. coal tar, creosote or another liquid with a high viscosity, e.g. > 20 cP (centipoise). Such liquids are expected to migrate very slowly and thus pose limited migration risks.
- A DNAPL pool contamination which has reached a barrier with a high hydraulic resistance. In such a case, provided that it can be proven that the barrier is continuous, the migration risks are limited.

In the case of scenarios with limited migration potential it could be concluded that migration risks are acceptable.

3. Make plausible that unacceptable migration risks are unlikely, using a multiphase flow model.

The application of a multiphase flow model for the assessment of unacceptable migration risks requires a detailed conceptual model of the contaminated profile. Such a conceptual model requires highly detailed mapping of the dimensions of the DNAPL pool contamination (i.e. the positions and sizes of DNAPL pools) and insight into the structure of the underlying, unpenetrated soil (alternation of more and less permeable soil layers). If incorrect data are used regarding the positions and thicknesses of the pools, and regarding the permeability of the underlying soil barriers, the results could be unreliable. Furthermore, only a few experts are able to fully understand these models. For these reasons, it is unlikely that, on the basis of application of a multiphase flow model only, a reliable assessment of migration risks is possible.

4.2.2 Light Non Aqueous Phase Liquids

Light Non Aqueous Phase Liquids (LNAPLs) often enter the groundwater as a result of accidents or leakage or spillage from storage tanks or transport pipelines. Two specific properties are essential for the development of LNAPLs:

a) The density of the organic liquid must be less than the density of water (1000 g/dm^3)
b) The water solubility must be low (less than approximately 1 g/dm^3)

After reaching the groundwater the contaminant tends to migrate laterally (often as a film) over the surface of the groundwater table due to these properties.
This section explains the risks, behaviour and determination of a LNAPL.

Risk caused by LNAPLs

LNAPLs can cause risks through the presence of high concentrations of toxic substances. Often an undissolved contaminant phase is present. This is a potential source of groundwater contamination. Substances dissolve in the surrounding groundwater at the interface of the water and contaminant phases. When these substances are exposed to the unsatured soil, evaporation of volatile substances can occur.

LNAPLs often exist as volatile contaminants which tend to evaporate to the soil surface. Possible human risks can be assessed using the human exposure model VOLASOIL (Waitz et al., 1996).

Behaviour

The migration of a NAPL in the unsaturated zone is driven by gravity, with a dominant vertical flow direction. When a LNAPL reaches the groundwater table the contaminant tends to migrate in a lateral direction (Kai et al., 2003). The effect of soil profile, preferential flow, ageing and groundwater level fluctuations on the migration of NAPLs is important but often neglected. Ageing of the contaminant often results in a decrease in water solubility, a decrease in volatility, oxidation and polymerization, resulting in a decrease in mobility. Chemical and microbial processes (degradation) occur at the soil-air boundary.

The determination of LNAPLs

The remediation urgency method gave some criteria for the determination of the presence of a LNAPL. However, the evaluation of the remediation urgency method showed us that users considered these criteria to be inadequate in some cases (Lijzen et al., 2003). In practice, risk assessors formulated other complementary criteria and the determination of a LNAPL is, in some cases, difficult (Van de Haar, 1999). For example, fluctuations in the groundwater table often confuse the picture of the situation and this can even lead to an apparently (temporarily) vanishing of LNAPL.

More robust evidence can be collected on the basis of the behaviour of LNAPLs and through the combination of different observations. Table 4.1 (based on Van de Haar, 1999) tabulates various useful observations that may help determine the presence of a LNAPL.

Table 4.1 Observations concerning the presence of LNAPLs.

	Observation	**Conclusion related to the presence of LNAPL**
a)	The appearance of an oil layer (>0.5 cm) in a groundwater monitoring well	Certain
b)	The observation of pure contaminant in subsoil samples drilled from the soil layer near the groundwater table	Likely
c)	The presence (determined by analytical analysis) of NAPL generating contaminants in high concentrations (> 1 percent) in samples drilled from the soil layer near the groundwater table	Plausible
d)	The presence (determined by analytical analysis) of NAPL generating contaminants in high concentrations (concentrations > 10% of water solubility) in the upper layer of the groundwater	Likely
e)	The presence of oil-like discolorations or the presence of an oil film in the subsoil samples	Possible
f)	The presence (determined by analytical analysis) of NAPL generating contaminants in the upper layer of the groundwater	Possible
g)	A combination of the mentioned observations (a–f)	Up to 100% certainty

Risk assessment of LNAPLs

According to the Circular on soil remediation (VROM, 2006), the presence of an LNAPL poses an unacceptable risk. The reason for that is the assumption that a LNAPL migrates autonomously. However, actual migration (see behaviour of LNAPLs) and the correspondent risk, are dependent on soil profile, preferential flow and groundwater velocity, amongst others. The actual risk depends also on the use of the contaminated zone. For actual risk assessment the same approach as given for DNAPLs (section 4.2.1.) can be followed.

4.3 Vulnerable objects

Vulnerable objects are biotic (living organisms) or abiotic (non-living) parts of the environment that can experience damage (effects) from exposure to contaminants. Vulnerable objects can be categorized on the basis of three important protection goals: human health, soil ecology and groundwater and surface water.

Concerning the risks of the migration of contaminated groundwater, the following vulnerable objects are mentioned in the Circular on soil remediation (VROM, 2006):

- Groundwater bodies used for the extraction of drinking water or industrial process water
- Surface waters which are part of a protected area
- Strategic groundwater bodies (regarding ecological quality or drinking water reserves)
- Water seepage areas

See also section 2.2.3.

4.4 Volume of contaminated groundwater

A clear indicator of unacceptable contaminant migration is the magnitude of the contaminated soil volume. The contour of the contaminated area is determined using the Intervention Value for groundwater. An unacceptable risk is considered to exist when the soil volume determined by the groundwater Intervention Value contour exceeds 6000 m^3 (VROM, 2006).

5. Tier 1: Generic risk assessment

5.1 Introduction

The migration of contaminants in groundwater depends strongly on groundwater velocity. The higher the groundwater velocity, the larger the advancement of a contaminant front in time and, consequently, the larger the increase of the volume of contaminated subsurface.

Other processes that play a major role in migration in saturated groundwater are sorption and degradation. Sorption leads to a delayed arrival of the contamination, while degradation causes a reduction in contaminant concentrations.

Until 2006 the prescribed procedure (remediation urgency method) for the assessment of risk due to contaminant migration was based on the ‘standstill’ principle: contaminants should not move from their current location. The object to be protected from further contamination is the groundwater body itself, namely the surrounding clean groundwater. The risk of contaminant migration was assumed to be unacceptable if the volume of contaminated water saturated soil increased by more than 100 m^3 within a period of one year.

It is expected that some details of the Circular (VROM, 2006) will be adjusted. Concerning the site-specific risk assessment of contaminated groundwater the migration can be expressed as the increase of contaminated groundwater volume in time. If the volume of contaminated water saturated soil increased by more than 1000 m^3 within a period of one year an unacceptable risk is present.

In this chapter the methodology for the calculation of the increase in contaminated groundwater volume (according the former remediation urgency method) will first be discussed. Secondly, the procedure for deciding whether a risk exists due to contaminant migration is discussed. Thirdly, groundwater velocity is considered. Finally, we briefly discuss the process of sorption and its effect on the migration of contaminants.
The methods selected for this tier are simple, but conservative, to prevent an underestimation of the risks.

An alternative for the method of this chapter is the use of the Webplume model (http://www.delftgeosystems.nl/ click on ‘e-consult’). Webplume might be suitable for a tier

1 or 2 assessment. In Appendix A5 the Webplume model is explained[3]. It should be mentioned that a comparison between both approaches is essential before an opinion about the suitability of Webplume (to support decisions about remediation measures) can be formed.

5.2 Assessing increase in volume of contaminated water-saturated soil

The current and proposed risk evaluation procedure applies the following simple equation:

$$d = p \times O \tag{5.1}$$

where:

$d =$	increase in time of the volume of contaminated water-saturated soil ($\mathrm{m}^3\ \mathrm{year}^{-1}$)
$p =$	advancement (forward movement) of the so-called Intervention Value (IV) concentration within one year ($\mathrm{m\ year}^{-1}$)
$O =$	largest cross-sectional area (m^2) of the currently contaminated groundwater body, delineated by IV-concentration for groundwater

The advancement p, as applied in equation (5.1), is calculated by:

$$p = v/R \tag{5.2}$$

where:

$v =$	groundwater flow velocity ($\mathrm{m\ year}^{-1}$), being the quotient of specific groundwater discharge (also known as Darcy flux or seepage flux) and effective porosity
$R =$	retardation factor (dimensionless), assuming linear equilibrium sorption. If no sorption, R takes the value of 1, otherwise R>1. For more information about sorption refer to section 5.5.

Note that equation (5.2) does not account for contaminant degradation. If this were the case then the advancement p and, consequently, the increase in the volume d would become smaller. The processes of degradation (decay) and its influence on concentrations are considered in section 6.4 and Appendix A5.

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[3] By K. Janssen-Roelofs (Geodelft)

The current procedure calculates the advancement, p, of the Intervention Value contour (Intervention Value (IV)-concentration front) within one year. The expression d = p × O, graphically illustrated in Figure 5.1, is based on the following assumptions:

- the one-year long pathlines starting from the surface of a contaminated groundwater body are straight lines
- all pathlines point in the same direction in x y z space (parallel pathlines)
- groundwater velocity is the same for all pathlines

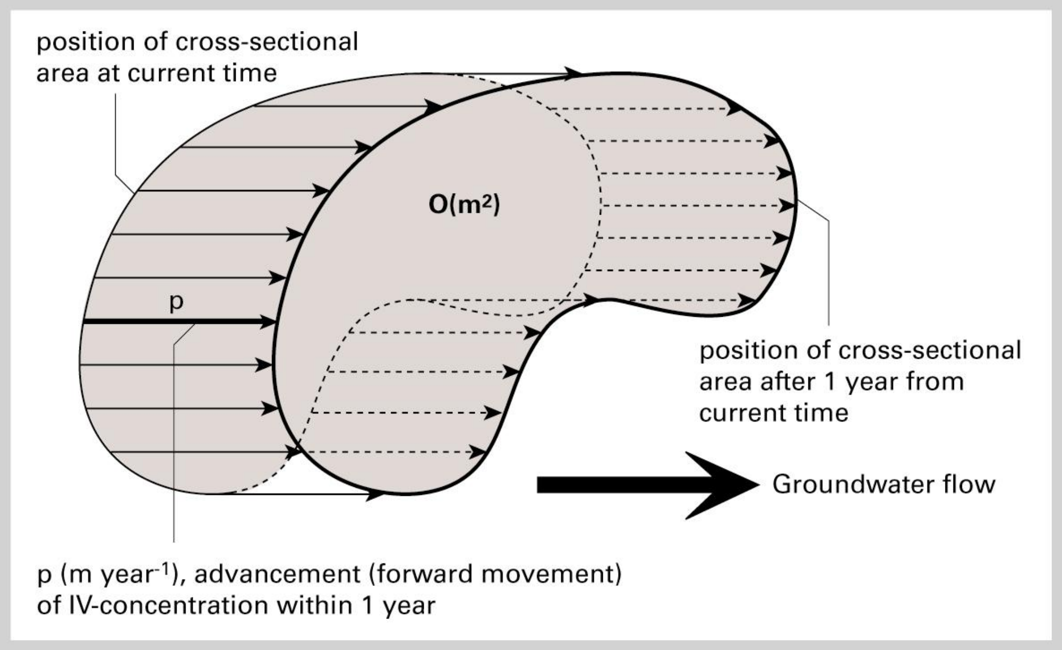

Figure 5.1 Schematic diagram of volume-increase calculation.

Figure 5.2 further illustrates the approach to calculating the volume increase *d*. The mean vertical velocity is 1 m per year while the mean horizontal velocity is 30 m per year (see section 5.4). Therefor, the assumptions that (a) all pathlines are parallel (unilateral flow) and (b) the one-year advancement *p* in space is identical at any point on the IV-concentration contour, are both plausible approximations of reality. However, it is recommended to control this assumption in practice. Equation 5.1 and 5.2 can be used, with area *O*, not being a vertical but a horizontal cross-section.

In case of negligible vertical movement, as Figure 5.2 shows, the Intervention Value concentration front c_0 moves, while retaining its original shape, to the Intervention Value concentration front c_1 within one year; the distance between c_0 and c_1 being *p* at any point in space. Therefore, it can also be assumed that the straight-plane area *O* moves forward, undistorted, by the distance *p* after one year (see Figure 5.1).

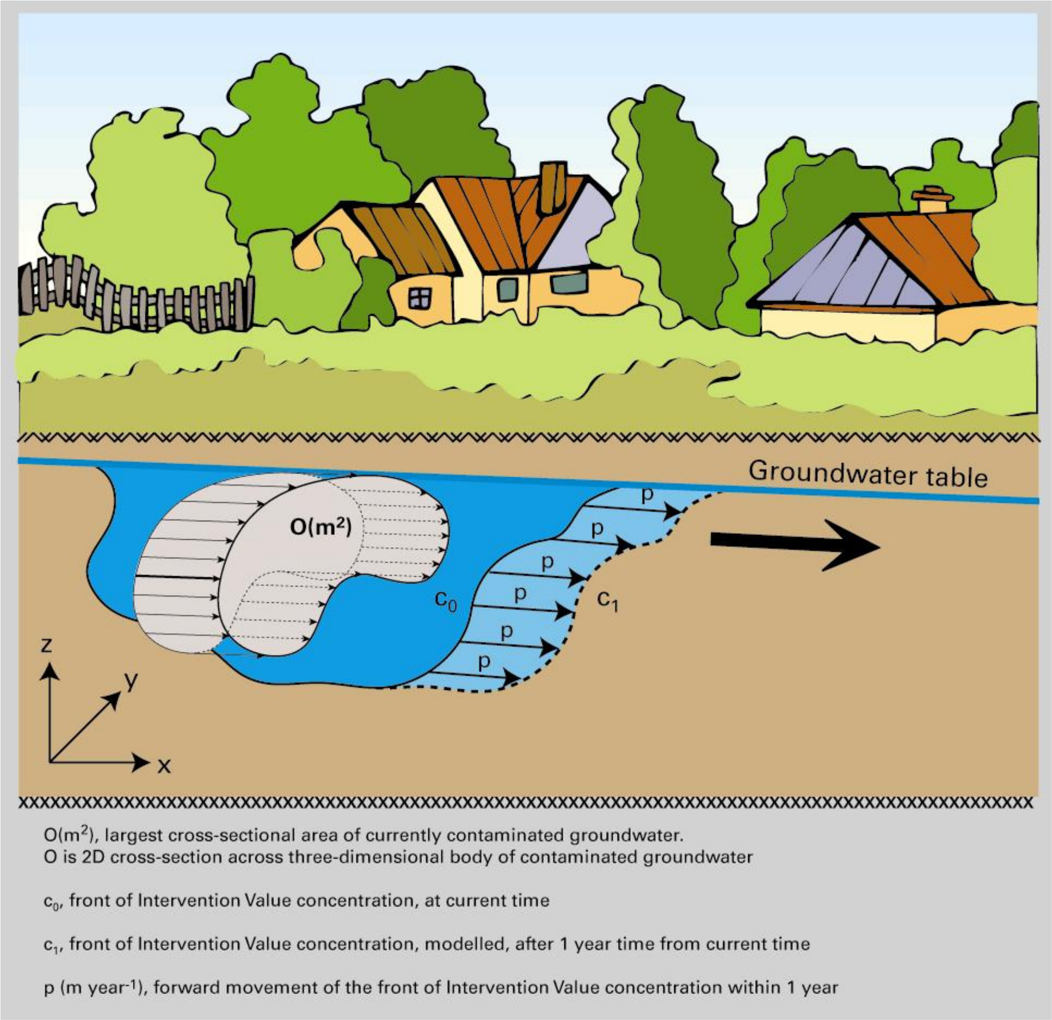

Figure 5.2 Schematic view of concentration front advancement due to unilateral flow.

5.3 Deciding about contaminant migration risk

The decision as to whether the migration of a contaminant results in an unacceptable risk is based on a simple rule, defined by the expression (5.3):

$$\begin{aligned}&\text{if } (d > 1000 \text{ m}^3 \text{ year}^{-1}) \text{ and, if so,}\\ &\text{if (potential exists for } 1000 \text{ m}^3 \text{ year}^{-1} \text{ pollution)} \Rightarrow \text{risk}\end{aligned} \tag{5.3}$$

If the volume of contaminated water-saturated soil, *d*, increases by more than 1000 m^3 within a period of one year, it is assumed that a risk exists due to migration of the contaminant. However, the outcome of this check alone is not conclusive. An additional constraint for a contaminated site being declared ‘at migration risk’ is that the yearly contaminant load should be sufficiently high to be actually able to contaminate the groundwater in a volume of 1000 m^3 water-saturated soil up to the level of the Intervention Value concentration for groundwater.

The basic principle is that new cases of ‘serious soil contamination’(defined as an exceedance of the Intervention Value for groundwater in a water-saturated volume of at least 1000 m^3) should not develop in a relatively short time frame. The check value of 1000 m^3 within one year is based on political policy considerations. The value is greater than zero –strictly speaking the goal– because a zero value would be impractical. Should the outcome of these two checks be positive (equation 5.3), it is possible to refer to a case of ‘risk due to contaminant migration’.

The volume criterion of 1000 m^3 is currently subject to political discussion. The criterion of the former remediation urgency method was 100 m^3 increase per year.

5.4 Groundwater velocity

Groundwater flow is a major process leading to the migration of contaminants in water-saturated subsurfaces. The relevant process is known as contaminant advection. The higher the groundwater velocity, the larger the advancement of a contaminant front.

The groundwater flow velocity, v [$L\ T^{-1}$], is also the velocity of non-reacting constituents (ideal tracers) transported by groundwater. The groundwater flow velocity is required for equation (5.2) and can be expressed as:

$$v = q/n \tag{5.4}$$

where:

q = specific groundwater discharge (also known as Darcy flux, or seepage flux) [$L^3\ L^{-2}\ T^{-1}$, i.e. $L\ T^{-1}$]

n = effective porosity of water-saturated soil [$L^3\ L^{-3}$, i.e. dimensionless]

The specific groundwater discharge, q, can further be written as:

$$q = k_h \times gradH \tag{5.5}$$

where:

k_h = hydraulic conductivity of water-saturated soil [$L\ T^{-1}$]

$gradH$ = gradient of groundwater potential [$L^1\ L^{-1}$, i.e. dimensionless]

If no information is available about the actual site-specific groundwater velocity v, the user can adopt, for equations (5.1) and (5.2), the value of v from the standard table (Remediation

Urgency, the Manual, VROM, 1995).

In the tiered approach proposed in this report, the table values are used in tier 1 for a first generic assessment of the risk of contaminant migration.

Table value for sandy regions (tier 1)

The standard (table) value v = 30 m per year can be regarded as the spatial average of groundwater velocities in sandy regions of the Netherlands. The relevant regions consist of Upper Pleistocene formations where the hydraulic conductivity varies between 10 m per day (cover sand, a mixture of aeolic sands with local materials) and 60 m day^{-1} (coarse sand), the average value being about 30 m per day (UN, 1991). In these regions the gradient *gradH* of the groundwater potential is on average 0.001 (Meinardi, 1994).

It should be noted that the table value of v = 30 m per year should not be used at locations where the velocity is locally higher, such as (a) in the vicinity of groundwater abstraction sites, (b) in the vicinity of surface waters (large rivers and canals) and (3) along the side (toe) of ice-pushed hills. An example of the latter is formed by the edges of the Veluwe region of which the groundwater drains into the Nederrijn and IJssel rivers.

More information on the background of the value v = 30 m per year is given in Appendix A2.

Table value for clay and peat regions (tier 1)

The risk-assessment procedure (VROM, 1995) allows the user to adopt a standard value for the groundwater velocity v if no information is available for the actual site-specific groundwater velocity. In clayey and peat subsurfaces, the tabled velocity values are:

- clay: v = 0.2 m per year
- peat: v = 0.1 m per year
- clay/peat: v = 0.15 m per year

Those velocities may seem very small at first sight, at least when compared to the velocity ranges in the sandy areas. However, the velocity is small because, in most cases, clay and peat are found in flat areas where the groundwater gradient *gradH* is practically zero. Consequently, referring to the relationship (5.5), specific groundwater discharge, q, and thus also the groundwater velocity, v, should also be very low. An additional factor leading to low velocities in clay and peat regions is the low hydraulic conductivity of clay and peat materials.

5.5 Sorption

As mentioned in section 5.2, the advancement of a contamination front is determined by the groundwater flow velocity and the retardation. The migration of a contaminant is retarded compared to water due to interaction with soil constituents. Several types of binding, covered by the term ‘adsorption’, have in common that they are considered reversible processes. Due to the reversibility of adsorption contaminants ‘stored’ on the soil, particles can be mobilized if the pollution source itself has been removed.

Major surfaces for adsorption are clay, organic matter and iron, manganese and aluminium oxides and hydroxides. As well as the presence and amount of these reactive surfaces, the acidity (pH) and redox conditions are of major importance because they affect the accessibility of the surfaces and the speciation of, mostly anorganic, substances. Changing pH or redox conditions, as a result of human activities in or on the soil, can result in mobilization or immobilization of contaminants.

The presence of dissolved organic carbon is an important factor to consider because it can stimulate migration of substances.

The relationship between retardation and adsorption is given by:

$$R = 1 + K_d * \frac{\rho}{\varepsilon} \tag{5.6}$$

R = Retardation factor (dimensionless)
K_d =Adsorption coefficient ($dm^3.kg^{-1}$)
ρ =Soil bulk density ($kg.dm^{-3}$)
ε =Pore volume (dimensionless)

There are several options available to account for retardation in the tiered assessment of migration risks.

1) Use of adsorption values found in literature. Table values for adsorption (K_d and K_{oc} values) can be taken from Otte et al. (2001).
2) Adsorption coefficients can be estimated based on empirical relationships between adsorption and soil properties (regression lines)
3) Adsorption coefficients can be computed using geochemical models. Geochemical models combined with transport equations do not require adsorption coefficients and

compute binding to soil using equilibrium constants for specific soil constituents
4) Site-specific adsorption coefficients or retardation can be measured in the lab

For the tier 1 generic assessment standard table values (1) is recommended. The use of regression relationships (2), simple geochemical models (3) or measured adsorption coefficients can be applied in tier 2 (see section 5.3).

Adsorption coefficients are widely used in environmental risk assessment frameworks. Many values for common contaminants have been published in the literature. However, most of these are measured in topsoil samples (0-30 cm). This part of the soil usually contains a larger amount of reactive surfaces, such as clay and organic matter, than subsurface soils. As a result, the adsorption coefficients are not considered representative for calculating the migration of contaminants in the saturated zone. This does not necessarily mean that migration in the subsoil is faster. Due to anoxic conditions sulphide complexes can form which are very insoluble and precipitate.

Since data for the subsurface is scarce, a reduction factor can be applied which gives a rough indication of how adsorption changes with depth, to extrapolate the topsoil adsorption coefficient to subsurface conditions. This is done in other frameworks such as pesticide assessments (European consensus) and leaching of inorganic contaminants of construction materials in the Netherlands. Reduction factors used are 0–0.1 for the saturated zone deeper than 1 m.

The typical range of adsorption coefficients for Dutch soil is given in Figure 5.3. In order to obtain a safe risk assessment for groundwater in the first generic tier, it is recommended to use the lower K_d value from the range and a reduction factor for the effect of depth.

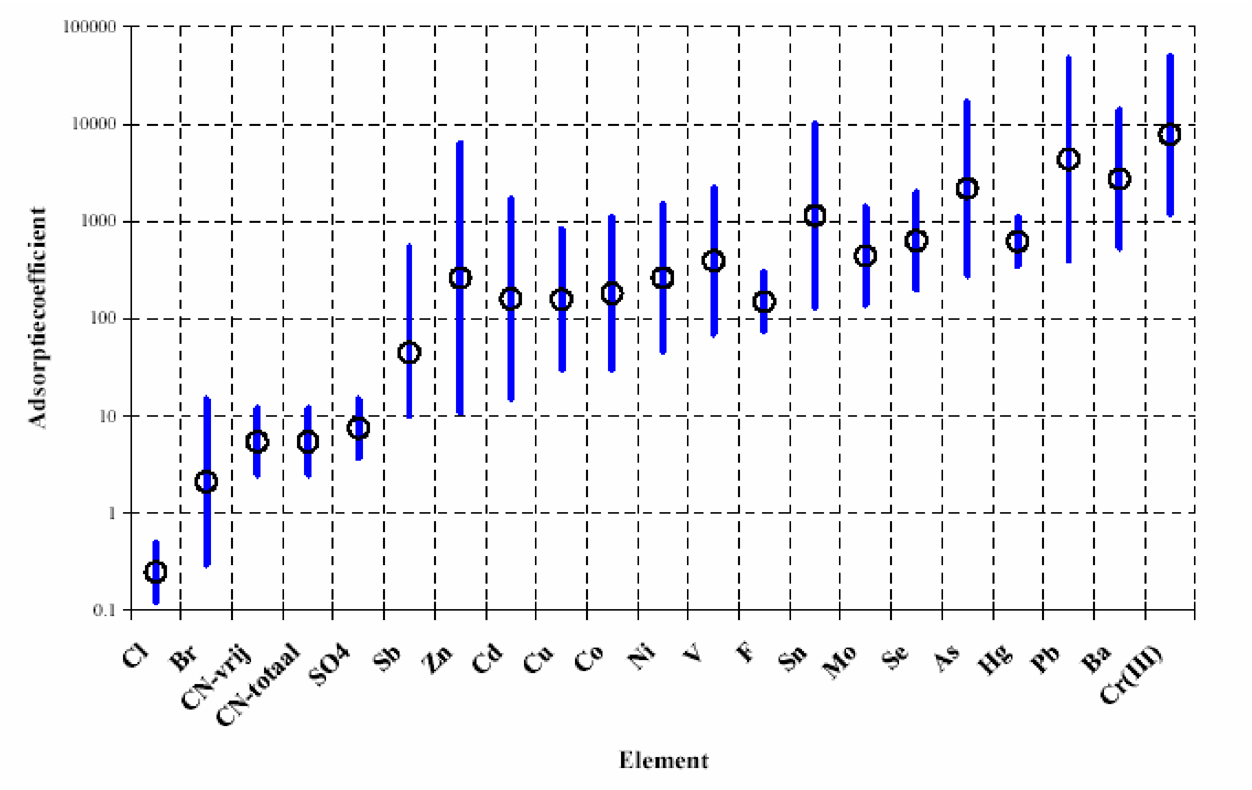

Figure 5.3 Typical ranges of adsorption coefficients of inorganic contaminants in Dutch topsoils (Verschoor et al., 2006).

The adsorption coefficient of organic substances is often expressed as a value normalized for the organic carbon content of the soil, K_{oc}. The adsorption coefficient in a particular soil is obtained by multiplication with the fraction of organic carbon:

$$K_d = K_{oc} * f_{oc} \qquad (5.7)$$

Table 5.1. Classification of mobility (FAO, 2000).

log K_{oc}	**Classification**
< 1	Highly mobile
1–2	Mobile
2–3	Moderately mobile
3–4	Slightly mobile
4–5	Hardly mobile
>5	Immobile

Note that adsorption is expressed as log $K_{oc.}$

6. Tier 2: Site-specific risk assessment

6.1 Introduction

In tier 2, the site-specific assessment, the concepts of tier 1 can be used. However, site-specific (i.e. measured) data should now be used instead of the generic data in order to increase the certainty of the risk assessment.

Alternative options for assessing contaminant migration are also proposed:

- Contaminant migration can be assessed based on historical data.
- The possibility of natural attenuation can be considered. Should trustworthy indicators for natural degradation be present, a remediation decision can be postponed, together with the monitoring of natural attenuation processes. Monitoring activities can be performed as part of a tier 3 assessment (section 7.3).

The use of these alternatives depends on the availability of site-specific data.

Furthermore, contaminant migration as a result of leaching processes can be considered. section 6.7 tackles the problem of the risk assessment of Total Petroleum Hydrocarbons (TPH, or mineral oil). TPH is a complex mixture of many components and can be assessed after analyzing the oil fractions. TPH is a frequently occurring contaminant in groundwater.

6.2 Assessment of site-specific groundwater velocity

The assessment concept used in tier 2 is the same as that for tier 1 and the following equation applies:

$$d = v \times O / R \tag{6.1}$$

where:

d = increase in time of the volume of contaminated water-saturated soil ($m^3.year^{-1}$)
v = groundwater flow velocity ($m.year^{-1}$)
O = largest cross sectional area (m^2) of the currently contaminated groundwater body, delineated by IV-concentration for groundwater
R = retardation factor (dimensionless), assuming linear equilibrium sorption. If no sorption, R takes the value of 1, otherwise R>1. For more information about sorption it is referred to section 6.5.

The groundwater flow velocity, v (m.year^{-1}), is also the velocity of non-reacting constituents (ideal tracers) transported by groundwater. This groundwater flow velocity, which is the actual velocity of groundwater, can be expressed by:

$$v = 365.25 \times k_h \times gradH \;\, / \, n \qquad (6.2)$$

where:

k_h = hydraulic conductivity of water-saturated soil (m.day^{-1})

$gradH$ = gradient of groundwater potential in the direction of flow (m^{1}m^{-1}, i.e. dimensionless)

n = effective porosity of water-saturated soil (m^{3}m^{-3}, i.e. dimensionless)

Please note that in (6.2) the expression $k_h \times gradH$ represents the specific groundwater discharge, also known as Darcy flux or seepage flux (m^{3}m^{-2}day^{-1}, i.e. m day^{-1}).

Unlike in tier 1, where the groundwater velocity values are taken from a standard table, the groundwater velocity v (m^3 year^{-1}) in tier 2 is defined by the user, based on hydrological characteristics from the location in question. From (6.2) it follows that three hydrological characteristics have to be assessed:

- kh, hydraulic conductivity of water-saturated soil (m day-1)
- gradH, gradient of groundwater potential in the direction of flow (dimensionless)
- n, effective porosity of water-saturated soil (dimensionless)

The value of hydraulic conductivity, usually varies rather strongly in space. It is therefore common practice to define its value at a series of locations within the area in which contaminant migration has taken place and, using these local k_h-values, to calculate the spatially-averaged value of hydraulic conductivity to be used for expression (6.2).

Compared with the k_h value, the gradient of groundwater potential varies much less within the area considered for contaminant migration. The gradient can be defined using the groundwater level observed at a number of monitoring wells. Obviously, to be able to define the gradient in real three-dimensional space, it is necessary to know the groundwater level at a minimum of three locations. Knowing these three groundwater levels, one can (a) generate the groundwater level contour map in space, (b) draw the direction of the flow on that map and (c) calculate the magnitude of the gradient *gradH* in the direction of groundwater flow. When three observations only are used, it is implicitly assumed that the groundwater contours are straight lines located on a straight plane. Although three groundwater level observations should be sufficient in theory, in practice it is preferable to use more than three observed values. This makes it possible to better capture the natural variability in groundwater levels – both on a local and on a larger spatial scale – due to the spatial variability in hydraulic conductivity and other factors.

It is a lot easier to determine the effective porosity of water-saturated soil, n, than k_h and $gradH$. The reason is that porosity values vary relatively little within a formation, i.e. within a sand layer.

6.3 Assessment of site-specific sorption

Site-specific adsorption coefficients can be obtained using:

- Regression relationships
- Geochemical models
- Measurements

Regression lines are mathematical relationships between soil properties and the adsorption coefficient. Organic matter and pH are often the dominant parameters in this relationship. Clay, Fe oxides and Al oxides are also involved in adsorption, but their contribution is not always expressed in regression relationships. Regression lines are based on large datasets of adsorption in topsoils. This implies that the relationships are not representative for subsurface soils. In subsurface soils the percentage of clay, Fe oxides and Al oxides are the dominant active surfaces, while these parameters are often not expressed in the regression relationship. If these parameters are not included in the regression relationship the adsorption coefficient is represented as a relatively low, conservative value. It can be used without a depth reduction factor and can be considered a ‘worst case’ estimate of mobility in the groundwater. Regression relationships are available for a limited number of anorganic substances.

Another way of obtaining a site-specific sorption coefficient is the use of a geochemical model, for example PHREEQC (Parkhurst and Appelo, 1999), MINTEQA (Allison et al., 1991) or ORCHESTRA (Meeussen, 2003). In general, the use of these models requires expert knowledge. Site-specific information on pH, redox potential, organic matter, types and amounts of clay minerals and the presence of other substances in the groundwater is required to obtain a realistic adsorption coefficient.

The adsorption can also be measured. Site-specific samples are taken to the lab and tested, preferably using a standard method (i.e. OECD test guideline 106, Adsorption/Desorption Using a Batch Equilibrium Method). Adsorption coefficients obtained by spiking fresh samples generally provide lower adsorption coefficients than samples containing a historical contamination.

6.4 Degradation; potential for natural attenuation[4]

In the Netherlands, the monitored natural attenuation (MNA) may be considered a risk management option if it is sufficiently protective for human and ecological receptors. Most protocols used to assess the efficacy of natural attenuation (NA) use the three lines of evidence (see Box 7.1). In this second tier only the first line of evidence is used. It documents the development of concentrations in wells, or the development of the plume. It is a straightforward evaluation, in which the actual NA processes and conditions are not yet taken into account. However it can prove that NA is sufficiently protective. The method is described in Appendix A4; section A4.5.

This second tier assessment implies that tier 3 needs not to be executed if:
1. there is no threat to receptors, and
2. concentrations show a decreasing trend, or
3. the plume is clearly stable or fading.

These considerations are further explained in Appendix A4, section A4.5. If concentrations are increasing or the plume is expanding over a time span greater than 30 years, then NA is not an option. However, if no clear trend can be recognized, or if the plume is expected to expand, but over less than 30 years, tier 3 needs to be executed (section 6.3).

6.5 Leaching

Leaching is a vertical migration pathway for contaminants. Leaching causes contamination of clean groundwater by transport of substances from the soil layer above.

There is a potential risk for leaching after reallocation of soil, land use changes or groundwater level changes. Once pollution reaches the groundwater, further migration is caused by a combination of horizontal flow and vertical transport. The relative contribution of horizontal and vertical pathways depends on the soil type, but, as stated above, leaching is the vertical transport from the unsaturated soil to shallow groundwater only.

Leaching can be assessed by measurement and by calculation. Measurement mainly enables the assessment of leaching under current soil conditions, whereas calculation makes it

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[4] By Hans Slenders (TNO)

possible to predict leaching in the future and for different scenarios, such as changing soil pH. For both possibilities, several options are available, differing in quality, i.e. reliability, and complexity. ISO 15175:2004 provides guidance on the principles behind, and main methods for, the evaluation of sites, soils and soil materials in relation to their role as a source of contamination of groundwater and their function in transporting, degrading and transforming contaminants. It identifies and lists relevant monitoring strategies, sampling methods and soil processing and analytical methods.

6.6 Risk assessment based on historical contaminant migration

In the remediation urgency method contaminant migration is estimated, based on groundwater flow, groundwater flow direction and retardation of the contaminant. There is also an alternative method for a first assessment of contaminant migration based on the increase in the amount of contaminated groundwater. Such a method is described in this section.

A minimal amount of data is necessary for this method and choices have to be made so that basic principles can be used. Based on this method a rough estimate, or range, of the horizontal and vertical contaminant transport per year can be derived. This method should initially focus on estimating the maximum flow rate. When this ‘historical approach’ is applied correctly the actual contaminant migration is assessed, including processes such as sorption, dispersion and degradation. This method should therefore be realistic, and not conservative.

The following information is required (see Figure 6.1):

- The volume of the contaminated groundwater above the Intervention Value (IV) at the time of measurement (Tm). The use of the Target Value would make the assessment more conservative.
- The period in which the contamination or discharge has taken place (Tb-Te). Most important is that the moment at which no more contamination was added to the groundwater (Te) is known
- The exact location or locations at which contamination /discharge took place (Pl)

Based on this data the following parameters can be derived:

- The largest distance (horizontal and vertical) between the original point of discharge (the largest or the one that is furthest upstream), Pl, and the contour of the Intervention Value (furthest downstream) (Lmax, v ; Lmax, h)
- The time between the last discharge and the moment the measurements were carried out for estimation of the size of the contamination (t=Te-Tm)

Division of these results in a rate of contaminant migration in metres per year (in horizontal, V_h, and vertical direction, V_v), based on the Intervention Value:
($V_h = L_{max,h} / t$ en $V_v = L_{max,v} / t$)

With the use of this information, the same procedure can be followed as in the current risk assessment method:

- Multiply the horizontal migration rate with the vertical surface area of the Intervention Value contour (dh= Vh*Ov);
- Multiply the vertical migration rate with the horizontal surface area of the Intervention Value contour (dv= Vv*Oh).

Addition of both volumes gives the maximum increase in the contaminated groundwater volume. This volume can be compared to the critical value of 1000 m^3 per year.

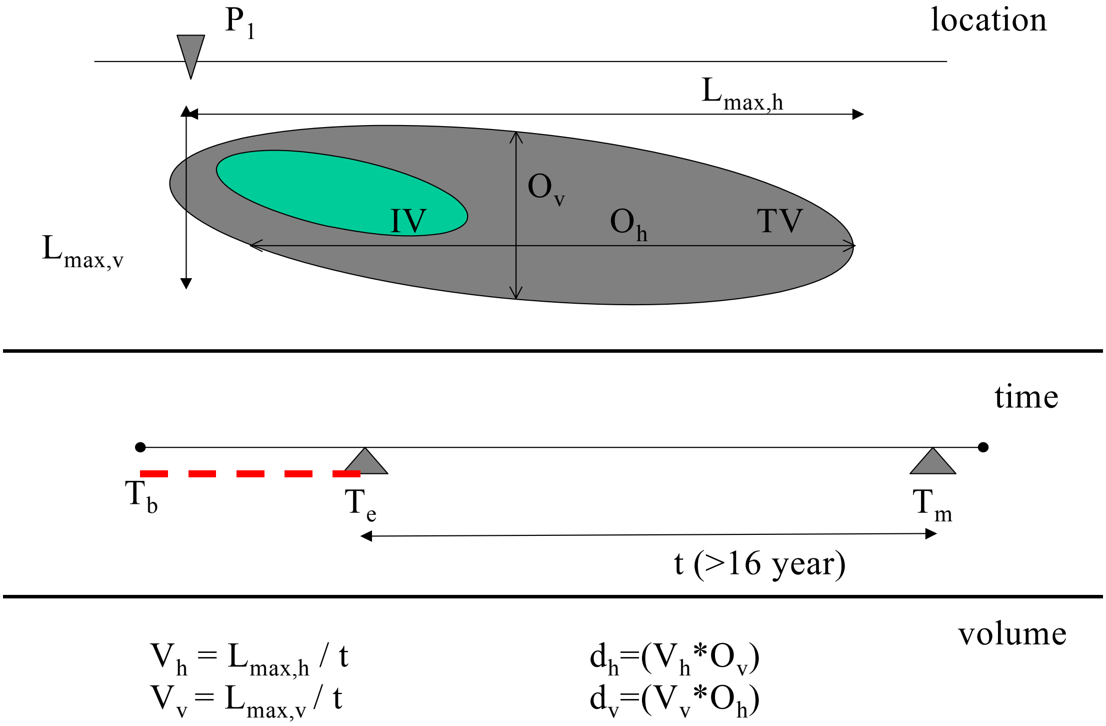


Figure 6.1 Sketch of a groundwater contamination and necessary data for risk assessment.

Rule of thumb

As well as this calculation, a rule of thumb is used for an initial assessment.

- *When the maximum size of the Intervention Value contour is known for a historical contaminated site (prior to 1987), the volume of contaminated soil must be greater than 1000 m3 multiplied by the number of years since 1987.*

The *rule of the thumb* is valuable for a first impression, but it is not recommended to use only this method for decisions concerning remediation urgency.

Critical aspects

- Background concentrations in groundwater. For the determination of the Target Value contour it is important to know the site-specific background concentration. This could be a problem in areas with naturally higher concentrations (e.g. arsenic).
- Determination of the contour. It can be difficult to make a good estimation of the contaminated volume based on scarce data. Unless additional measurements are carried out, the maximum volume should be used in the risk assessment.
- More sources. At many industrial sites there will be many points in space and time. All points should be recorded and the worst case scenario should initially be followed.
- Extrapolation into the future. When circumstances remain unexpectedly stable within the relevant period the results can be extrapolated. When changes in the groundwater flow rate and direction are expected in the near future, this should be included in the risk assessment.

6.7 Total Petroleum Hydrocarbons

6.7.1 Introduction

Total Petroleum Hydrocarbons (TPH), also named mineral oil, form a frequently occurring contaminant in groundwater. Risk assessors frequently stress that, in cases of oil-contaminated soil and groundwater, the remediation urgency method has its shortcomings (Lijzen et al., 2003). Assessment of TPH contamination tends nowadays to be carried out using the ‘fraction approach’, in which petroleum hydrocarbons are subdivided into equivalent carbon fractions with toxicological similarities. This approach has been applied in human risk assessment (Franken et al., 1999) and proposals were done for new soil quality criteria, the so-called Serious Risk Concentrations (Lijzen et al., 2001). In regard to ecological risk assessment, maximum permissible concentrations and serious risk concentrations were derived for TPH. For each fraction or block separate risk limits are derived. The toxic unit approach must be applied to these blocks to calculate the environmental risk limits for the total (sum) toxicity of a specific oil type (Verbruggen, 2004).

In this section an approach for risk assessment of the migration of TPH based on the above-mentioned fraction approach is discussed.

6.7.2 Approach according to the remediation urgency method

When the TPH concentration in groundwater exceeds the Intervention Value of 600 µg/l and the volume of contaminated groundwater exceeds a volume of 100 m^3, a case of seriously contaminated groundwater exists. According to the remediaiton urgency methode, TPH is considered as a single component with a retardation factor of one. This means that TPH moves with the same velocity as the groundwater. In practice this approach leads rapidly to an urgent case of seriously contaminated groundwater.

6.7.3 The TPH fraction approach

The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) proposed basing the assessment of human risk due to mineral oil on individual TPH-fractions. These fractions are defined on the basis of homogeneous physical-chemical properties. An analytical method for the characterization, and quantification, of petroleum hydrocarbons in line with the proposed TPH fraction method was developed by the TPHCWG (Weisman, 1998). Other methods for the characterization of TPH are currently under development (http://www.oliekarakterisatie.nl/, 1-08-2007; Gemoets et al., 2003).

Table 6.1 shows the defined TPH fractions and the corresponding proposed soil and groundwater quality standards (colomn 2 and 3). The fifth colomn tabulates, for each TPH fraction, the log K_{oc}. Based on this K_{oc} value and assuming an organic matter content of 1 % in the subsoil the retardation (R) is calculated. The volume increase under standard conditions in m^3 per year per 100 m^2 cross-sectional area is given in the seventh colomn.

Table 6.1 Proposed ecotoxicological and human SRC values and characteristics of TPH fractions (Verbruggen, 2004; Lijzen et al., 2001)

TPH	Ecotox. SRC soil (mg/kg)	Ecotox. SRC groundw. (µg/l)	Human SRC soil (mg/kg)	SRCgroundw. (µg/l)	log K_{oc}	R (1%OM)	Volume increase in $m^3 . y^{-1}$ per 100 m^2 cross-sectional area
Reference	Verbruggen, 2004		Lijzen, 2004		Franken, 1999		
Aliphatic							
EC 5-6	16	330	35	613	2.9	18	164
EC >6-8	15	74	109	444	3.6	88	34
EC >8-10	14	9.4	28	15	4.5	689	4
EC >10-12	26	2.4	152	10	5.4	5460	1
EC >12-16	280	- [a)]	55000	- [a)]	6.7	1.09E+05	0
EC >16-21	- [a)]	- [a)]	1280000	- [a)]	8.8	2.18E+07	0
Aromatic							
EC 5-7	39	2300	29	492	3	23	132
EC > 7-8	44	1600	62	850	3.1	28	106
EC > 8-10	49	1000	59	640	3.2	36	85
EC > 10-12	56	600	305	1331	3.4	56	54
EC > 12-16	68	260	1500	1331	3.7	110	27
EC > 16-21	88	71	15800	543	4.2	346	9
EC > 21-35	200	- [a)]	19100	- [a)]	5.1	2740	1

SRC: Serious Risk Concentration for soil and groundwater

R: Retardation factor (-)

K_{oc}: Organic carbon normalized adsorption coefficient

Ecotox SRC: For details and backgrounds see Verbruggen (2004)

[a)] : Due to low solubility no relevant risk based value could be derived

6.7.4 Presence of a case of seriously contaminated groundwater

A case of seriously contaminated groundwater can be determined on the basis of TPH fractions, which corresponds to the proposals for revised quality standards. Measured concentrations should be tested against the Serious Risk Concentrations for groundwater (SRCgw).
Note that the higher TPH fractions have very low Serious Risk Concentrations (SRC). This is not because of human or ecological toxicity but caused by the very low water solubility and the applied method for the derivation of quality criteria (Lijzen et al., 2001). Definite quality criteria for groundwater for TPH fractions are not yet set.

Another aspect of importance is that it is considered that the TPH fractions have the same toxic mode of action (Lijzen et al., 2001). Therefor the toxic unit (TU) approach should be applied to sum the different TPH fractions. A case of serious contamination exists when the ratio of the measured concentrations and the SRCgw of each TPH fraction exceed 1, as shown:

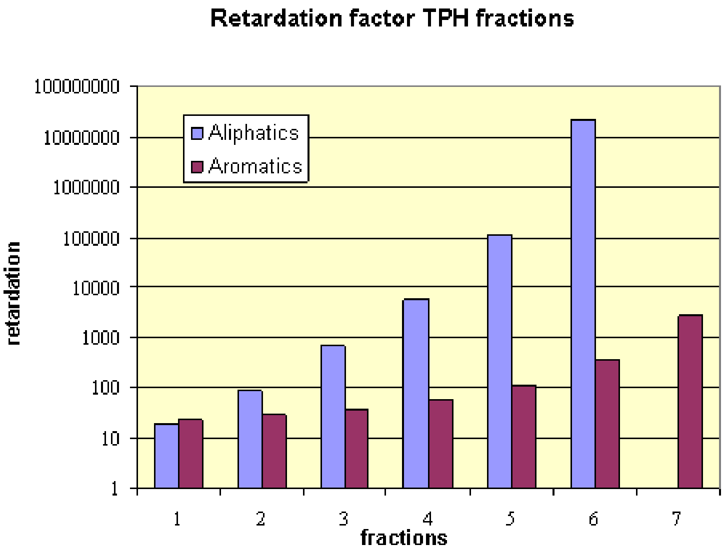
$$\sum_{1-n} \frac{C_{TPH1}}{SRC_{TPH1}} + \frac{C_{TPH2}}{SRC_{TPH2}} + \ldots + \frac{C_{TPHn}}{SRC_{TPHn}} > 1$$

Use of the TPH fraction approach does not mean that the assessor should not test for BTEX, PAHs and other frequently occurring carcinogens in TPH against their SRCs.

In the last column of Table 6.1 an impression of the increase in volume under standard conditions is given. Quality standards are taken from the report by Lijzen et al. (2001) and Verbruggen (2004). Note that the soil quality standards of aromatics EC>10-12, EC>12-16, EC>16-21 and EC>21-35 deviate slightly from the figures in the report of Lijzen et al. (2001), due to a recent correction.

6.7.5 Mobility and retardation

The retardation factor is one of the main factors with respect to mobility. Based on the K_{oc} of the different TPH fractions the retardation factor ranges from 18 for the most mobile fraction to over 100000 for the most immobile contaminants assuming an organic matter content of the subsoil of 1% (Figure 6.2). When the Dutch standard soil is assumed (the organic matter content 10%), the retardation factor becomes 10 times higher.



fraction	Aliphatic	Aromatic
1	EC 5-6	EC 5-7
2	EC >6-8	EC > 7-8
3	EC >8-10	EC > 8-10
4	EC >10-12	EC > 10-12
5	EC >12-16	EC > 12-16
6	EC >16-21	EC > 16-21
7		EC > 21-35

Figure 6.2 Retardation factors of TPH fractions for 1% organic matter content.

6.7.6 Assessment strategy for TPH fractions

Seriousness and extent

As mentioned in section 6.7.3 and 6.7.4., TPH concentrations are tested against the SRC for groundwater in combination with the toxic unit approach. It is questionable whether, regarding the risk of migration, all TPH fractions must be tested against their respective SRCs. Testing aliphatic EC5-6 and EC>6-8 and aromatic EC5-6, EC>6-8, EC>8-10 and EC>10-12 will possibly supply sufficient information to determine the seriousness and volume of with TPH contaminated groundwater.

Table 6.1 shows that the ‘higher’ aliphatic TPH fractions have very low SRCs. Because of the very low water solubility risk based SRC values could not be derived . Low solubility and low vapour pressure values together with high K_{oc} values are typical for a low mobility (see Table 6.2).

Table 6.2 Physico-chemical properties of aliphatic and aromatic TPH fractions.

compound	S (in mg/dm^3	Vp in Pa	K$_{oc}$
Aliphatic			
EC 5-6	2.8E+01	5.1E+04	1.9E+03
EC >6-8	4.2E+00	8.6E+03	9.8E+03
EC >8-10	3.3E-01	8.2E+02	7.8E+04
EC >10-12	2.6E-02	7.9E+01	6.2E+05
EC >12-16	5.9E-04	3.6E+00	1.2E+07
EC >16-21	1.0E-06	1.7E-01	2.5E+09
Aromatic			
EC 5-7	2.2E+02	1.1E+04	2.5E+03
EC > 7-8	1.3E+02	3.2E+03	3.1E+03
EC > 8-10	6.5E+01	8.2E+02	3.9E+03
EC > 10-12	2.5E+01	7.9E+01	6.2E+03
EC > 12-16	5.8E+00	3.6E+00	1.2E+04
EC > 16-21	5.4E-01	1.7E-01	3.9E+04
EC > 21-35	6.6E-03	8.0E-04	3.1E+05

Verbruggen (2004) derived ecotoxicological maximum permissible concentrations (MPC) and serious risk concentrations for TPH. The method is also based on a fraction analysis approach, in which aliphatic and aromatic compounds are regarded separately and are each further divided into different fractions. Separate risk limits are derived for each fraction or block. The toxic unit approach must be applied to these blocks to calculate the environmental risk limits for the total, or sum, toxicity of a specific oil type.

The above-mentioned observations lead us to propose simplifying the testing of TPH fractions against the groundwater standards as follows:

a) The risk assessment should focus on the following fractions
Aliphatic EC5-6 and EC>6-8
Aromatic EC5-7, EC>7-8, EC>8-10 and EC>10-12

b) The annual increase of contaminated groundwater volume above Intervention Value can be assessed for each TPH fraction seperately. The TPH fraction which contribute to the largest increase in contaminated volume is normative for the remediation decision.

Characterization of the case problem

Where there is a case of serious groundwater contamination caused by TPH, often a NAPL is present too. According to the assessment method, the location in such a case is potentially indicated as being an urgent case. However, determination of the contaminated groundwater volume is still recommended to assess the risk of migration. Note that if the increase in contaminated groundwater volume is less than the criterion, removal of the source (i.e. the NAPL) will probably be sufficient.

7. Tier 3: Monitoring and specific modelling

7.1 Introduction

Complex sites, complex groundwater systems and/or complex contaminations require a tier 3 assessment. These extensive risk assessments and additional monitoring are valid when estimated remediation costs and social consequences are high. Processes to take into account are natural attenuation, sorption, vulnerable objects, NAPLs, leaching and the function of groundwater in the area. This chapter does not go into detail on these subjects, as every complex case is different and this is not the place to describe all possible situations. An expert is required to develop a site-specific protocol for tier 3 assessment on location. This chapter does provide a general introduction to groundwater modelling and the monitoring of natural attenuation.

7.2 Role of groundwater models in tier 3

The process of groundwater modelling, in general, involves the following steps:

Step 1: Develop groundwater potential model

Select model boundary (horizontally and in depth) and parameterize the model. Parameterization, i.e. specification of model input values (hydraulic conductivity etc.), should always be done by calibration, using observed groundwater heads.

Step 2: Apply groundwater potential model to simulate groundwater heads

The modelled map of groundwater heads (or groundwater potential), variable in the horizontal plane and with depth, is the basis for the determination of pathlines and travel times. This map is also needed for calibration of the groundwater model.

Step 3: Develop model for simulation of pathlines and travel times

Take the groundwater potential model as a starting point and parameterize parameters additionally required, such as effective porosities. Model calibration is not possible at this stage, on the scale of a polluted site.

Step 4: Apply model to simulate pathlines and travel times

The modelled output – due to advection only – is pathlines, curved in the 3D or quasi 3D flow field, and travel times of water ‘particles’ along these pathlines. Pathlines and travel times give a good first impression of contaminant transport.

Step 5: Develop contaminant transport model

Select model boundary and model processes and parameterize the model. Parameterization, i.e. specification of model input values (sorption, decay and dispersion), can be done either by assuming expert judgment supported by lab experiments, or by calibration using observed concentrations. However, other than for groundwater potential models, calibration of concentrations is cumbersome and is therefore not mandatory here. The spatial dimension of a contaminant transport model can be (a) fully 3D or quasi-3D, (b) 2D in the horizontal plane or 2D in the vertical cross-section or (c) 1D along curved pathlines from a 3D or quasi 3D flow field. We distinguish two approaches for simulating concentrations, namely the ‘complex concentration-based method’ and the ‘simple pathline-based method’.

Step 6: Apply contaminant transport model to simulate contaminant concentration

The modelled output is the variation of contaminant concentration in space and time. Specifically, we want to calculate the increase in time of the volume (m^3 $year^{-1}$) of contaminated water-saturated soil, associated with the Intervention Value concentration.

Tier 3 is characterized by the highest complexity, in terms of the possibility of including the physical, physico-chemical and biochemical processes. Another identifying mark of a tier 3 model is the ability to specify the spatial variability of model input, including model boundary and river topology, and its capability to calculate the development of concentration in time at any location.

In most cases it may be expected that in tier 3 more site-specific data need to be collected. All in all, activities in this tier will involve higher costs compared with the previous two tiers. In return however, and if the modelling is carried out by a qualified hydrologist modeller, it can be expected that the contaminant migration modelled in tier 3 will be a better reproduction of actual future conditions than the assessment achieved under tier 2. Evidently, tier 3 should by definition yield more reliable, or more realistic, results than tier 1. Ultimately, the higher expenditures involved in tier 3 will have to weighed up against the advantage of acquiring more well-founded information regarding contaminant migration.

In our opinion, an integral part of the information available to authorities deciding on risk assessment should also be the reliability, or uncertainty, of the model input parameters and, where possible, the model output.

In summary, tier 3 groundwater modelling will probably most often be carried out at those contaminated sites (a) where monitoring natural attenuation is chosen as the remediation method or (b) when it is clear from the beginning that a site will have to be cleaned up anyway and the modelling is required to design the remediation strategy.

For more information about the groundwater models – specifically about the approaches to simulate concentration of solutes – it is refered to Appendix A3. The appendix also includes a short discussion of model calibration and the reliability of model input.

7.3 Monitored natural attenuation (MNA)[5]

The second tier evaluated the plume development on the basis of field data (section 6.4), but did not go into detail concerning NA processes. This third tier is the place to consider natural attenuation. It consists of the commonly-accepted 3 lines of evidence, leading to documented loss of contaminants, documented NA conditions or documented microbial activity.

All protocols state that to support remediation by MNA, the site owner must convincingly demonstrate that attenuation, or degradation of site contaminants, is occurring at rates sufficient to protect human health and the environment. So not only the sole occurrence of NA should be satisfactory, the rates of attenuation have to be high enough to be protective. The data and type of information that can be used to underpin the demonstration of NA can be classified in three ‘lines of evidence’. The three lines are described in Box 7.1.

The first line of evidence is already used in a simplified form in tier 2. In tier 3, additional modelling is required for this line. Whereas in most protocols and guidelines the first two lines of evidence are indispensable, the third line is usually considered additional. This third line is used as additional evidence, for instance in the case of complex situations and compounds, or to narrow the bandwidth of predictions, or to reduce uncertainty. It may sometimes even provide conclusive evidence for the occurrence of NA (e.g. presence of specific bacterial enzymes for degradation of contaminants).
In Appendix A4, section A4.6 you will find a stepwise protocol for gathering the necessary data and combining data into a structured evaluation of applicability.

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Textbox 7.1 Three lines of evidence for the occurrence of Natural Attenuation:

1. ***First line: documented loss of contaminants or direct proof of decreasing contaminant concentrations***
   Means: historical contaminant data for the plume or single wells, application of screening models.
   Historical groundwater data and/or soil chemistry data which demonstrates a clear and meaningful trend in decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points. In the case of a groundwater plume the decreasing concentrations should not be solely the result of plume migration. In that case, simple transport or screening models can be useful. In the case of inorganic chemicals the primary attenuation mechanism should be identified.
2. ***Second line: documented NA conditions***
   *Means: geochemical indicators (e.g. redox), biochemical indicators (electron balance), presence of metabolites and stable isotope shift***.**
   Geochemical and bio-geochemical data can be used to demonstrate that favourable conditions for NA processes are present. In addition, the presence of metabolites directly proves the degradation of the primary contaminant. This does indicate that natural attenuation processes are active at the site and the rates at which such processes can reduce contaminant concentrations to required levels can be estimated. Stable isotope data is not obligatory, but may be very useful as in certain cases it can prove that the occurrence of metabolites is caused by degradation and not transport from upstream.
3. ***Third line: documented microbial activity***
   Means: additional laboratory or field data such as RNA-DNA analysis, enzyme data, bacterial counts, microcosm studies.
   Data from field or microcosm studies which directly demonstrates the occurrence of particular natural attenuation processes at the site and its ability to degrade the contaminants concerned.

A detailed description is given in Appendix A4 section A.5.7.

8. Conclusions

This report provides a tiered procedure for the assessment of risks due to migration of contaminants in groundwater. The proposed procedure can be used as a practical interpretation of the Circular on soil remediation.
Risk assessors can use this procedure to decide on remedial action, to underpin measures or to pursue further research on the risks.
For each tier of the procedure, the report provides in practical assessment tools. The tools differ in complexity.
The procedure is not meant as a rigid protocol, but serves as a guideline that can be geared to site-specific conditions.

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Appendices

Appendix A1: The DNAPL tiered approach; background information

(By: A. van de Haar, Elementair Utrecht)

An important difference between the assessment of risks related to groundwater migration and risks related to migration of DNAPL (Dense Non-Aqueous Phase Liquid) pools is the applicability of the data that are generally available after the field and laboratory phase of a phase II site assessment ('nader onderzoek'). After such an assessment the dimension of the actual groundwater contamination is normally known, which enables a initial characterization (tier 0) and if necessary a generic assessment (tier 1) for risks related to groundwater contamination with sufficient reliability. However, the results of a phase II site assessment usually do not account for the possible existence of a DNAPL pool contamination with sufficient reliability. This problem will be briefly explained in the following paragraphs.

A1.1. DNAPL pool contamination

A1.1.1 Formation and migration of a DNAPL pool contamination

DNAPLs (dense non-aqueous phase liquids) are liquids with a density higher that water and a limited water solubility. As a result of their high density relative to water they tend to migrate vertically through the saturated zone. Besides, as a result of their low solubility they can remain in the soil as a pure liquid for many years or even centuries.

The most common DNAPL classes, some specific DNAPL substances and some of their properties are listed in Table A1.1 (Environment Agency, 2003). Based on EPA Superfund data, chlorinated solvents are by far the most abundant DNAPL forming substances in the groundwater at Superfund sites (EPA, 1993).

Table A1.1 most common DNAPL classes, DNAPL substances and major properties

Substance	**Density (kg/l)**	**Solubility (mg/l)**	**Viscosity (cP)**	**K_{oc} (l/kg)**
Chlorinated solvents; some examples:				
- TCE ('tri')	1.46	1100	0,57	126
- PCE ('per')	1.62	200	0,9	364
- CT'(tetra')	1.59	790	0,97	439
Creosote (mixture of a.o. carrier fluid (often diesel oil), PAH, phenol, cresols, pentachlorophenol, etc.)	1.01 – 1.13	n.a.	20 – 50	n.a.
Coal tar (coal gasification product; contains a.o. a wide range of light to heavy mineral oil fractions, BTEX and PAH)	1.01 – 1.1	n.a.	20 – 100	n.a.
PCB; some commercial products:				
- aroclor 1221	1.18	200	5	n.a.
- aroclor 1242	1.38	240	24	n.a.

Source: An illustrated handbook of DNAPL transport and fate in the subsurface, Environment Agency, June 2003.

DNAPL pool contaminations are formed if a DNAPL enters the soil in sufficient quantity and if the soil is sufficiently permeable. Under those conditions the DNAPL sinks to the groundwater table, breaks through it and migrates vertically through the saturated zone to greater depths. The migration pattern is controlled by the alternation of layers of higher and lower permeability. More permeable layers are generally penetrated in a vertical direction through narrow channels (a process called fingering), while less permeable layers act as barriers at which DNAPL pools are actually formed. As a pool fills, the thickness of the pool and thus the overpressure at its base increase (due to its density higher than water). If the overpressure is sufficient to penetrate the pores of the barrier layer below, the vertical migration will continue. If the barrier layer is inclined, the DNAPL may actually flow over its surface and thus migrate horizontally. An example of the resulting contamination pattern is given in Figure A1.1.

During the migration process, the amount of DNAPL available for further migration decreases as a result of trapping of DNAPL in the pores of the penetrated soil and as a result of dissolution (and in the unsaturated zone due to vaporization). Finally, the migration process comes to a halt when there is no longer sufficient DNAPL available for the penetration of new barrier layers or for further horizontal spreading over such layers. At that moment a metastable equilibrium is reached and the DNAPL pool is subsequently strengthened as a result of further dissolution. Renewed mobilization may occur as a result of events that will be discussed later in this text.

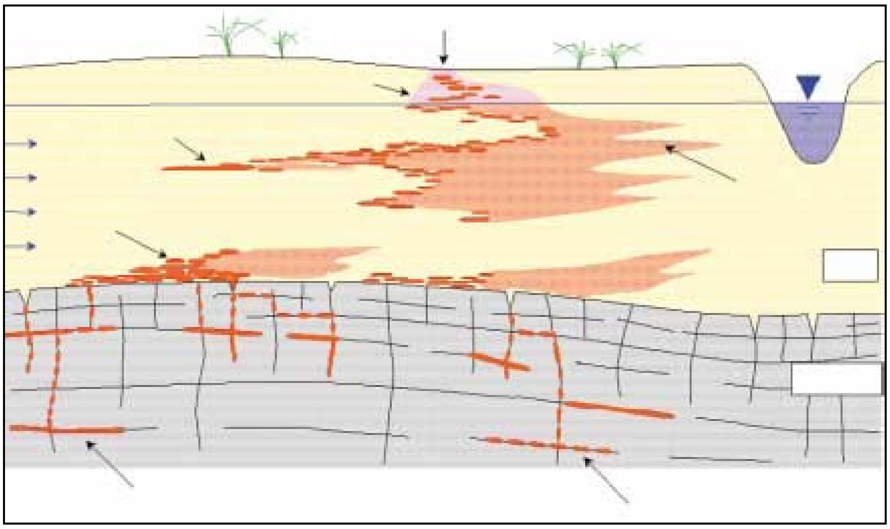

Figure A1.1 Illustration of a DNAPL pool contamination pattern.

Source: An illustrated handbook of DNAPL transport and fate in the subsurface, Environment Agency, June 2003.

The duration of the migration process and the maximum thickness of the resulting pools are dependent on the viscosity and density of the DNAPL and on the soil and aquifer characteristics. In case of chlorinated solvents, which have a very low viscosity and a relatively high density, the formation process may have ceased within 2 or 3 years and may have led to relatively thin DNAPL pools. Creosote on the other hand, which has a relatively high viscosity and low density, may take over 50 years to reach a state of equilibrium, but may form relatively thick DNAPL pools. In Table A1.2, an indication is given of the maximum pool thickness for several soil types and DNAPL classes (Environment Agency, 2003).

Table A1.2 Maximum pool thickness for several soil types and DNAPL classes.

DNAPL class **Soil type**	**Chlorinated solvents**	**Creosote**	**Coal tar**
Silt	0.7 m	5 m	5 m
Fine sand	0.4 m	2.5 m	2.5 m
Medium sand	0.1 m	0.8 m	0.8 m
Coarse sand	0.02 m	0.1 m	0.1 m

Source: An illustrated handbook of DNAPL transport and fate in the subsurface, Environment Agency, June 2003.

A1.1.2 Assessment of a DNAPL pool contamination

The assessment of a DNAPL pool contamination is often difficult as the DNAPL tends to migrate irregularly through the unsaturated and the saturated zone. As a result, depending on the DNAPL class and the permeability of the soil, there may be limited proof of the contamination at shallow depths. In case of chlorinated solvents, due to their generally low viscosity (even lower than water), limited solubility and high volatility, traces of an old contamination in the unsaturated and phreatic zone may even have disappeared completely. As a result, the chances for missing a DNAPL pool contamination in case of a preliminary soil investigation (screening level evaluation; ‘verkennend onderzoek’) which is limited to the saturated and phreatic zone, are substantial.

The importance of proper preliminary soil investigations is highlighted by the results of an EPA study on the likelihood of DNAPL presence (EPA, 1993). The motive for this study was that, despite the widespread use of DNAPL compounds at so called NPL sites (National Priorities List sites) and the common detection of these contaminants dissolved in groundwater, for very few sites direct observations of DNAPLs in the subsurface were reported. An informal poll of the EPA Regions conducted as part of the study revealed that at less than 5% of the total number of investigated sites DNAPLs had been directly observed. Further, most of these encounters were accidental.

The study included a screening level evaluation of 712 NPL sites. At 44 of these 712 sites, DNAPLs were observed directly in the subsurface. The likelihood of DNAPL occurrence at the remainder of these sites was estimated based on more detailed analysis of a subset of 310 sites, including 40 of the sites where DNAPLs were observed directly. Finally, these results were extrapolated to all NPL sites. Detailed information for each site studied was obtained from Remedial Investigation and other site characterization reports, direct discussions with Remedial Project Managers, and regional hydrogeologists. Nearly all major physiographic regions in the US and virtually all categories of site types were covered by the study.

A1.1.3 Example: an assessment based on site history ranking

Based on the results of the described EPA study, using the subset of 310 sites, a ranking method was developed for the assessment of the likelihood of a DNAPL pool contamination at a site, based on site historical information and available site groundwater contamination data. First, the subset of 310 sites is classified based on facility type, usage of hazardous substances and site operations practices. This results in six ranking classes. Second, a ranking is assigned based on DNAPL indicators (facility type, site operations, hazardous substances, aqueous or unknown form, non-aqueous form). Third, a ranking is assigned based on maximum percentage solubilities of DNAPL compounds, resulting in four ‘likelihood classes'. Finally, the two rankings are combined in an overall ranking assignment.

In The Netherlands, a ranking method comparable to the method explained above is normally not used. Conventionally, the final assessment of the presence of a potential DNAPL pool contamination and hence the decision to initiate a phase II investigation ('nader onderzoek') is based on soil and groundwater contamination data only.

The assessment of the presence of a DNAPL pool contamination is often indirect, as direct assessment is both difficult and dangerous. Difficult because the size and horizontal and vertical position of a pool are dependent on subtle variations in soil structure and are therefore highly unpredictable. And dangerous, because the penetration of an underlying barrier layer may lead to further migration of a trapped DNAPL pool. Thus the presence of DNAPL pools is generally assessed based on indirect proof, focused on the following criteria:

- The presence of pure DNAPL in the source zone;
- The presence of a strong vertical variation in dissolved DNAPL concentrations downstream of the source zone; especially if the variation can be related to the presence of barrier layers;
- The presence of dissolved DNAPL at a position which is difficult to explain as a result of migration of dissolved DNAPL from the source zone only (i.e. the occurrence of DNAPL deep below the source zone or in an upstream position);
- The presence of a dissolved DNAPL in high concentrations (typically concentrations greater than 1% - 10% of solubility, not taking into account correction for mixtures of DNAPL substances).

A1.2. Elaboration of the DNAPL stepwised approach

A1.2.1 First outline of the stepwise approach

As explained above, the assessment of risks related to migration of DNAPL pools normally start after the field and laboratory phase of a phase II site assessment. As a consequence of the facts explained in the previous text, and based on general practice in the Netherlands, it is often difficult to assess the presence of a DNAPL pool contamination at that stage. It is even more difficult to assess the risks related to such a contamination from the results of a phase II site assessment.

However, based on the results of a phase II site assessment it is possible to assess the likelihood that a DNAPL pool contamination is *not* present. For such an assessment, the EPA ranking method explained in paragraph A1.1.3 could be used.

Thus: ***Step 0/1: assess the likelihood that a DNAPL pool contamination is*** **not** ***present***

If the presence of a DNAPL pool contamination cannot be excluded from a step 0/1 assessment with sufficient certainty, step 2 should be initiated.

The aim of a step 2 assessment should be to verify the presence of a DNAPL pool contamination, and if present, to determine its dimensions and geohydrological setting. This assessment enables a first assessment of the migration risks related to the DNAPL pool. Thus step 2 has three possible outcomes:

1. no DNAPL pool contamination present;
2. a DNAPL pool contamination is present, but based on its dimensions and/or geohydrological setting, migration risks are probably limited;
3. a DNAPL pool contamination is present, and based on its dimensions and geohydrological setting, migration risks could be unacceptable.

Thus: ***Step 2: verify presence, dimensions and geohydrological setting, and make first assessment of likelihood of migration risks***

The aim of step 3 is simple: to verify whether the migration risks as identified in step 2 are actually unacceptable or not.

Thus: ***Step 3: verify the presence of unacceptable migration risks.***

The outline of the stepwised approach is visualized in the flow chart in Figure A1.2.

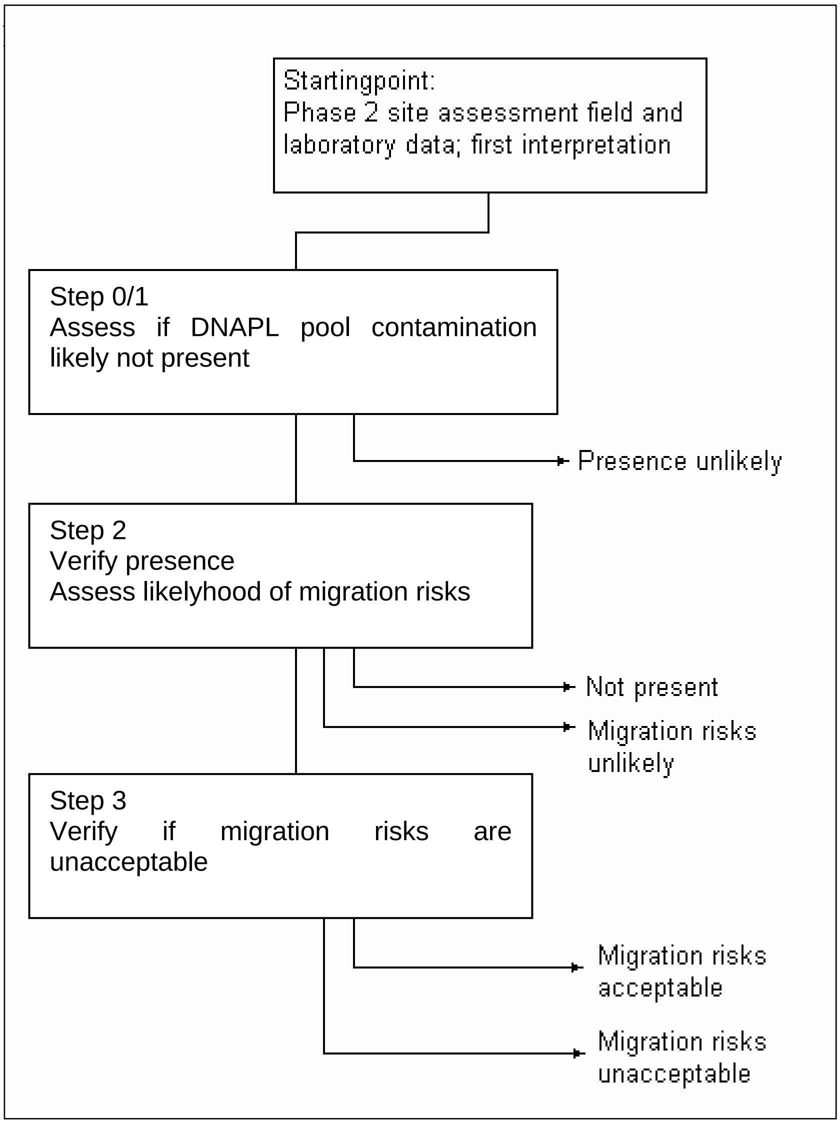

Figure A1.2 flow chart of stepwised approach to assess risks due to migration of DNAPLs.

A1.2.2 The Circular on soil remediation 2006

Recently, the *Circular on soil remediation 2006* took effect. It includes a 3 tier approach for the assessment of risks related to soil contamination. In short these 3 tiers are as follows:

1. If a soil contamination is encountered (normally in a preliminary soil investigation) then assess if it is a ‘case of serious soil contamination’ (‘geval van ernstige bodemverontreiniging’);
2. if it actually is a case of serious soil contamination then execute a generic risk assessment;
3. if the generic risk assessment shows that there probably is an unacceptable risk, then take remedial action or execute a site-specific risk assessment to further assess these risks.

In the tiered approach as defined in the Circular, the aspect of DNAPL pools is included as follows:

- In tier 1, the presence of DNAPL pools does not play a role (in theory this could mean that a DNAPL pool contamination is not regarded as a case of serious soil contamination);
- In tier 2, the presence of a DNAPL pool implies that there is an unacceptable migration risk, unless proven otherwise (i.e. tier 3 has to be executed or remedial action must be taken);
- In tier 3, the presence of a DNAPL pool implies that there is an unacceptable migration risk, unless it can be made plausible that there is not an uncontrollable situation (‘onbeheersbare situatie’ in Dutch).

In tier 3 the following aspects must be taken into account:

- At first, one must define the actual or (in case of an intended change in land-use) future soil and aquifer layer under human influence (‘gebruikszone’). This is the reach below the soil surface that is influenced by human activities, such as construction works, groundwater withdrawal and infiltration.
- Second, one must determine if there are possibly significant DNAPL pools present in the soil and aquifer layer under human influence. If this is the case, an uncontrollable situation is assumed, unless it can be made plausible that the intended human activities will not lead to significant further migration of the DNAPL pools and the contaminants they contain.

The Circular does not explain in detail how the latter assessment must be made. However, it gives some approaches that could be used in the assessment and that generally require additional investigation:

- Make plausible that there are no DNAPL pools present in the usage zone;
- Make plausible that the amount of DNAPL in the usage zone is too small to pose an unacceptable migration risk;
- Make plausible that based on the properties of the DNAPL present in the usage zone (a.o. viscosity), combined with the permeability of the soil, unacceptable migration risk are unlikely;
- Make plausible that unacceptable migration risks are unlikely, based on the application of a multiphase flow model.

A1.2.3 Combination of the stepwised DNAPL approach and the tiered approach for risk assessment related to soil contamination.

In this section the DNAPL stepwised approach is combined with the tiered approach as described in the Circular.

Step 1 – assess the likelihood that a DNAPL pool contamination is present

This element is not included in the tiered approach as defined in the Circular. It can be based on the results of a ‘verkennend bodemonderzoek’. Such an investigation provides both site historical information and soil and groundwater quality data. The assessment could be as follows:

- If based on site historical information a DNAPL pool contamination is unlikely and if no DNAPL substances are encountered in both soil and groundwater in significant concentrations, it is assumed that a DNAPL pool contamination is not present.
- If based on site historical information a DNAPL pool contamination is not unlikely and/or if DNAPL substances are encountered in soil and/or groundwater in significant concentrations, it is assumed that a DNAPL pool contamination may be present.

In the former case, further action is not necessary. In the latter case, tier 2 should be initiated. For the assessment of the site historical information, the approach described in paragraph A1.1.3 could be used.

Step 2 – assess the likelyhood that a DNAPL pool contamination is present in the zone under human influence (‘gebruikszone’)

Following the tiered approach as described in the Circular, this tier focuses on the presence of a DNAPL pool contamination in the zone under human influence. As explained in paragraph A1.1.2 this assessment is normally based on indirect proof. Such proof could include:

- There is no indication of the presence of dissolved DNAPL substances in the zone under human influence in high concentrations (typically concentrations greater than 1% of solubility, not taking into account correction for mixtures of DNAPL substances).
- There is no indication of the presence of a strong vertical variation in dissolved DNAPL concentrations (due to the presence of DNAPL pool layers) in the zone under human influence;
- There is no indication of the presence of dissolved DNAPL substances in a position in the zone under human influence which is difficult to explain as a result of migration of dissolved DNAPL substances from the source zone only (a.o. in an upstream position);

If one or more indications of the presence of a DNAPL pool contamination are found, tier 3 should be initiated. If not, it is assumed that there is no (significant) DNAPL pool contamination present in the zone under human influence. It should be stressed that this assessment is highly dependent on the quality of the assessment of the horizontal and vertical variation in dissolved DNAPL concentrations in the groundwater in the zone under human influence.

Step 3 – assess the likelyhood that a DNAPL pool contamination present in the zone under human influence poses unacceptable migration risks

Following the tiered approach as described in the Circular, this tier focuses on the potential of a DNAPL pool contamination in the zone under human influence to substantially migrate. For the assessment of this potential, the latter three of the four approaches as given in the Circular and described in paragraph A1.2.2 are used.

Make plausible that the amount of DNAPL in the usage zone is too small to pose an unacceptable migration risk

It is probably very difficult to discern between absent or very small DNAPL pools, based on indirect evidence. Thus this method probably is less applicable.

Make plausible that based on the properties (a.o. viscosity) of the DNAPL present in the usage zone, combined with the permeability of the soil, are unlikely

This method could be applied by comparison with standard scenarios with variable migration potential. Some examples of such scenarios are given below:

- A DNAPL pool contamination with viscous DNAPL, e.g. coal tar, creosote or another liquid with a high viscosity (e.g. > 20 Cp). Such liquids are expected to migrate very slowly and thus pose limited migration risks.
- A DNAPL pool contamination which has reached a barrier with a high hydraulic resistance. In such a case, provided that it can be proven that the barrier is continuous, the migration risks are limited.

In case of scenarios with limited migration potential it could be concluded that migration risks are acceptable.

Make plausible that unacceptable migration risk are unlikely, using a multiphase flow model

The application of a multiphase flow model for the assessment of unacceptable migration risks requires a detailed conceptual model of the contaminated profile. This conceptual model requires a highly detailed mapping of the dimensions of the DNAPL pool contamination (i.e. the positions and sizes of DNAPL pools) and insight into the structure of the underlying, unpenetrated soil (alternation of more and less permeable soil layers). If incorrect data are used regarding the positions and thicknesses of the pools and the permeability of the underlying soil barriers, the results could be unreliable. Furthermore, only a few experts are able to fully understand these models. For these reasons, it is unlikely that based on the application of a multiphase flow model only, a reliable assessment of migration risks is possible.

A1.3 Monitoring of a DNAPL pool contamination

As explained in the previous chapters, it is difficult to assess the presence and dimensions of a DNAPL pool contamination, let alone to assess the likelihood of further migration. Thus it is of great importance to be able to monitor DNAPL pool contaminations, especially after it has been decided that migration risks are acceptable and no remedial action has to be taken.

A proper monitoring of DNAPL pool contaminations requires that their dimensions (i.e. the position and size of DNAPL pools) are known to a sufficient degree. Subsequently, the actual monitoring can focus on the detection of DNAPL below and downstream of the known DNAPL contamination, i.e. below previously unpenetrated barrier layers. The disadvantage of this method is that further migration will only be detected some time after it has taken place.

Remark: DNAPL pool contaminations are normally accompanied by significant groundwater contamination. In such a case, the monitoring of the eventual further migration of the DNAPL pool contamination will actually be a part of the monitoring of the development of the groundwater contamination itself.

A1.4 References

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Appendix A2: Table value of groundwater velocity in sandy regions of the Netherlands

A2.1 Introduction

In this appendix we examine the representativeness of the table value 30 m year^{-1} of the groundwater-flow velocity for sandy areas in the Netherlands. In the tiered approach proposed here, the table values are used in the tier 1 for a first-estimate (generic) assessment of the risk.

The velocities are analysed statistically, using the GENSTAT statistical computer package. Since large velocities imply a potentially greater risk of contaminant migration, we have performed an analysis of groundwater transport behaviour in the sandy areas. A specific question is whether the current table value (30 m year^{-1}) for groundwater-flow velocity for sand is compatible with a 'realistic worst case assumption'. As a basic assumption, a 'realistic worst case' has been defined as a groundwater velocity that is exceeded in circa 20% of the cases. In other words, in 80% of the cases the actual groundwater velocity is lower than the 'realistic worst case' groundwater velocity.

The groundwater flow velocity, v [L T^{-1}] can be expressed by:

$$v = q/n \qquad \text{(equation A2.1)}$$

where:

q = specific groundwater discharge (also known as Darcy flux, or seepage flux) [L^3 L^{-2} T^{-1}, i.e. L T^{-1}];

n = effective porosity of water-saturated soil [L^3 L^{-3}, i.e. dimensionless]. For example, the value of n in sandy regions of The Netherlands is around 0.35 (Meinardi, 1994).

The specific groundwater discharge, q, can further be written as

$$q = k_h \times gradH \qquad \text{(equation A2.2)}$$

where:

k_h = hydraulic conductivity of water-saturated soil [L T^{-1}];

$gradH$ = gradient of groundwater potential [L^1 L^{-1}, i.e. dimensionless].

A2.2 Table value for sandy regions (tier 1)

The hydraulic conductivity in sandy regions of the Netherlands –Upper Pleistocene formations– varies between 10 m day^{-1} (coversands, a mixture of eolic sands with local materials) and 60 m day^{-1} (coarse sand), the average value being about 30 m day^{-1} (UN, 1991). The thickness of the 'water saturated' aquifers varies between 200 m and more in the central and southern part of the Netherlands (Veluwe, North Brabant) to a few meters in eastern Netherlands. The gradient of the groundwater potential in the sandy regions of the Netherlands is on average 0.001 (Meinardi, 1994). The gradient is higher:

a) in the vicinity of groundwater abstraction sites;
b) in the vicinity of surface waters (large rivers and canals);
c) along the side (toe) of ice-pushed ridges (hills). If groundwater is deep at a hill, the recharge water cannot be drained off at the hill region itself and flows with continuously increasing velocity speed to the sides of the hill where it is captured (drained) by rivers and ditches. An example of this is the sides of the Veluwe region draining to the Nederrijn and IJssel River.

With the before mentioned average values of the hydraulic conductivity and the gradient of the groundwater potential one can – applying expressions (A2.1) and (A2.2) – conclude that the average value of the groundwater flow velocity is around 30 m year^{-1}. Thirty meters is the distance an ideal tracer would travel in groundwater – as an average in sandy regions – within the period of 1 year.

The reader should note that the table listing groundwater velocities (VROM, 1995) is considered to represent a spatial average within a certain area, e.g. a block of 0.5 by 0.5 km. The situations where the velocity is locally affected, e.g. by groundwater abstractions or presence of surface waters, are not intended to be covered by the table, but rather will be handled in the tier 0 (special and extreme conditions), tier 2 (site-specific evaluation), and in tier 3 (monitoring and specific modelling). This 'spatially-averaged' conception of velocity is consistent with the generic purpose of the table listing groundwater velocities. The table values should be high enough to ensure that – if one decides to apply those table values – in most cases (e.g. 80%) the actual groundwater velocity at a specific location will be smaller than the table value.

As groundwater velocity cannot be observed in the field, one has to calculate the velocity one way or the other. In principle, two approaches could be followed:

a) Interpolation from observed groundwater potentials: calculate the velocity using observed values of the groundwater potential, e.g. the observations from the TNO-NITG OLGA database. Those point values would have to be spatially interpolated into a continuous image of the groundwater-potential gradient, required as input for expression (A2.2).

However, because the number of observation values is limited and because of the purely mathematical nature of the spatial interpolation algorithm (disregarding local conditions of groundwater flow), the resulting map of the gradient would be rather unreliable;

b) Interpolation by a groundwater model: calculate the velocity by using a groundwater flow model. The observed groundwater levels also can be used for the model calibration, thus ensuring that the model adequately simulates the reality. The advantage of the model-calculated velocities is that the local hydrological conditions – such as aquifer heterogeneity, groundwater abstractions and rivers – are intrinsically incorporated. In essence, the model serves as a physically based interpolator.

Figures A2.1 and A2.2 show the horizontal groundwater velocity calculated by the RIVM's LGM model (Kovar et al., 1998).

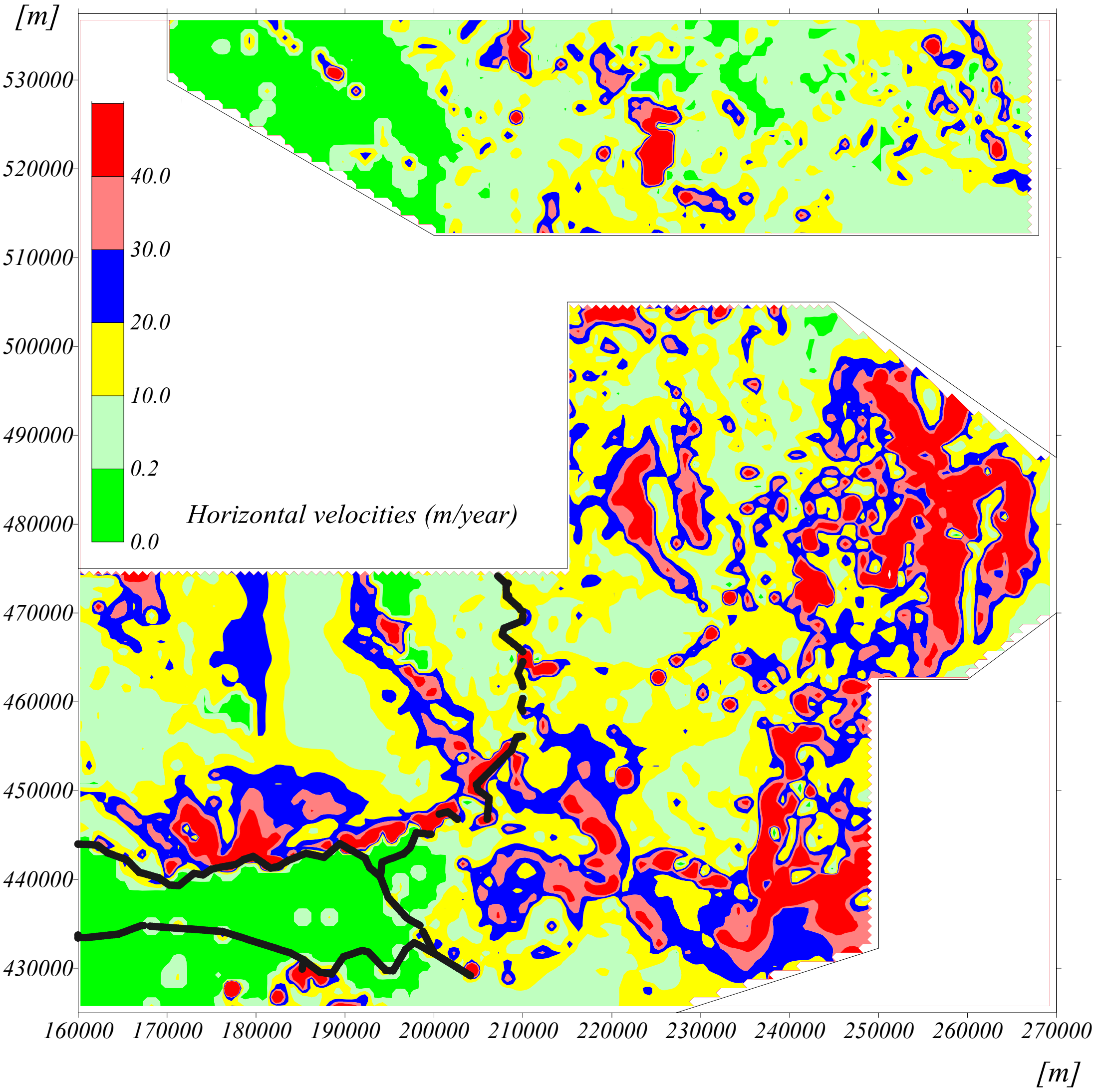

Figure A2.1 Groundwater velocity (Kovar et al., 1998) in the area of Veluwe, Achterhoek, Twente and southern part of Drenthe. Contour lines of horizontal velocity (m year^{-1}) at top of upper aquifer or phreatic water table. Figure prepared by G. Uffink, RIVM.

Though the relevant study regarded all sandy soil areas of the Netherlands, the figures contain only the models Veluwe, Achterhoek, Twente and Hoogeveen (southern part of Drenthe). Most of the area shown consists of sandy soils – where the top aquifer is not covered by peat or clay. The ‘non sandy’ soils are those where in Figure A2.1 the velocity is smaller than 0.2 m year^{-1} (the darkest green colour).

As mentioned before, the high velocity (e.g. >30 m year^{-1}) occurs (a) in the vicinity of abstraction sites (see localized ‘red spots’) and (b) along the outflow side of ice-pushed hills. Since there are no drainage systems on those hills, the water collected on top of the hills flows down to the nearest rivers or polder areas. A typical example for this are the Veluwezoom hills north of the Nederrijn River. Figure A2.1 gives further insight into the behaviour of the geohydrological system. Obviously, the groundwater velocity on top of the recharge areas – hills like Veluwe– is small.

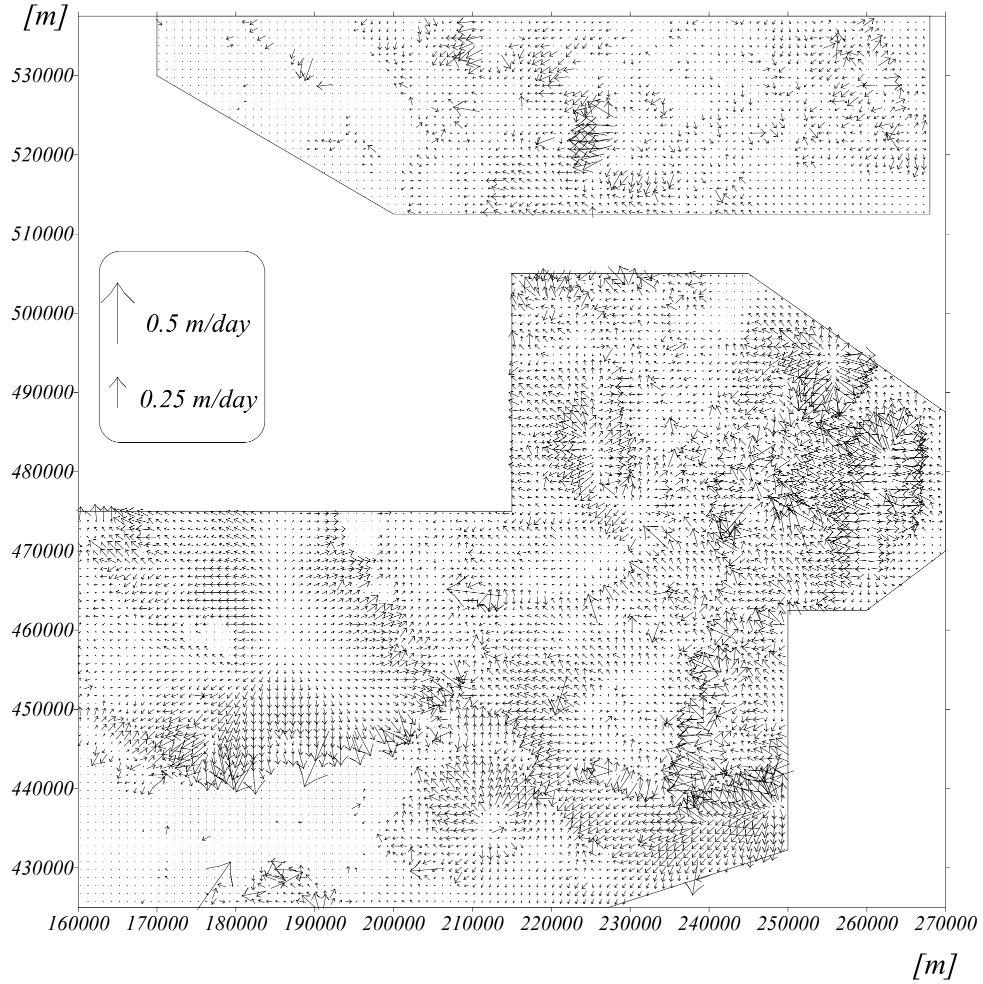

Figure A2.2 Groundwater velocity (Kovar et al., 1998). Vectors of horizontal velocity (m day^{-1}) at top of upper aquifer or phreatic water table. Figure prepared by G. Uffink, RIVM.

When carrying out the statistical analysis, it was assumed that the sandy-soil region velocities shown in Figure A2.1 are – in statistical terms – representative for the entire sandy soil area of the Netherlands. This assumption can be made because other sandy regions (North Brabant, Drenthe) also feature both large non-draining recharge areas and lower-lying draining regions in-between those recharge areas. In terms of morphology, geology and hydrology, all sandy areas in the Netherlands are rather similar.

When discussing the correctness and representativeness of groundwater velocities shown in Figure A2.1, one should bear in mind the following:

- The effective porosity used in LGM was 0.3. According to others (Meinardi, 1994), the effective porosity for Upper-Pleistocene sandy aquifers is about 0.35. As a consequence, the LGM output contains velocities about 17% higher than it would be for the effective porosity of 0.35.
- The modelling (Kovar et al., 1998) was carried out in steady-state mode applying groundwater recharge based on the meteorological data for the year 1988 (precipitation and grass reference evapotranspiration). However, as the year 1988 was relatively wet, it is not representative for the average situation. Locally, the 1988 recharge rate could be up to 20% higher than it would be for an 'average' meteorological year. As a consequence, the LGM output contains groundwater velocities about 20% higher than it would be for an 'average' meteorological situation.

Summarising, as the effect of a too-low value of the LGM-used effective porosity is – to a great extent – compensated by a too-high value of groundwater recharge used in LGM input, it is concluded that the LGM-generated groundwater velocities reasonably well represent the actual time-averaged hydrological conditions. The calculated velocities can be slightly higher than the actual groundwater velocities.

The contour map of velocities in Figure A2.1 was prepared at the midpoint of 1 by 1 km blocks, by interpolation of the LGM-calculated velocities at nodes of the LGM finite-element grid of about 250 by 250 m. In other words, Figure A2.1 does not contain block-averaged values. The darkest green colour in the map depicts regions where ground surface is more or less flat, and clayey and peaty soils occur. After all, as one might expect, because groundwater level more or less mimics the ground level, the groundwater velocity is around zero in those flat regions. Specifically, the velocity was zero in by far most of the dark-green blocks, or between zero and 0.2 m year^{-1} (in 13 dark-green blocks only). After having omitted the zero-velocity values, and six velocities higher than 140 m year^{-1}, 6941 values for velocity remain for the statistical analysis. The percentile values of the groundwater velocity are shown in Table A2.1.

Table A2.1 Percentile values of groundwater velocity from Figure A2.1. Analysis carried out by GENSTAT for 6941 points where velocity >0 and <140 m year^{-1}.

Percentile	Groundwater velocity (m year^{-1})
5%	2.70
10%	4.02
20%	6.39
30%	8.88
40%	11.32
50% median	14.10
60%	17.46
70%	21.62
80%	27.69
90%	39.45
95%	51.13

The estimate of the mean value is 18.81 m year^{-1}, and the standard error of observations (i.e. standard deviation) is 16.7 m year^{-1}, respectively. However, one can clearly see from Figure A2.3 that the velocities are not normally distributed, but rather form a sort of log-normal distribution. The latter was tested – not shown here – by creating a histogram with 10log transforms of the velocities. The resulting '10log histogram' indeed resembled closely a normal (Gaussian) distribution. The estimate of the mean 10log value was 1.11541, which corresponds with a geometrically averaged groundwater velocity of 13.04 m year^{-1}. As the groundwater velocity is a linear function of hydraulic conductivity (see equation A2.2), and as the 10log transform of hydraulic conductivity is also normally distributed, it should indeed hold that also the 10log transform of groundwater velocity is normally distributed, as has been illustrated in our case.

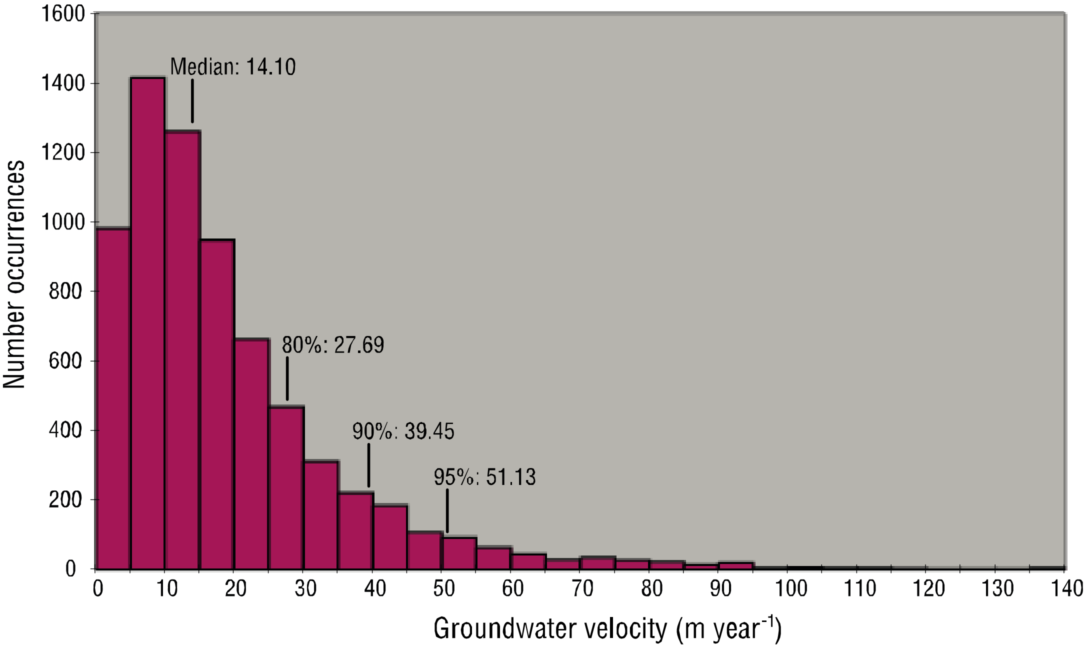

Figure A2.3 Histogram of 6941 groundwater velocity values in sandy areas (>0 and <140 m year^{-1}) from Figure A2.1. Also included are some percentile values.

The conclusion one can draw from the statistical analysis of groundwater velocities in sandy areas – specifically from Table A2.1 – is that the current value 30 m year^{-1} used in the risk evaluation method captures at least 80% of cases of groundwater velocity occurring in these areas. This is because the 80-percentile from Table A2.1, 27.69 m year^{-1}, is smaller than 30 m year^{-1}. One should note that the 6941 values also include about 5% of relatively high groundwater velocities (>51.13 m year^{-1}). These high groundwater flow velocities probably occur in the vicinity of groundwater abstraction sites and along the outflow side of ice-pushed hills. As those high velocities do not fall into the category of 'an average case', it is intended to treat those cases separately in the tiered approach. Once those extreme cases have been handled separately, the 80-percentile will become somewhat smaller than 27.69 m year^{-1} and, consequently the table value 30 m year^{-1} – to be used in tier 1– will even more decrease the probability that a case of migration risk is not detected.

A2.3 References

Kovar, K., Pastoors, M.J.H., Tiktak, A., van Gaalen, F.W. (1998) Application of the Netherlands Groundwater Model, LGM, for calculating concentration of nitrate and pesticides at abstraction wells in sandy soil areas of the Netherlands. RIVM report no. 703717002.

Meinardi, C. R. (1994) Groundwater recharge and travel times in the sandy regions of the Netherlands. RIVM report no. 715501004.

UN (1991) Ground Water in Western and Central Europe. Natural Resources, Water Series No. 27. United Nations, New York, 1991.

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Appendix A3: Assessing contaminant transport in tier 3, by groundwater modelling

A3.1 Outline of groundwater models – contaminant transport models

Groundwater models are used to predict (simulate) behaviour of the subsurface system, in terms of groundwater heads, direction and speed of contaminant migration, and concentration of contaminants. Within the variety of groundwater models, it is the **contaminant transport models** (also named solute transport models) that are used to simulate the changes in the contaminant concentration in space and time. A contaminant transport model jointly deals with (a) transport of one or more (interacting) solutes due to subsurface flow, and (b) the fate these solutes undergo due to chemical and/or biological transformations.

Groundwater models can be used as a tool assisting a risk assessor in his/her determination of the risk of contaminant migration and the forthcoming remediation urgency. Subsequently, the models can also be used for the design of the remediation method, or to simulate natural attenuation processes to facilitate understanding and management of the contaminated site. Another model application, especially related to the monitored natural-attenuation 'remediation' approach, is for the design of the monitoring system, that is, the parameters to be sampled, the location and depth of monitoring wells screens, and the sampling frequency in time.

In the context of this report, a groundwater model is composed of mathematical equations that follow from the physical, physico-chemical and biochemical laws pertaining to flow of groundwater and to a variety of different processes affecting the solute concentration. A model is constructed for a particular part of subsurface (aquifer system) by specifying (a) the boundary of the area to be analyzed, (b) conditions at the periphery of this area, (c) stresses within the area (groundwater pumping, groundwater recharge, etc.), (d) processes to be taken into account, and (e) numerical value of parameters within the modelled domain. Analytical solution methods can be used only in a limited number of cases, for the simplified (often trivial) assumption that all parameters are constant in space. Therefore, to accommodate more realistic (complex) topology in all three dimensions (variability in aquifer thickness, location of rivers and groundwater pumping, etc.) and spatial variability in model parameters (hydraulic conductivity, sorption, etc.), numerical methods have to be used to solve the resulting mathematical equations.

Currently, many computer codes are commercially available to solve these equations for any question at any contaminated site. Usually the discretization method of finite differences (FD) or finite elements is used. The most popular of the FD-based codes is MODFLOW and associated MODPATH, MT3D and MT3DMS, developed by the US Geological Survey. The MODFLOW computer programmes are capable of simulating (a) groundwater heads, with the possibility to use a calibration module, (b) pathlines and travel times, and (c) contaminant concentrations. In the Netherlands, in addition to MODFLOW, one other groundwater modelling package exists with the functionality similar to that of MODFLOW, namely TRIWACO of Royal Haskoning. Though the kernel of TRIWACO is based on the finite element method, the TRIWACO user interface, TriShell, allows the user to use also MODFLOW and MT3D. FEMFLOW is another modelling system available in the Netherlands. It is based on finite elements and has been used successfully for assessing the risk of contaminant migration. However, FEMFLOW does not contain a module to calculate the contaminant concentrations by solving the dispersion-advection equation.

Apart from the finite difference and finite element approach, other numerical techniques are available to simulate the contaminant concentrations, such as the random walk method and the method of characteristics. It is the modeller who decides which method or modelling package will be used. Each modelling package has its own solution method and the sophistication of software implementation, thus offering the modeller different levels of flexibility (options) to handle irregular domain geometry, processes and their interactions, nonlinear behaviour, spatially variable properties, and boundary conditions.

A3.2 Processes in contaminant transport models

The following processes, affecting the contaminant concentration, can be incorporated in a contaminant transport model:

- **Advection.** Movement (spreading) of contaminants due to average flow of groundwater;
- **Dispersion.** Spreading out of contaminant due to the mixing of groundwater in pores and variability of hydraulic conductivity at microscale. Dispersion causes the dilution of the solute: sharp concentration fronts dampen out, the contrasts in concentration becoming smaller;
- **Diffusion.** Unlike dispersion, that is caused by mechanical mixing during fluid advection, the molecular diffusion is due to the thermal-kinetic energy of the solute particles. Diffusion is of importance only at low groundwater velocities and (very) long periods of time. Therefore for the migration-risk assessment considered here, diffusion will hardly ever be a factor of importance;
- **Sorption.** A contaminant may be transported conservatively (due to advection and dispersion), but it may undergo sorption: (a) equilibrium sorption according to linear or

nonlinear (Freundlich or Langmuir) isotherms) or (b) non-equilibrium (kinetic) sorption. To put it simply, sorption delays the arrival time of a concentration front and, if nonlinear or non-equilibrium, similar to dispersion, 'flattens' the concentration in time;
- **Decay.** Decay, also named degradation, regards a vast number of processes that all have in common that a solute decays due to chemical and/or biological transformations, leading to a decrease in its concentration. A special case involves a sequential decay of a solute in two or more other decay products, which can be modelled as a chain of sequential first-order decay processes. Examples of decay mechanisms are aerobic biodegradation and anaerobic (methanogenic) biodegradation.

In addition to the 'regular' contaminant transport models, special models exist for the simulation of the fate and transport of NAPL's in contaminated aquifers. These models can include multiple organic NAPL phases, chemical and microbiological transformations, the mobilization and/or dissolution of NAPL's by nondilute remedial fluids, and changes in fluid properties (density, viscosity) during the remediation. Also can be included nonequilibrium interphase mass transfer and the temperature dependence of chemical and physical properties, in an environment where density, temperature and viscosity are variable (constitutive relationships). These (biodegradation) models have been developed as a tool for the analysis of bioremediation processes for site cleanup, and can also be used when analysing the potential of natural attenuation.

Table A3.1 gives an overview of the processes and constitutive relationships included in tiers 1 through 3. When comparing tier 1 and 2, one can see that in both tiers the processes are the same, namely only advection and linear sorption. However, while in tier 1, the parameter value of groundwater velocity v and retardation factor R are taken from a standard table, the value of v and R in tier 2 are defined by the modeller using local field data and observations for the site. The potential advantages of tier 3, over tiers 1 and 2, is the possibility:
- To include dispersion;
- To include nonlinear and kinetic sorption;
- To include decay.

Especially decay is a factor that can lead to a considerable decrease in solute concentration in time and space.

Table A3.1 Overview of processes and constitutive relationships for tiers 1, 2 and 3.

	Tier 1 (generic assessment)	**Tier 2 (site-specific)**	**Tier 3 (modelling)**
Advection	Yes, groundwater velocity *v* from standard table	Yes, groundwater velocity *v* defined from site-specific data	Yes
Dispersion	No	No	Yes, (a) 3D, quasi-3D and 2D: longitudinal dispersivity and transversal dispersivity, or (b) 1D along pathlines: longitudinal dispersivity only
Sorption	Yes, linear sorption, retardation factor *R* from standard table	Yes, linear sorption, retardation factor *R* defined from site-specific data	Yes, both linear and nonlinear (Freundlich, Langmuir) sorption. Also equilibrium or kinetic
Decay (degradation)	No	No	Yes Multiple interacting solutes possible
Constitutive relationships, e.g. for fluid density and viscosity as function of concentration and temperature	Not taken into account	Not taken into account	Yes, can be taken into account. For example, density effects are important for petroleum hydrocarbons (mineral oil) and DNAPL's (chlorinated solvents: tri- and per-chloroethylene, etc.)

A3.3 Groundwater modelling in tier 3 – Comparison with tiers 1 and 2

As noted before in this report, the kernel of the current risk evaluation procedure is (a) the determination of the increase of the volume of contaminated water-saturated soil, indicated by variable *d* (m^3 $year^{-1}$), and (b) the check whether this increase *d* is larger than a check value, e.g. 100 m^3 $year^{-1}$. Assuming that:

– the one-year ‘long’ pathlines starting from the three-dimensionally curved surface of a

contaminated groundwater body are straight lines,
- all pathlines point in the same direction in x-y-z space (parallel pathlines),
- groundwater velocity at all pathlines is the same,

then the value of d can be calculated with the following simple equation:

$$d = p \times O \qquad \text{(equation A3.1)}$$

where:

d = increase in time of the volume of contaminated water-saturated soil (m^3 $year^{-1}$);

p = advancement (forward movement) of the so-called Intervention Value (IV) concentration within one year (m $year^{-1}$);

O = largest cross-sectional area (m^2) of the currently contaminated groundwater body, delineated by IV-concentration for groundwater.

The principle of this so-called *simple pathline-based method*, applicable in each of the three tiers, is shown in Figure A3.1.

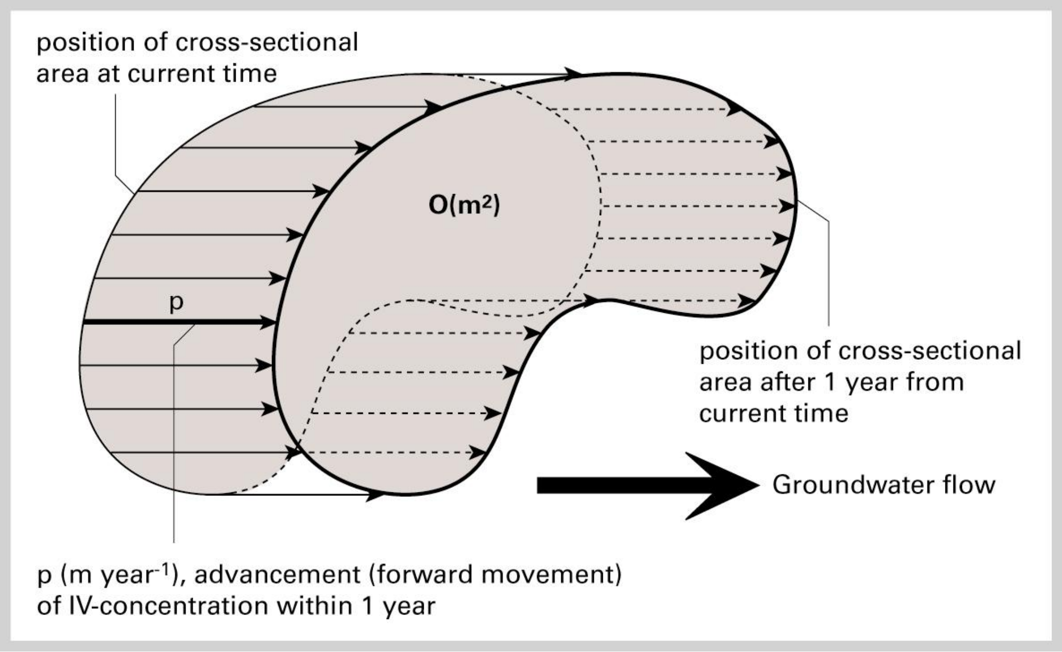

Figure A3.1 Schematic diagramme of volume-increase calculation by simple pathline-based method.

Figure A3.2 further illustrates the approach to calculating the volume increase d. The mean vertical velocity is 1 m per year while the mean horizontal velocity is 30 m per year (see section 5.4). Therefor, the assumptions that (a) all pathlines are parallel (unilateral flow) and (b) the one-year advancement p in space is identical at any point on the IV-concentration contour, are both plausible approximations of reality. However, it is recommended to control this assumption in practice. Equation A3.1 can be used, with area O, not being a vertical but a horizontal cross-section.

In case of negligible vertical movement, as Figure A3.2 shows, the Intervention Value concentration front c_0 moves, while retaining its original shape, to the Intervention Value concentration front c_1 within one year; the distance between c_0 and c_1 being p at any point in space. Therefore, it can also be assumed that the straight-plane area O moves forward, undistorted, by the distance p after one year (see Figure 5.1).

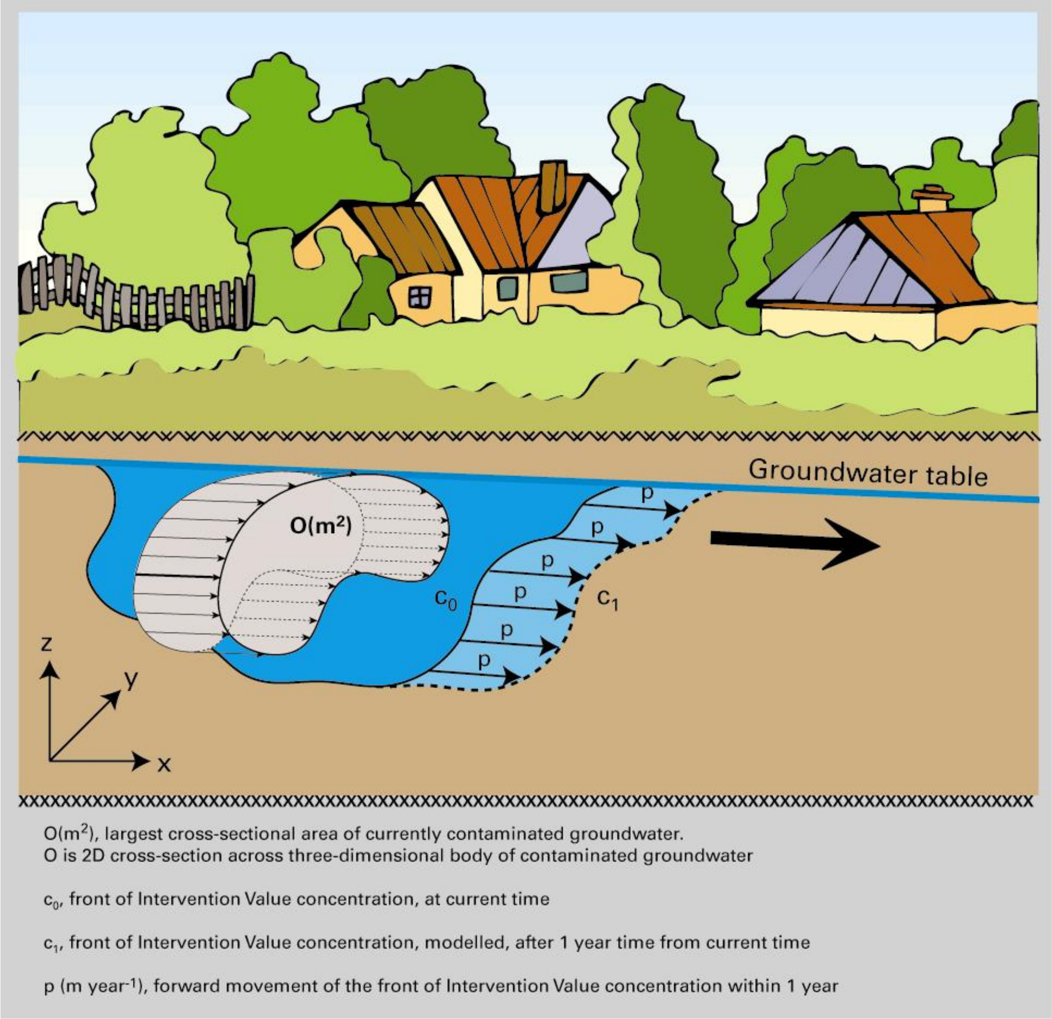

Figure A3.2 Schematic view of concentration front advancement due to unilateral flow.

One should recall that in tiers 1 and 2, the advancement p, as applied in equation A3.1, was calculated by:

$$p = v/R \qquad \text{(equation A3.2)}$$

where:

v = groundwater flow velocity (m year^{-1}), being the quotient of specific groundwater discharge (also known as as Darcy flux or seepage flux) and effective porosity;

R = retardation factor (dimensionless), assuming linear equilibrium sorption.

If no sorption, R takes the value of 1, otherwise R>1.

In tier 1, the values of v and R are taken from a standard table, for example, v = 30 m year^{-1}, for sandy areas. In tier 2, however, the values for the parameters v and R are based on site-specific information, for example using local groundwater head observations to assess v, and lab experiments (organic carbon content) to obtain information about the sorption characteristics, eventually resulting in a value for R.

The *simple pathline-based method* (equation A3.1 and A3.2) in tier 3 for the calculation of d, the increase in time of the volume of contaminated water-saturated soil, is discussed in section A3.4 ‘Calculation of contaminated-volume increase in tier 3 – Complex or simple’. However, anticipating the discussion in aforementioned section, the volume increase d can also be calculated directly, avoiding simplifying assumptions, from the change in the three-dimensional position of the IV-concentration front. We refer to this, formally correct, method as ‘*complex concentration-based method*’, also considered in section A3.4.

Table A3.2 gives an overview of a number of selected features typical for the three tiers. We wish to dispel the misconception that the main distinguishing feature of any groundwater model is the complexity of its input data. In other words, we oppose the false expectation that the model input should vary in space, on the scale of adjacent model cells or, at least, gradually over the model space. It may be fully sound to have a model with only one input value for each parameter. It is not the spatial variability of model input that makes a model in tier 3 different from models in tiers 1 and 2, but rather the possibility to take into account the physical, physico-chemical and biochemical processes affecting the contaminant concentration.

The capability to simulate contaminant concentration is crucial for a model being suitable for tier 3. Obviously, a tier-3 model should, in either case, be capable of simulating groundwater heads, and pathlines and travel times.

One of the special, uncommon, situations where a tier-3 model is also applicable is one where the processes are complex but the input is spatially simple. An example of such situation could be for a relatively small model area of, say, 200-300 by 200-300 m. As one can imagine, on many occasions the model parameters, such as hydraulic conductivity, do not vary that strongly on the scale of a few hundred metres. Therefore, it is often sensible and ‘good enough’ to assume only a single input value of a model input parameter for the entire area of the model. Rephrasing, please note carefully that the fact of little or no variability of model input in space does not exclude that the modelling is done in a spatially complex mode, for example in a 3D or quasi-3D approach.

Table A3.2 Overview of selected features typical for tiers 1, 2 and 3.

	Tier 1 (generic assessment)	**Tier 2 (site-specific)**	**Tier 3 (modelling)**
Spatial dimension for concentration modelling, e.g. concentration front advancement in time	0D, along a hypothetical (generic) pathline. Modelling is not done in actual space	1D along one/more typical straight site-specific pathline(s)	(a) fully 3D or quasi-3D, (b) 2D in horizontal plane or 2D in vertical cross-section, or (c) 1D along curved pathlines from (quasi)3D flow field
Approach to calculate the volume increase *d* (m^3 $year^{-1}$)	Assume 1D straight parallel pathlines and use equation $d=p\times O$ (eq. A3.1)	Assume 1D straight parallel pathlines and use equation $d=p\times O$ (eq. A3.1)	(a) complex: calculate volume increase *d* from simulated concentration front advancement, or (b) simple: assume 1D straight parallel pathlines and use equation $d=p\times O$ (eq. A3.1)
Boundary conditions along model periphery, and surface water levels in horizontal space	Not relevant because not dealing with actual space	Cannot be explicitly specified, are implicitly included via site-specific gradient of groundwater head	Yes, possible to specify groundwater heads and/or fluxes along model boundary, and surface water levels
Stresses (abstractions, groundwater recharge)	Not relevant because not dealing with actual space	Cannot be explicitly specified, are implicitly included via site-specific gradient of groundwater head	Yes, possible to specify groundwater abstractions (any location and depth) and recharge rate. Steady-state or transient mode
Spatial variability of model input	Constant value, groundwater velocity *v* and retardation factor *R* from standard tables	Constant value, one site-specific value for each input parameter involved	(a) constant value for input parameter, or (b) spatially variable input parameter, or (c) any combination of constant and variable parameters
Possibility to simulate stress to receptors (groundwater abstraction, ecologically valuable areas, etc.)	Not possible because in tier 1 not dealing with actual space.	Physically based assessment is not possible because actual location of receptors in space cannot be specified.	Possible, at any desired level of complexity. Evaluation can be done either by analysing: (a) pathlines and travel times, or (b) movement of a concentration front.
Possibility to simulate concentration variation in time	Not possible	Not possible	Possible, at any location. Variability in time is especially required to assess potential of natural attenuation processes to manage contaminated site

In contrast to the modelling approaches used in tiers 1 and 2, the typical features (advantages) of tier-3 modelling are:

- The possibility to include complex processes, other than only advection and linear sorption;
- The possibility to account for spatially variable parameters (model input);
- The possibility to incorporate complex topology (laterally and in depth) of model boundary, surface waters and abstractions; and
- The possibility to calculate the variation of contaminant concentration in time.

A3.4 Calculation of contaminated-volume increase in tier 3 – Complex or simple

Two approaches will be discussed: so-called '*complex concentration-based method*' and so-called '*simple pathline-based method'*.

The '*complex concentration-based method*' is illustrated in Figure A3.3(a). This method is nothing more and nothing less than using straightforward a contaminant transport model – with processes and constitutive relationships as listed in Table A3.1– in two or three spatial dimensions, i.e. without resorting to the simplification to one dimension. The increase of the volume, d (m^3 $year^{-1}$), of contaminated water-saturated soil is calculated is the volumetric difference between the contaminated volume at the current time and that occurring one year later. As is usual, the body of contaminated groundwater is spatially delineated by the so-called Intervention Value (IV) concentration. One should note that the advancement vectors of IV-concentration not only are not parallel but have also different length. This is can be caused by nonlinear sorption and concentration dependant decay. Since the '*complex concentration-based method*' takes into account, without simplifications, all spatial aspects, one may refer to it as a formally correct method. Since the concentration should vary at least in two spatial dimensions, the method has to be applied in fully 3D, quasi-3D, or 2D (horizontal plane or vertical cross-section).

For the very reason that the 'complex concentration-based method' is capable of producing the concentration variation in time at any point within the model (Figure A3.3(b)), it can also be used for the design of the remediation method, including the design of the monitoring system for the monitored natural-attenuation 'remediation' approach.

Examples of the computer codes capable of simulating the concentration changes in space and time are MT3D and MT3DMS.

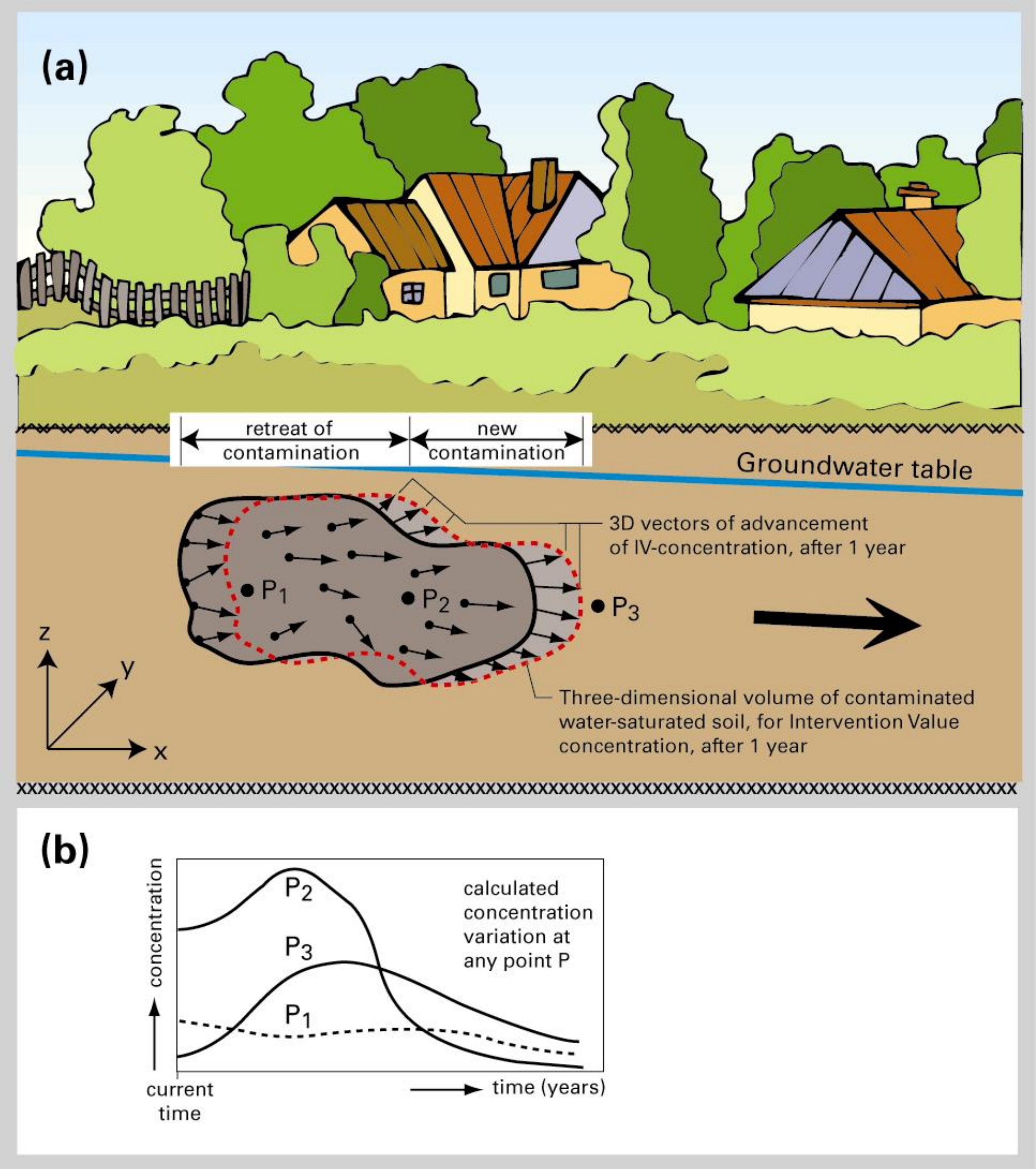

Figure A3.3 (a) Principle of complex concentration-based method to calculate volume increase in tier 3, (b) concentration variation in time simulated at a location within model.

The '*simple pathline-based method'* is an approximation of the '*complex concentration-based method*'. The hydrologist-modeller has, sometimes, to resort to this simplification if the '*complex concentration-based method*' becomes computationally too demanding, involving running a contaminant transport model in 2D or 3D for grids of tens of thousands of cells at small time steps, even in the range of seconds. The kernel of the simplification is that the concentration variation is calculated in one dimension only, namely along a selected pathline. However, and this is important, the same processes as for the 'complex method' are taken into account for the 1D solution along the pathline, namely advection, dispersion, sorption and decay.

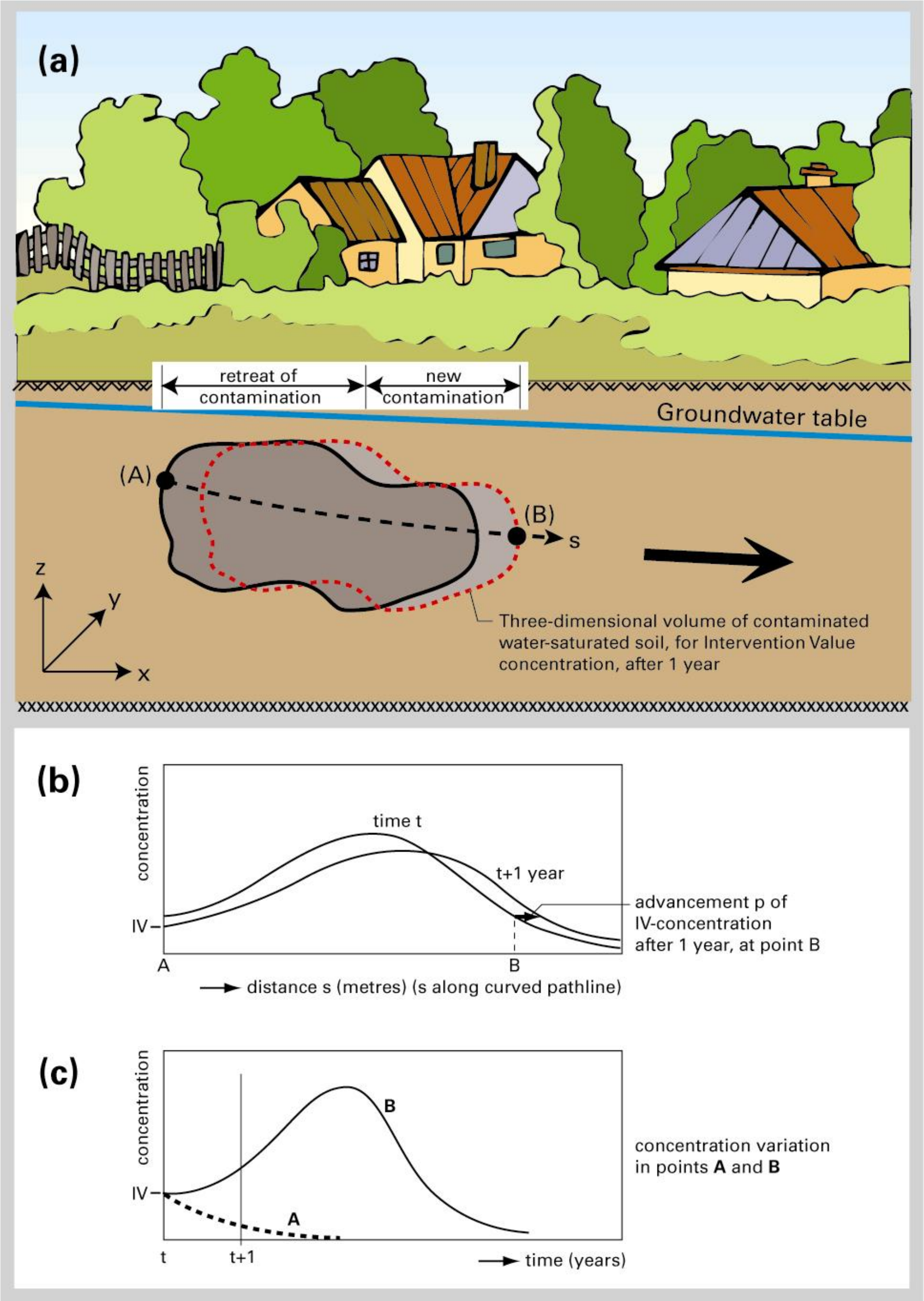

Figure A3.4 (a) Principle of simple pathline-based method to calculate volume increase in tier 3, (b) concentration variation at various times along a pathline, (c) concentration variation in time, at points along pathline.

The '*simple pathline-based method*' is illustrated in Figure A3.4. It consists of the following steps:

- Generate the groundwater-potential field in fully 3D or quasi-3D mode (MODFLOW, TRIWACO-FLAIRS, etc.). This can be done for spatially variable model-input parameters and complex topology of model boundary, surface waters, etc.;

- Generate a series of pathlines through the current three-dimensional contaminated groundwater body (MODPATH, TRIWACO-TRACE, etc.). Note that pathlines are, in principle, curved lines in space (Figure A3.4(a));
- Analyse (visually) the pattern of pathlines;
- Select a number of representative pathlines for further analysis;
- Assume that the current concentration, at time t, along a pathline is known, derived from observations at the contaminated site;
- Use 1D contaminant transport model (advection, dispersion, sorption, decay) to calculate the concentration along the pathline for 1 year after the current situation (Figure A3.4(b)). Obviously, all relevant input parameters for the 1D model should, where required, vary along the pathline. Examples of these parameters are the specific flux, effective porosity, dispersivity, sorption and decay. Examples of computer codes capable of simulating concentration in one dimension – while taking into account all mentioned proceses – are MT3D, Webplume (Grondmechanica Delft) and TRIWACO-SORWACO (Royal Haskoning);
- Calculate the advancement p (m year-1) of the IV-concentration front (p calculated with respect to point B in Figure A3.4(b)) after 1 year;
- Assuming that (a) all pathlines are parallel and (b) the one-year advancement p in space is identical anywhere around the IV-concentration contour carry, calculate the increase of the volume of contaminated water-saturated soil, d (m3 year-1), from d=p×O (equation A3.1).

The volume-increase equation $d=p\times O$ is the same one as it is used in tiers 1 and 2. However, the difference between tiers 1 and 2 on the one hand and tier 3 on the other, is that advancement p in tier 3 is calculated by taking into account three-dimensional flow, spatial variability of model input, complex topology, and, particularly, all processes affecting the contaminant concentration. One should recall that in tiers 1 and 2 only advection and linear sorption are considered.

Like the '*complex concentration-based method*', the 1D modelling approach can also yield the concentration variation in time, namely at any point along the selected pathline (see Figure A3.4(c)). This temporal variation can serve as basis for the design of site cleanup, for example by the monitored natural-attenuation 'remediation' approach.

A3.5 Calibration of groundwater model in tier 3 – Reliability of model input parameters

We argue that for a groundwater model in tier 3 to become a reliable and useful tool for the assessment of contaminant migration, it is required –or, if one prefers that word, desirable– that the model is calibrated using the field-observed behaviour of the reality. Mostly only observed groundwater heads are used, for calibration of the groundwater potential model. In addition to groundwater heads, observed concentrations can also be used to calibrate a contaminant transport model. Doing this, however, is computationally very demanding. Moreover, unlike for groundwater heads where observations are in relative abundance, the number of available concentrations is very limited. Therefore, in practice, the parameters for the processes in a contaminant transport model (sorption, decay, dispersion) will mostly be carried out by assuming expert judgement, supported by lab experiments.

Calibration is mostly done by means of an inverse method approach, by minimizing an objective function that compares observed data with those simulated by the model. The aim is to design such set of model input parameters that –while also taking into account hydrologists' perception about the structure of the geohydrological system– leads to the minimal difference between the observed and modelled values.

Considering the scope of this report, it would go too far to discuss the issue of model calibration in more detail. We merely wish to reiterate the importance of parameterization by means of calibration-optimization techniques, usually referred to as inverse modelling. We advise against the use of the trial-and-error calibration method where one decides about 'the optimum' subjectivelly, based on the visual inspection of the differences between observed and modelled values. Applying calibration-optimization techniques has two clear advantages over the the trial-and-error calibration method:

- The calibration-optimization method is objective because it uses a well-defined mathematical procddure to minimize an objective function. The resulting calibrated parameter values do not depend on the individual decision of the groundwater specialist. In other words, the results are reproducible and unambiguous.
- The calibration-otimization method not only generates the optimized parameter values but also the information about the reliability of calibrated parameters. As one can imagine, the more field observation are used for the calibration, the higher the reliability of the resulting calibrated parameters. In groundwater modelling practice, alongside with the term 'reliability' also the term 'uncertainty' is used, the meaning of both words being identical.

Figure A3.5 illustrates the way of expressing (visualizing) the reliability of a calibrated model input parameter *T*. For this, it is assumed that the parameter probability p(*T*) follows a Gaussian (normal) distribution:

$$p(T) = \frac{1}{\sigma_T \sqrt{2\pi}} \exp\left(-\frac{(T-\mu_T)^2}{2\sigma_T{}^2} \right)$$

where μ_T is the calibrated mean value of parameter *T*, and σ_T is the standard deviation. In practice, one often uses the variance of the calibrated parameter, which is Var(*T*)= $\sigma^2{}_T$. A typical example of a calibrated parameter, for modelling in tier 3, is transmissivity or hydraulic conductivity of an aquifer, or hydraulic resistance of a less permeable layer (e.g. clay). If observed concentrations are available, *T* could also be a sorption or decay parameter that was calibrated for.

Intuitively, one can conceive that a greater uncertainty (low reliability) in model input parameters will result in greater uncertainty in contaminant concentration simulated by the groundwater model and, consequently, greater uncertainty in the simulated increase of the volume of contaminated water-saturated soil, *d* (m^3 $year^{-1}$).

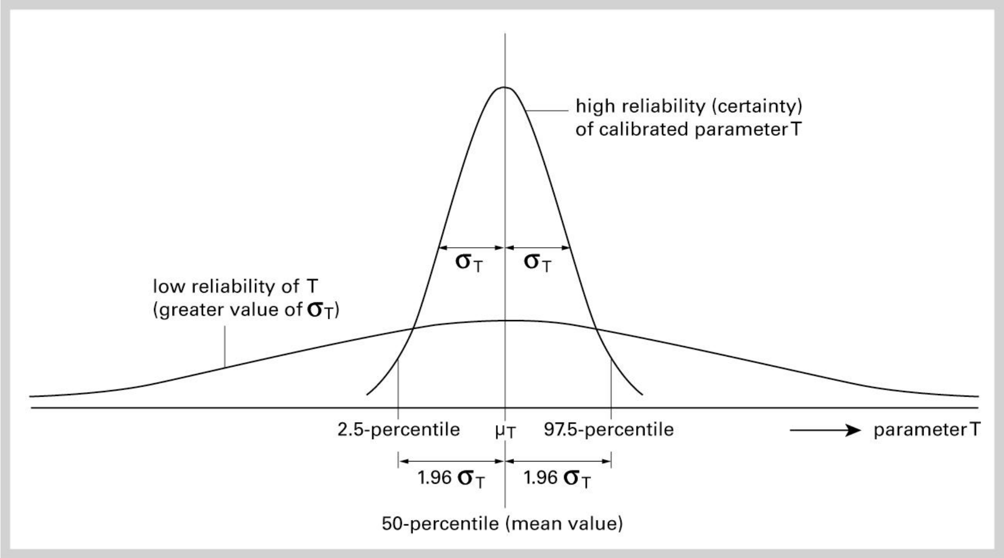

Figure A3.5 Reliability of calibrated model input parameter T, assuming normal probability distribution function.

Appendix A4: Monitoring Natural Attenunation

By Hans Slenders (TNO)

A4.1 Introduction

This appendix on monitoring of natural attenuation (MNA) is written bij Hans Slenders (TNO). It describes the policy aspects of NA, and gives (M)NA assessement tools for the different tiers of the procedure to assess risk due to contaminant migration in groundwater.

A4.2 Policy aspects of the risk assessment

A4.2.1European policies towards NA in groundwater

By now most countries in Europe have formulated a policy or a position on MNA. In order to implement MNA at a site, it has to be approved by the authority as a remedial strategy. Also there have to be clear-cut agreements on the monitoring strategy, the performance criteria, the contingency plan, the remedial objectives and the timeframe of the remediation. But very often there are regional differences in the interpretation of the authorities; it may depend on the country or ‘county’ or ‘provincie’ or ‘region’ or ‘Bundesland’. The major trend however is that MNA is an accepted option for cost-effective management of contaminated groundwater that cannot be ignored. There is awareness that a rapid and complete cleanup of mobile contaminants in groundwater in many cases is not feasible, both technically and financially.

***European Legislation*:**

In the EU Groundwater directive, Annex IV, indent 1.4 (version submitted to the EU parliament) it is stated that:

‘Specific trend assessment shall be carried out for relevant pollutants in bodies of groundwater that are affected by point sources of pollution, including historical point sources, in order to verify that plumes from contaminated sites do not expand over a defined area and deteriorate the chemical status of the groundwater body.’

The application of MNA in Europe can therefore be accepted. Groundwater plumes are even allowed to remain and expand within a defined area, unless the chemical status of the groundwater body is deteriorated according the definitions of the EU directive. The plumes however are not allowed to pose any risk for possible receptors such as surface water or public water supply wells.

A4.2.2 Policy in the countries of the demonstration sites

UK, Belgium and the Netherlands

There are similarities in the regulatory approach to MNA in these countries. MNA may be considered as a risk management option if it is sufficiently protective of human and ecological receptors. The efficacy of NA has to be demonstrated clearly beforehand, with an assessment of the current and future conditions for NA (sustainability). The remedial goals have to be achieved within 30 years, leading to a stationary or receding plume, without a significant increase. If at any time NA does not meet the criteria a fall-back contingency plan has to be activated. Furthermore MNA is considered as one of the remedial options in a decision process, which is obligatory. In this process benefits and burdens can be weighed to demonstrate cost-efficiency (see A4.2.3). The EA for England and Wales have produced detailed guidance on the steps to go through to demonstrate that MNA is a technically robust risk management strategy for a site.

Differences do occur in the fact that in Netherlands and Belgium additional criteria can be put on residual concentrations and that a problem owner is asked to remove as much contaminant load as is cost-effectively feasible. In the Netherlands specific legal possibilities have been created that allow MNA to be used, even with a slightly expanding plume, if it can be ascertained that within a reasonable time frame (30 years), the contaminant concentrations are stabilized to such an extent that no further care or control is needed.

Germany

Currently only a sparse body of legislation exists in the Federal German Republic which takes into account natural attenuation processes in soil conservation administration. A position paper from the Commission on Contaminated Sites (ALA) of the German National/Federal States Committee on Soil Protection (LABO) was published recently, which proposes classifying MNA as self-monitoring measures in terms of Article 15 of the German Federal Soil Protection Act. A possible classification of MNA as remediation measure (decontamination measures and securing containment measures, Article 2 (7)) or protection and restriction measure (Article 2(8)) was refused by the commission.

As a general rule MNA is more and more accepted as a supplement or replacement of remediation measures, but the determining process regarding organic pollutants should be microbial decomposition and must not be dilution. The number of approved projects is still limited, but twenty four sites are currently under investigation within the BMBF-funding priority KORA - Retention and Degradation Processes Reducing Contaminants in Groundwater and Soil.

France and Italy

In France and Italy the acceptability of MNA as such is still in its infancy. In both countries only a few projects focussed on MNA have been proposed and approved. These projects were mainly prepared in compliance with international protocols and guidelines.
However, the French approach for managing contaminated sites leaves open how far natural processes may or must be taken into account when determining rehabilitation values. If natural processes are referred to, enough evidence of their occurrence must be provided.

A4.2.3 Cost-effective remediation of groundwater ROSA

Besides the prerequisite that all risks for receptors have to be dealt with, the current policy in the Netherlands offers the possibility to consider cost-effective solutions. This means that there is more than one alternative for a remedial approach. As in many decision processes, choosing an objective is choosing between alternatives. The final remedial objective is the outcome of a weighing process between the burdens and the benefits of remedial actions. This is a more specific expression of cost-effectiveness. If the costs for a full clean-up are too high in relation to its economical and societal benefits, the balance may switch over in favour of a prolonged MNA process that is often also safer and environmentally friendly. In all cases it should be ascertained that the site-specific remediation is protective of human health and the environment. Recently a Guidance was published in the Netherlands on how to make decisions dealing with mobile contaminants Slenders et al., 2005 (ROSA).

This guidance is a description of the balancing process leading to the choice of a remedial alternative, and contains:

- An inventory of stakes and commitment of all parties concerned in the process;
- A clear and unequivocal definition and mutual choice of relevant benefits and burdens;
- An open balancing of realistic remedial alternatives;
- A stepwise reduction of the number of remedial alternatives, leading to the choice of the preferential alternative.

Table A4.2.1: Decision aspects.

Burdens	Benefits
Cost	Risk reduction
Remediation time and aftercare	Restoration of functional use
Risk of failure	Plume behaviour
Emissions and exhaustion of resources	Amount contaminant removed
Other	Other (e.g. decrease of liability)

A4.3 Proposed tiered risk assessment procedure

The Assessment of NA within the risk of contaminant transport in tier 1-3:

1) No NA, transport and risks are determined on the basis of generic site information about groundwater velocity, sorption and extent. If this preliminary assessment indicates probable risks, the second tier has to be executed.
2) The second tier does not go into the detail of NA processes, but evaluates plume development on the basis of field data. If the plume is not obviously shrinking, than the third tier has to be executed. Also stationary plumes need a rough assessment of the durability of NA.
3) The third tier of the assessment of NA consists of the commonly accepted 3 lines of evidence, leading to documented loss of contaminants, documented NA conditions or documented microbial activity.

In section A4.4 – A4.6 assessment tools are described per tier. A4.7 gives some more background information.

A4.4 First tier assessment tools

No Natural Attenuation

A4.5 Second tier assessment tools

A4.5.1 Decreasing contaminants and plume life cycle as proof for NA

Most protocols that are used to assess the efficacy of NA use the 3 lines of evidence. In this second tier, the first line of evidence is used. It documents the development of concentrations in wells, or the development of the plume. It is a straightforward evaluation, in which the actual NA processes and conditions are not yet taken into account. However it can already prove that NA is sufficiently protective. One can use data from individual wells and evaluate the development of concentration levels (if historical data are available) or, more convincing, demonstrate the historical behaviour and development of the source and plume zone (see section 6.6). Obviously, the impact of the first line of evidence increases significantly when data trends are consistent with time and have been followed for a series of years. A good impression of the overall first order natural attenuation rate constants can be obtained by plots of concentration versus time or by plots of concentration versus distance along the plume axis (Newell et al., 2002). The first can be used as indicative for the remediation timeframe and the latter for plume length. Normally the first line of evidence can be demonstrated at different levels of detail and persuasion. For this second tier assessment one or two time series are considered to be sufficient, and at this stage a computer model of the plume is not yet considered necessary.

The second tier assessment implicates that tier 3 need not to be executed if:

1) There is no thread to receptors, and;
2) concentrations show a decreasing trend, or;
3) The plume is clearly stable or fading.

Considerations 2 and 3 are explained below. If concentrations are increasing or the plume is expanding over a time span longer than 30 years, than NA is not an option. However, if no clear trend can be recognized, or if the plume is expected to expand, but no longer than 30 years, tier 3 needs to be executed.

A4.5.2 Concentrations in individual wells

The concentration data of individual wells can be used to underpin the occurrence of natural attenuation. Without pretending to have characterized the full dimensions of the plume in all directions, this type of evidence gives information on several single locations and/or depths. The crucial factor in this is the positioning of these individual wells with respect to the source zone and the groundwater direction and velocity. A test that can be used to identify concentration trends is the Mann-Kendall statistical test (Gilbert, 1987). In Figure A4.5.1 the decreasing trend in individual wells is demonstrated in an example.

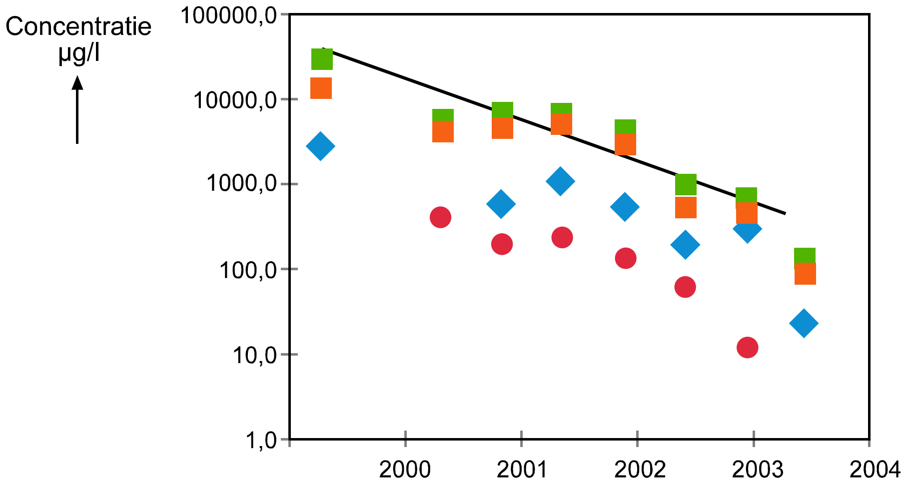

Figure A4.5.1: Concentration trends in individual wells (flow field with high velocity).

Plume behaviour

In a series of well-described and investigated cases, trends can be observed in the development of a plume and plumes can be grouped in different categories (Figure A4.5.2):

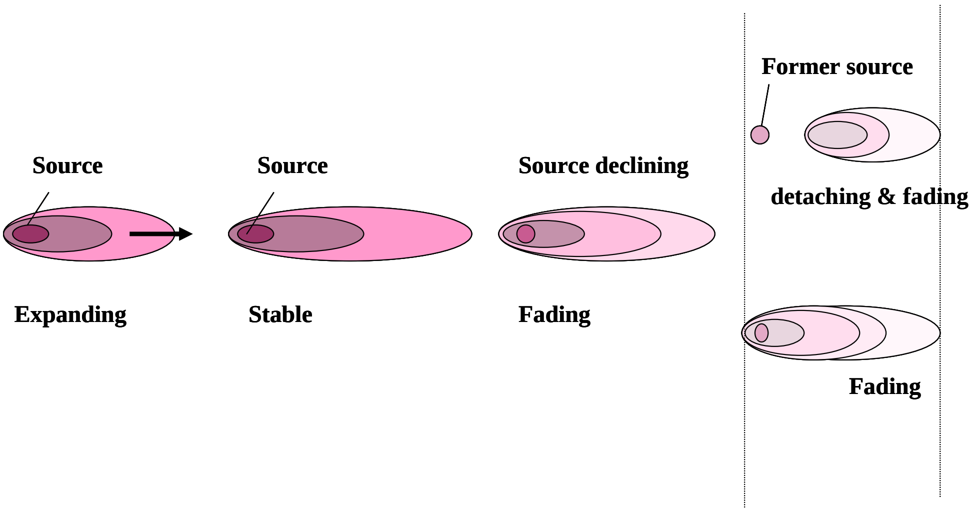

Figure A4.5.2: The life cycle of a contaminant plume that is naturally attenuated with the four succeeding stages of expanding, stable, fading and vanishing.

- Expanding: residual source present. Mass flux of contaminants exceeds the assimilative capacity of the aquifer,
- Stable: insignificant changes in both plume dimensions and mass, the level of attenuation processes equals the amount of leaching,
- Fading: residual source (nearly) exhausted. Significantly reduction in plume mass as inferred from either plume dimensions or concentrations,

- Fading and-or detaching: average plume concentration very low and changing slowly over time. Plume may detach from the original source zone.

A stabilized or receding plume is direct and irrefutable evidence of natural attenuation. Several studies addressed the changes in plume length and concentration for dissolved petroleum hydrocarbon plumes and plumes of chlorinated solvents (Mace et al., 1997, Newell et al.,1990, Rice, et al. 1995). As a general trend it can be seen that Benzene-, Toluene-, Ethylbenzene-, and Xylenesplumes (BTEX plumes) are shorter than plumes of chlorinated ethenes or other chlorinated solvents (Newell and Connor, 1998). Most of the studies on plume behaviour were carried out at sites in the United States (US) where aerobic background conditions prevail. Generally aerobic conditions are favourable for the degradation of petroleum hydrocarbons including BTEX. In the US the majority of the petroleum hydrocarbon plumes appear to be either stable or fading and only as little as 5-10% is still expanding (Newell and Connor. 1998).

Documented data on the historical plume behaviour are rare. A consistent historical picture of the plume behaviour, even with several information gaps, is important evidence. It rarely happens that the plume dimensions have been followed with time for all relevant aspects such as depth distribution, size, volume and mass. Besides, the interpretation of the plume behaviour and the reliability of the often scattered historical data, are not in all cases straightforward as different analytical methods have been used through time and wells have not been positioned optimally. Also at sites with multiple source regions and mixed contaminants, the historical development of the plumes is seldom described with confidence. Collecting conclusive data, preferably at an early stage, is therefore important.

In most cases the immediate risks for receptors are limited, and the collection of time series should be given sufficient possibilities.

A4.6 Third tier assessment

A4.6.1 NA assessment with 3 lines of evidence

All protocols state that to support remediation by MNA, the site owner must convincingly demonstrate that attenuation, or degradation[6] of site contaminants is occurring at rates sufficient to be protective of human health and the environment. So not only the sole occurrence of NA should be satisfactory, the rates of attenuation have to be high enough to be protective. The data and type of information that can be used to underpin the demonstration

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[6] In the Netherlands and Germany degradation must be the key mechanism responsible for NA.

of NA can be classified in three ‘lines of evidence’. The first line of evidence is already used in a simplified form in tier 2. In tier 3 additional modelling is required for this line. Where in most protocols and guidelines the first two lines of evidence are indispensable, the third line is usually considered as additional. This third line is brought up as additional evidence, for instance in case of complex situations and compounds, or to narrow the bandwidth of predictions, or to reduce uncertainty. Sometimes it may even provide conclusive evidence for the occurrence of NA (e.g. presence of specific bacterial enzymes for degradation of contaminants).

The three lines are:

1. ***First line: documented loss of contaminants or direct proof of decreasing contaminant concentrations***
   Means: historical contaminant data for the plume or single wells, application of screening models,
   Historical groundwater data and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points. In case of a groundwater plume the decreasing concentrations should not be solely the result of plume migration. In that case simple transport or screening models can be useful. In case of inorganic chemicals the primary attenuation mechanism should be identified.
2. ***Second line: documented NA conditions***
   *means: geochemical indicators (e.g. redox), biochemical indicators (electron balance) presence of metabolites and stable isotope shift***.**
   (Bio-)geochemical data can be used to demonstrate that favourable conditions for NA processes are present. In addition, the presence of metabolites directly proves the degradation of the primary contaminant. This does indicate that natural attenuation processes are active at the site and the rates at which such processes can reduce contaminant concentrations to required levels can be estimated. Stable isotope data are not obligatory, but can come in very useful, because in certain cases they can prove that the occurrence of metabolites is caused by degradation and not transport from upstream.
3. ***Third line: documented microbial activity***
   means: additional laboratory or field data such as RNA-DNA analysis, enzyme data, bacterial counts, microcosm studies
   Data from field or microcosm studies which directly demonstrate the occurrence of particular natural attenuation processes at the site and its ability to degrade the contaminants of concern.

A detailed description of the content of these lines is given in A.4.7.1. In this chapter you will find a stepwise protocol to gather the necessary data and to combine data into a structured evaluation of the applicability of NA.

A4.6.2 A NA protocol: Is MNA sufficiently protective?

All protocols and guidelines that can be find in literature use stepwise procedures to investigate the possibilities for MNA at a site. The aim is to make as early as possible and with as little expense as necessary, a good estimation on the probability that MNA is an appropriate strategy to achieve site-specific remediation objectives within a reasonable time frame. The number of steps, the amount of detail and the sequence of steps, differ between the different protocols but are essentially comparable. Typically, the first steps are focussed on obtaining information for the first line of evidence while at a later stage the guidelines focus on the screening and modelling required for the second line of evidence. The third line of evidence, referring to experiments under field conditions or in the laboratory to demonstrate biological abilities to degrade the contaminants of concern, is not specifically included in these protocols.

1. The first step is the collection of basic information such as historical, technical and field data. The field data comprise contaminant data, biochemical and geochemical data. The structured evaluation of these data and the graphic representation allows the identification of data gaps.
2. A conceptual model has to be formulated to describe the origin and behaviour of the contaminant in the environment, including a hypothesis on the natural attenuation processes and the source-pathway-receptor approach. A qualitative procedure can be applied to assess the potential for NA. Some of the protocols (Appendix A: Wiedemeier et al., 1998, Sinke et al., 1998) use a type of quick scan giving points for field parameters but these ‘score lists’ only serve as indication for the occurrence of NA and can never be used as such to ‘demonstrate’ the efficacy of NA. In the case of chlorinated solvents the presence of daughter products are a strong indication for the occurrence of degradation processes. Also the redox conditions are included here as, for example, the degradation of petroleum hydrocarbons is favoured under aerobic conditions. Special attention has to be paid to the evaluation of the sustainability of the processes (the continuation of NA processes in the future), which is important for the long-term NA capacity.
3. A third step, that is not included in all protocols, includes different types of experiments under field conditions or in the laboratory measurements to demonstrate biological activity and the abilities of the soil biota to degrade the contaminants of concern.
4. The next step is to simulate NA processes using a transport and fate model to predict the long-term behaviour of the plume. In some cases, simple models can be used such as BIOSCREEN but in other cases a more complex modelling approach using MODFLOW and RT3D is more suitable.

5. The comparison of field data and the model output allows conclusions on the efficacy and the sustainability of NA and enables the risk assessment of current and future plume conditions.
6. Finally, provided that the authorities also approve, MNA can be implemented as remedial strategy. Additional agreements have to be made about a contingency plan and a long term monitoring strategy. The future plume development has to be followed, to validate or refine the modelling results.

Table A4.6.1: Overview of evaluating steps (after Sinke, 2001).

Step	Line of evidence	Activity
1		Collect information on available site data; history and hydrogeology
	1st	concentrations of contaminants
	2nd	redox conditions, macro chemistry, concentrations of metabolites
2	2nd	Formulate conceptual model including hypothesis to explain NA Assess potential for NA Identify additional data requirements and collect data
3*	3rd	Field and laboratory experiments to underpin microbial activity
4	2nd	Use transport & fate model to confirm NA hypothesis and predict future plume behaviour
5	2nd	Test hypothesis and carry out risk evaluation
6		Getting MNA approved, and integration of Natural Attenuation in long-term management strategy & verification of MNA

*not obligatory in all protocols, depending on evidence in 1st and 2nd line and type of contaminant.

Steps 1, through 5 are explained in A4.7.1 en A4.7.2 of this appendix. Step 6: How to get MNA approved and agreed with the authorities was already detailed in A4.2.

At the end of step 6 it is clear whether or not (M)NA is an accepted remedial option. If not, other remedial options should be considered. If yes, MNA can be applied. In many cases however MNA will be combined with other remedial activities in source or plume.

A4.7 Background information on MNA

A4.7.1 Detailing lines of evidence for tiered approach

First line of evidence

The first line of evidence is greatly dealt with in TIER 2. For TIER 3 the first step however is a more extended evaluation of plume behaviour, consisting of a conceptual model and computer modelling.

Site description, conceptual model and risk assessment

From site data to conceptual model

Site investigation data should first be used to develop a site-specific conceptual model with source-pathway-receptor linkages. It should represent the origin of the contaminant, preferably both in time and location, and the hypothesis on how the contaminants behaved after liberation into the environment. Crucial parameters such as type of contaminant (DNAPL, LNAPL), mass, groundwater transport and type of natural attenuation processes have to be included.

There is some confusion to whether MNA is a remedial measure only for plumes or also for source zones. Actually this is very site-specific and depends on the balance between the mass flux out of the source zone, the rate of NA and the location of the plume. If, despite the presence of a source zone, the plume is stable, there is no scientific reasoning against MNA. The NA processes can keep up with the supply of contaminants from the source zone and the plume will remain in position. However, the presence of a source zone may increase the duration of the MNA significantly.

From conceptual model to risk assessment

The conceptual model should identify and describe the behaviour of source and the main processes in the pathway. From that point the conceptual model converts into a risk assessment, when it comes down to the threats to possible receptors. An ISO description of an exposure assessment comprises:

- Source identification and characterization;
- Identification of exposure routes (pathways);
- Identification of relevant receptors;
- Actual exposure assessment (possibly).

If receptors are not, or not directly, exposed to a contaminant, the exposure assessment needs to consider the various ways by which exposure might occur in the future and their significance. This includes: extractions, surface water, evaporation etc. The contaminant might also undergo biological or chemical transformations, affecting its toxicity, availability and mobility. The risk depends on both the concentration of the contaminant and the pathway/exposure route (skin, ingestion etc.).

For the risk assessment in MNA studies the main focus is on pathways and the chance that the contaminant actually reaches a receptor.

Screening and fate & transport models

By the use of solute transport models the groundwater transport and, after correction for retardation, the contaminant transport can be calculated (e.g. Bioscreen, Biochlor, Aziz et al., year). These models are typically used to quantify groundwater flow, sorption, dilution and biodegradation. The comparison of for instance the expected plume length with the actual plume length can be used as evidence that other processes, besides transport and dilution, have influenced the plume behaviour. The model is used to predict the plume behaviour, to identify mass loss of contaminants in relation to groundwater flow, and additional data to be collected at specific locations. The evidence grows stronger if a comparison can be made with a conservative tracer (e.g. chlorine) or with a relatively recalcitrant compound (e.g. Methyl-tert-butylether (MTBE) to total petroleum hydrocarbons).
For more complex situations a full analytical or numerical model can be used such as (combinations of) MODFLOW, RT3D.

Often fate and transport models are used with either analytical or numerical solutions to predict the effectiveness of MNA into the future. Preferably site-specific data and time series are used in the model. The model can be used to identify the key-processes by a sensitivity analysis of input parameters.

Second line of evidence: NA conditions

Understanding plume conditions and processes

The second line of evidence involves the determination of redox- or biochemical and geochemical conditions. This also involves the occurrence of metabolites, supported by modelling and perhaps stable isotope data.
The main questions for this line of evidence are:

1. Are the prevailing redox-conditions optimal for the microbial degradation of the contaminants present?
2. Are the available amounts of electron donor or acceptor sufficient for the complete transformation of the amount of contaminant?
3. Can the presence of metabolites be explained by degradation or transport (from the source zone)?

Redox conditions and availability redox species

The different redox-conditions are often referred to as to which Terminal Electron Acceptor Process is dominant (oxygen, nitrate-reducing, iron-reducing, sulphate-reducing or methanogenic).The change in these conditions can already demonstrate that the observed decrease in concentrations (first line) can be attributed to intrinsic processes such as degradation or chemical destruction.

Necessary redox conditions

Depending on the type of contaminant the type of dominating redox condition is crucial:

- *Chlorinated solvents*
  Dechlorination of the higher chlorinated solvents such as PerChloroEthylene (PCE) and TriChloroEthylene (TCE) can only be achieved under strongly reducing (anaerobic) conditions. In a homogonous situation complete dechlorination will only occur if sulphate is completely reduced. The chlorinated solvents can be used directly as primary substrate (electron acceptor). Prerequisite for this process is the supply and the quality of dissolved organic carbon (electron donor). If there is an imbalance between the amount of chlorinated compounds and the supply of organic carbon, the natural attenuation process may come to an end before all chlorinated solvents have been degraded.
- *(petroleum) Hydrocarbons*
  In general, the microbial degradation of these compounds can take place under oxidative, nitrate reducing, and sometimes iron- or sulphate reducing conditions. The oxidative capacity determines the extent and rate of the degradation of these compounds. The supply of electron acceptors must be sufficient to degrade the entire load of contaminants. In cases where the oxidative capacity is sufficient to balance the amounts of hydrocarbon present, natural attenuation is likely to take place and the plume will be stable or fade. In cases where the oxidative capacity is insufficient and the supply of electron acceptor is limiting, the plume will certainly expand further.

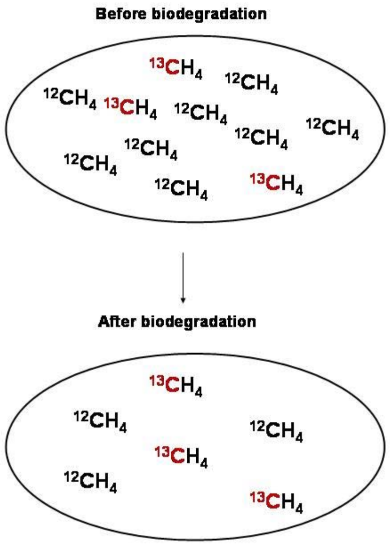
Electron acceptor – electron donor balance

The balance between the amount of electron donors (ED) and the available electron acceptors (EA) determines continuation of the degradation processes. If, for example, the contaminant is PCE (normally an electron acceptor) than the amount of electron donor (hydrogen, organic matter etc.) available or becoming available, must theoretically be sufficient to lead to complete transformation. This calculation can be done in simple tables with total amounts of EA-ED equivalents or with the use of a model. However other species compete in the consumption of electron donors, and the solid state species (e.g. Fe/Mn) are often overlooked. In active bioremediations, often a surplus of 20-times the calculated amount of electron donor or acceptor is needed to accomplish degradation of the contaminant. In A4.7.3 a box model is presented that can be used to calculated steady state plume lengths (Watson et al., 2005).

Metabolites

Depending on the type of contaminant and the situation, the presence of metabolites may be used as indication for the occurrence of NA. For instance chlorinated solvents such as trichloroethene (TCE) can be dechlorinated stepwise under anaerobic conditions and the presence of daughter-products such as cis-1,2-dichloroethene (cis-1,2-DCE), vinyl chloride (VC) and ethene, indicate that NA is occurring. However, cisDCE and VC are even more toxic than PCE or TCE. The final product ethene must be found as indication that NA possibly is sufficiently protective. For BTEX compounds elevated levels of carbon dioxide can be a proof of degradation.

Additional modelling or stable isotope data often are needed to state that the metabolites are a result of degradation in the plume, and not in the source zone. Metabolites formed in the source zone, can be transported to the plume zone, without degradation taking place in the plume.



Stable isotope fractionation

Recent research has shown that compound specific stable isotope analysis can be useful to demonstrate degradation at contaminated sites. Carbon, hydrogen, and chlorine isotope ratios are used to assess degradation. The theory behind this is that organic contaminants have a characteristic isotope ratio (e.g. $^{13}C/^{12}C$-ratio or $\delta^{13}C$) that changes during biodegradation. In microbial degradation processes, light isotopes are preferentially used and the heavier isotopes are enriched in the residual substrate fractionation (Figure A4.7.1). This process is called fractionation.

Figure A4.7.1: Changes in isotope ratio during biodegradation.

Non biological processes like adsorption, dilution and volatilization have no significant influence on the fractionation. However not all compounds show fractionation under different conditions. This means that an absence of fractionation does not mean that there is no degradation. A stable isotope shift however does prove that degradation took place.

The isotope ratio of a compound is given with the δ-value (in ‰). The δ-value is calculated from the isotope ratio from a sample relative to the isotope composition of an internationally recognized standard. A typical δ-value of petroleum related compounds is around -28 ‰.

An increase in isotope ratio along the central flow path of a groundwater plume can be evidence for biological degradation. The interaction of transport differences of different compounds along the flow field and the stable isotope shift however can complex to interpret. In Figure A4.7.2 an example is given of a cisDCE/VC plume. It shows a very significant shift of cisDCE from -21‰ to +3 ‰. VC is first being produced out of cisDCE (so first a decrease from -28‰ to -34‰) and is then being degraded and shows a shift to -20‰. In this case the flow field and transport mechanisms were well known, and the stable isotope numbers could be interpreted.

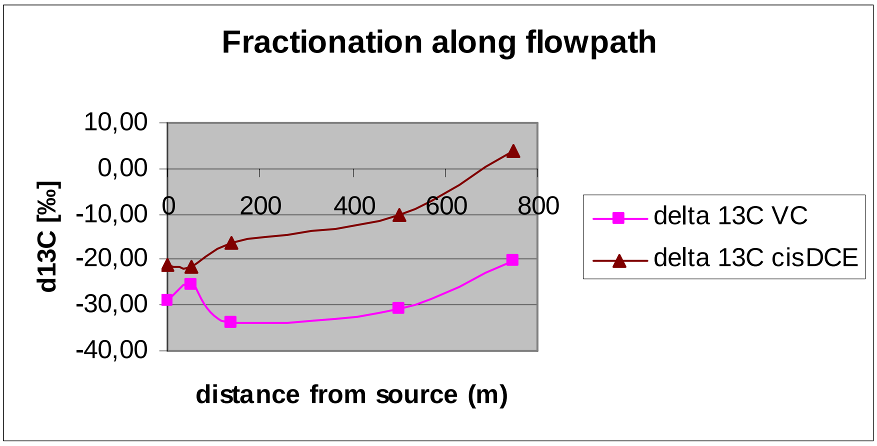


Figure A4.7.2: Fractioning along flow path (source Lerner et al., 2005).

An increase in ratio in time in a specific monitoring well can be used similarly.

For a compound like benzene, the carbon ratio and/or hydrogen ratio can be used (Figure A4.7.3). The carbon fractionation of benzene under anaerobic conditions is known to be maximum 2 ‰, and only significant after more than 60% degradation. The maximum hydrogen fractionation is much higher, and occurs already at less than 30% degradation. The disadvantage of hydrogen isotope analyses is however a higher detection limit.

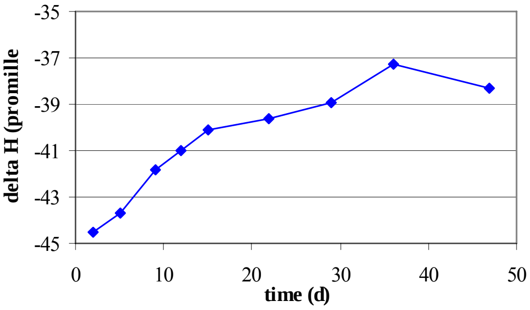


Figure A4.7.3: Fractionation of benzene in a monitoring well in time (source Langenhoff, pers. comm.).

At this moment knowledge and experience is obtained with compound specific stable isotope analyses of mono-aromatic compounds (e.g. Benzene, Toluene, Ethylbenzene and Xylenes (BTEX)), chlorinated ethenes (Perchloroethylene (PCE), Trichloroethylene (TCE), Dichloroethylene (DCE) and Vinyl chloride (VC)) and Methyl-tert-butylether (MtBE).

Third line of evidence

This line includes additional evidence from field, laboratory or mesocosm systems, directly aimed at microbial activity. Usually when the first two lines of evidence are strong enough, the third line is not required. However, additional evidence might help to strengthen the other observations, and to prove that decreasing concentrations are a result of microbial degradation. Several techniques are currently being developed that might be used to demonstrate that degradation occurs or to prove the presence of the ‘right’ bacteria in the aquifer capable of degrading the site contaminants. In general there are two ways to verify biotic degradation: conventional microbial techniques and molecular techniques.

Conventional microbial techniques

These are the commonly used standard techniques such as bacterial plate counts, most probable number counts, batch experiments and column experiments. The advantage is that only the active bacteria are counted, whilst the disadvantage is that only a small fraction of the soil bacteria can be detected. The obtained data give a rough indication for the third line of evidence.

Counts: An indication of the presence of culturable (pollutant-)metabolising micro-organisms can be obtained by plate counts (colony forming units, cfu’s). For these plate counts either selective media can be used on which only specific bacteria can grow with for instance phenols as carbon source, or non-selective media giving a rough indication of total culturable bacteria. Plate counts can be carried out under aerobic or anaerobic conditions.

For most probable number counts (MPN), multiple samples and dilutions in fluid media are used which are after incubation either scored positive or negative for growth. Also this type of measurement can be selective or non-selective and redox specific. A typical example is the MPN counting of sulphate reducing bacteria.

Batch and column experiments: classical laboratory assays showing that micro-organisms in field samples are able to metabolize the contaminants under site conditions (temperature; geochemistry; substrates). Laboratory techniques used are mainly microcosm studies (batches) and soil / groundwater column systems, partly combined with in situ mesocosm systems. Advantages of these classical methods are the clear distinction between biotic / abiotic effects, the analysis of complex ‘ecosystems’ under in situ conditions, and the option of combination with other techniques. Also the possible bottle-neck situations (pH, co-

contaminants) or nutrient limitation (N,P) can be examined. The main disadvantages are the duration of the biodegradation tests, the physiological adaptation of the micro-organisms to laboratory conditions, thus the lack of comparability with field conditions.

Molecular techniques

Recent progress in molecular biology has made it possible to detect microbes by the analysis of their universal intracellular components (e.g. DNA, RNA, proteins, lipids) and provides insight into the regulation and expression of degradative genes via mRNA analysis. The use of these recently developed methods (A4.7.2) poses the possibility of direct analyses of biological processes in field derived samples. Here are some relevant techniques:

- Determination of specific pollutant transforming micro-organisms by epifluorescence microscopy, flow cytometry or fluorescence activated cell sorting.
- Direct extraction of nucleic acid components of the microbes from environmental samples.
- PCR products of rRNA approaches are used to analyse the composition of complex bacterial communities using 16S rDNA fingerprinting techniques (e.g. DGGE, RFLP) or clone libraries for gene sequence analyses. With these tools general changes in the composition of bacterial communities directly or indirectly influenced by biodegradation activities are examined.

For the verification of biodegradation, the detection of specific bacterial species or groups and their spatial dispersion over the plume can be useful (e.g. chlorinated solvents dechlorinating *Dehalococcoides ethenogenes*; naphthalene degrading *Pseudomonas putida* G7; sulphate reducing bacteria; iron-(III)-reducing Geobacteriaceae). Combining the power of PCR with molecular probing and fluorescence analysis in ‘real-time’ enables direct quantification of the pollutant-degrading bacteria.

An even more elegant tool is the organism independent detection of genes responsible for enzymes, specifically necessary for e.g. aromatic ring cleaving Catechol-dioxygenases in BTEX. In Figure A4.7.4 the effects of air-sparging to enhance BTEX-degradation have been monitored by the quantitative detection of genes coding for catechol-2,3-dioxygenase. During the airsparging there is a significant increase in specific genes pointing at growth.

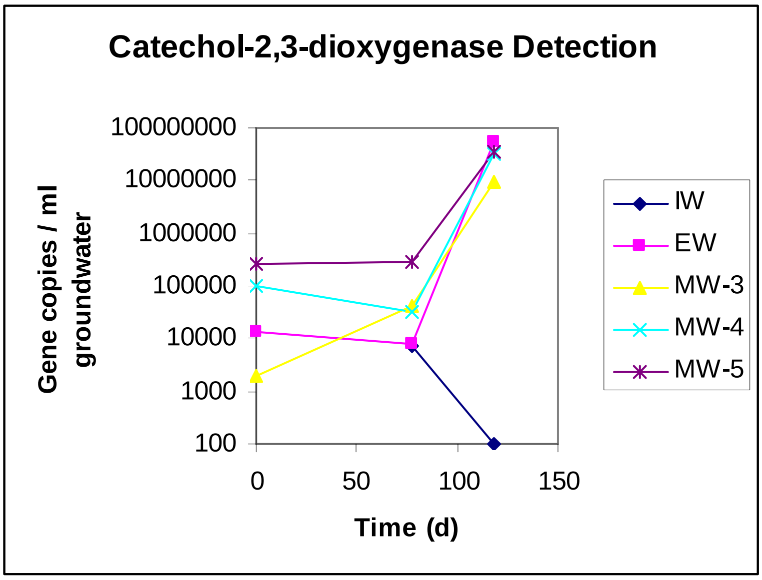


Figure A4.7.4: Increase of gene copies Catechol-2,3-dioxygenase in groundwater samples during air sparging of BTEX-contaminated soil. With IW influent water and EW effluent water.

A4.7.2 Acquisition of field data

The type of data to be collected to characterize a site and to determine the possibilities for NA can be divided into two categories:

- Hydro geological (determines transport of the contaminants),
- Chemical and biological (determines fate of the contaminant).

Hydro geological data

The properties of an aquifer that have the greatest impact on contaminant transport include hydraulic conductivity, hydraulic gradient, and porosity. In Table A4.7.1 the parameters are listed that have to be determined to characterize the hydrogeology of the site and the presence of potential receptors. These data are used as a basis for the site-specific conceptual model.

Table A4.7.1: *Parameters advised to be measured to characterize the hydrogeology and receptors of the site.*

	Chlorinated compounds	Petroleum hydrocarbons
Characterization of aquifer		
Regional hydrogeology	Yes	Yes
Definition of site lithology and stratigraphy	Yes	Yes
Porosity	Yes	Yes
Water level elevations	Yes	Yes
Direction of ground water flow	Yes	Yes
Travel rate of ground water	Yes	Yes
Range of seasonal water level fluctuations	Yes	Yes
Depth of pollution	Yes	Yes
Extent of unsaturated soil impact	Yes	Yes
Potential for vertical migration	Yes	Yes
Push-pull tests or pumping tests	Optional	Optional
Risk assessment and characterization of receptor		
Current use	Yes	Yes
Survey of nearby water supply wells	Yes	Yes
Location of potential receptors	Yes	Yes
Identification of high conductivity pathways	If possible	If possible
Locations of groundwater recharge and discharge areas	Yes	Yes

Chemical and biological parameters

Measurements of the concentration and spatial distribution of the major contaminants and, in case of chlorinated solvents, the daughter-products are important to characterize the extent of the pollution (Table A4.7.2). Also the distribution of contaminant in the aquifer has to be determined, and whether it is present as pure product (LNAPL or DNAPL), or whether it is sorbed or dissolved in the groundwater. Finally, the conditions in the aquifer as indicated by the chemical and biological parameters determine which reactions may proceed: sorption, degradation, or chemical transformation. The amount of organic carbon determines the sorption, and consequently, the retardation of contaminants. A factor that is often overlooked in many protocols is the presence of species that are available in the solid phase. Organic matter, iron- and manganese complexes do play a significant role in redox processes, but can be difficult to interpret.

The redox conditions determine the type of degradation process that might proceed in the aquifer as well as the rate at which degradation takes place. Aerobic conditions favour the degradation of petroleum hydrocarbons and lesser chlorinated solvents such as DCE and VC but inhibit the degradation of the higher chlorinated solvents such as PCE and TCE. For the aerobic degradation of petroleum hydrocarbons, the balance between the amount of organics (electron donor) present and the flux of oxidizing equivalents (electron acceptor i.e. oxygen, nitrate etc) determines the efficacy of the degradation and thereby the plume behaviour.

Under strongly reducing conditions (e.g., sulphate reducing or methanogenic) the reductive dechlorination of the higher chlorinated solvents (PCE, TCE) is favoured. Under these reduced conditions, organic carbon is used as electron donor for the dechlorination of chlorinated solvents that are thereby used as electron acceptor. The electron donor source, present as dissolved organic carbon, total organic carbon or as co-pollutant (BTEX), relative to the amount of electron acceptor (chlorinated solvent), determines the sustainability of the degradation process. Also the quality of the electron donor is important but can not yet be determined with standardized methods. The amount of volatile fatty acids may give information on the ‘quality’ of the energy source.

Several other parameters can be determined that help to describe the conditions present in the aquifer. Generally these parameters are not measured in all samples or are only measured in a later tier to get additional, more detailed information:

- Levels of phosphate and ammonia give an indication on the nutritional state of the bacteria,
- pH: when the pH is too low (< 5) or too high (> 9) the bacterial activity might be hampered,
- Heavy metals: the presence of large amounts of heavy metals might inhibit the bacterial activity,
- Temperature influences directly the rate of chemical, physical and biological processes,
- Alkalinity: an increased alkalinity compared to background indicates the production of carbon dioxide,
- Conductivity and chloride concentration: an increase in these values compared to background indicates the release chlorine.

Table A4.7.2: Recommended parameters to characterize the dimensions of the contamination and the biological and chemical conditions in an aquifer for chlorinated solvents and petroleum hydrocarbons.

	Chlorinated compounds	Petroleum hydrocarbons
Characterization of contaminant		
PCE	Yes	No*
TCE	Yes	No*
DCE	Yes	No*
VC	Yes	No*
Ethene, ethane	Yes	No*
Chloroethane	Yes	No*
1,1,1, trichloroethene	Yes	No*
1,1 dichloroethene	Yes	No*
Aromatic hydrocarbons (BTEX)	No*	Yes
Trimethylbenzene	No*	No*
Methyltertiairybutylether (MTBE)	No*	Yes
PAH's	No*	No*
Other contaminants (metals, arsenic)	No*	No*
Carbon dioxide	Optional	Optional
Ketones	Optional	Optional
Volatile hydrocarbons	Yes	Yes
Characterization of energy source		
Dissolved organic carbon	Yes	No
Total organic carbon #	Yes#	Yes#
Quality natural organic matter	Optional	No
Volatile fatty acids	Optional	No
Propane/propene	Optional	Optional
Characterization of redox		
Oxygen	Yes	Yes
Nitrate	Yes	Yes
Manganese	Optional	Optional
Iron(II)	Yes	Yes
Sulphate	Yes	Yes
Sulphide	Optional	Optional
Methane	Yes	Yes
Hydrogen	Optional	Optional
Oxidation reduction potential	Optional	Optional
Biologically available iron	Optional	Optional
Characterization of geochemistry		
Iron(III) species	Yes	Yes
Manganese species	Optional	Optional
Organic matter (%)	Yes	Yes

* Contaminants marked with *: only if historic data indicate that these contaminants might have been used

\# is important with respect to calculation of retardation factor for transport

o optional parameters might add to the lines of evidence in some cases

A4.7.3 Monitoring of NA (post NA-decision)

A fate and transport model often forms the basis for the monitoring strategy as it indicates the plume behaviour both in time and space, the expected trends in concentration of parent and

daughter products, and time-scale for remedial targets to be achieved. A model can provide insight in the optimized well position and the sampling frequency.
For the requirements that should be set for the monitoring strategy there can be a difference between: **I.** plume/process monitoring and **II.** early warning monitoring to protect possible receptors. The monitoring program should specify the location, frequency, and type of samples and measurements to evaluate remedy performance as well as the possible threat to receptors.

In addition an adequate monitoring program should:
I. plume oriented:
- Identify any potentially toxic transformation products resulting from biodegradation,
- Determine if a plume is expanding (either down-gradient, laterally or vertically),
- Detect new releases of contaminants to the environment that could have an impact on the effectiveness of the natural attenuation remedy,
- Detect changes in environmental conditions (e.g., hydrogeologic, geochemical, microbiological, or other changes) that may reduce the efficacy of any of the natural attenuation processes.

II. Early warning:
- Ensure adequate warning of potential impact to down-gradient receptors,
- Demonstrate the efficacy of institutional controls that were put in place to protect potential receptors.

For ideal cigar like plumes a monitoring network could look like the one drafted in Figure A4.7.5, where R stands for Reference, S for Source, P for Plume, M for the Early Warning Monitoring and L for lateral wells.

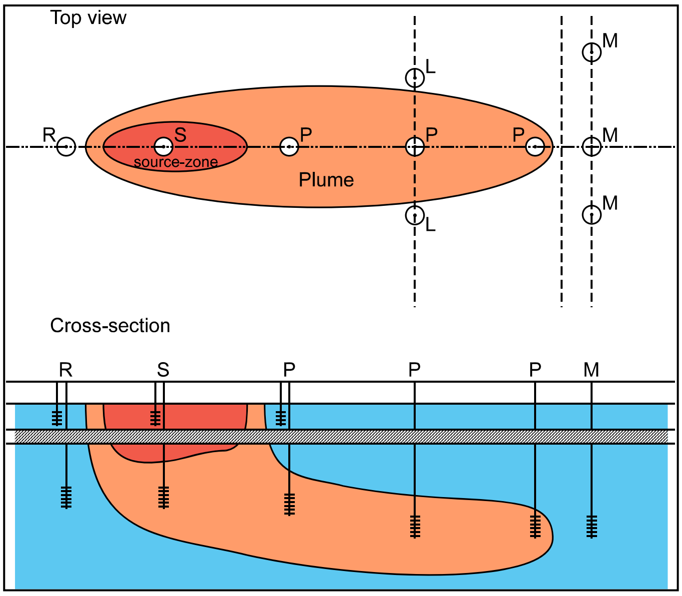


Figure A4.7.5: Monitoring network for ideal cigar shape plume

Performance criteria and contingency plan

Performance criteria

The evaluation on the efficacy of the MNA remedial action should be based on pre-defined performance criteria. These criteria should be realistic and process based. There is a noticeable growing trend towards a dual objective containing the following two performance indices:

1. A strict criterion that checks the actual plume development versus the agreed development. For example, if a plume keeps on expanding, this can be a direct reason to activate the contingency plan;
2. A target or expected trend or level of residual concentrations. This is not a strict criterion, but a switch to adjust the monitoring and aftercare programme or to check the plume prediction/modelling.

This split in performance criteria makes it possible to set clear fall-back criteria, but at the same time avoid the dependency on variations in concentration levels. Often these levels are put as an aim, not a realistic target. Variations in concentration levels can be the result of natural processes such as (temporal) non-equilibrium situations due to for instance groundwater fluctuations, heavy rainfall or temperature shifts, but also changing conditions. Also man-induced variations occur due to sampling procedures or minor analytical variability.

Contingency planning

The implementation documents for MNA should include a contingency plan in case the MNA does not meet the performance criteria or is even failing. Important aspects that should be included in the contingency plan are:

- Clear definition of the activation procedure for the contingency measures. Preferably, the decision criteria should be based on process parameters and not purely on concentration data (see above), but the national legislation must offer this liberty. The contingency plan should be activated for example when several wells or sequential measurements indicate a deviation from the assumed trend. Obviously, concentrations in one well exceeding the expectations cannot be the basis for activation of the contingency plan.
- Type of contingency measures. It should be indicated at least which contingency measures could be used. The contingency measures often refer to ‘conventional’ techniques such as pump and treat or hydrological containment to prevent the plume from migration and/or further expansion. In some cases also an additional active remediation of the source zone could be considered.

- The changed use of the site that might result in an increase of the risk should automatically start a process of re-evaluating the possibilities of MNA. This concerns both the altered use (e.g. housing instead of industry) and changes in hydro geological conditions (e.g. increase or decreased groundwater extraction regime, long lasting changes in groundwater level, changes in groundwater fluctuations).

A4.8 References

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Appendix A5: Webplume

By K. Janssen-Roelofs (GeoDelft)

A5.1 Objective of WebPlume

Webplume (http://www.delftgeosystems.nl/ go to ‘e-consult’) is a simplified version of the modelling tool Plume developed by GeoDelft. The model concerns an analytical model and intends to support the assessment of the risks of contaminant migration. Therefore, it is one of the options to use in tier 2 of the tiered approach described in this report. WebPlume also might be of use for educational purposes. It uses powerful analytical algorithms, thereby requiring no difficult boundary conditions to be entered. Plume is based on the program AT123D. WebPlume calculates contaminant transport using fixed parameters: a deterministic calculation.

A5.2 Range of application

Webplume is valid for a homogeneous and uniform aquifer in terms of soil properties, fate of the contaminant and site-specific hydraulic characteristics like the hydraulic conductivity and specific velocity of the groundwater. The model does not account for stratified aquifers, e.g. the presence of clay lenses in a sandy aquifer. Besides, WebPlume takes into account a regular groundwater migration pattern and, hence, does not include the presence of surface waters, polders or groundwater extraction points. If the actual situation does not meet this presumptions than a more complex modelling approach could be used.

A5.3 Risk-based assessment with WebPlume

The risk-based Assessment in WebPlume is along a tiered approach. This means that for relative simple situations a simple assessment is carried out. For the more complex problems, more site-specific inputs need to be taken into account. Therefore, the tiered approach supports the assessment for simple situations as well as the structure of more complicated problems.

A5.3.1 Tier 1

The first level (tier 1) focuses on the source of contamination and its direct surroundings. The question that needs to be addressed is whether or not an ‘urgent’ situation is present based upon the migration of specific contaminants in an aquifer. The answer is given from a generic perspective. This means that tabulated generic data is used as much as possible. The user gives information (inputs) about:

- Soil type (sand clay or peat);
- Contaminant;

- Source area;
- Source concentration.

In Webplume tabulated information is incorporated about:

- The Dutch Intervention Values;
- Relation between soil type and specific discharge of the groundwater;
- Relation between soil type and bulk density of the soil;
- Distribution coefficients of contaminants in terms of kd or koc values;
- Solubility of contaminants;
- Density of pure product of organic species;
- Viscosity of pure product of organic species.

A5.3.2 Tier 2

In tier 2, additional site-specific data must be included, in order to determine the risk for migration in more detail. With the site-specific information the mathematical formulas given for tier 1 are recalculated. The result will be a more accurate assessment of the risk due to contaminant migration and, hence, the urgency of remediation at the site. Parameters that can be taken into account are:

- Fraction of organic matter or organic carbon (-);
- Measured value for the distribution coefficient kd (l/kg);
- Specific data of the bulk density of the soil (kg/m^3);
- Specific value of the specific discharge (m^3/day/m^2);
- Specific value for the porosity or water content of the saturated zone (m3/m3);
- Information about vulnerable objects present downstream of the contaminated area.

A5.3.3 Tier 3

Thus far, in tier 1 and tier 2, only advection and adsorption (retardation) are taken into account to determine the risk for migration and the urgency for remediation. Additionally biodegradation of organic species and dispersion in the aquifer are taken into account, in tier 3. To show the effect of these processes, a simplified version of an analytical fate and transport model (DG>Plume) is used interactively in a user friendly manner.
Additional parameters that could be included by the user are:

- Specific discharge (or hydraulic conductivity or the fall in groundwater head);
- Porosity or water content in the saturated zone;
- Dispersivity or dispersion length: (Longitudinal, Transversal horizontal and Transversal vertical)
- Retardation coefficient, or bulk density and distribution coefficient;
- Half life for biological decay.

As a result WebPlume gives the following output:

- The concentration as function of distance along the flow direction, at several time steps;
- The concentration as function of time at several distances from the source.
- Calculated time at which stability occurs: stable (or stationary) plume of contaminated groundwater
- Calculated length of the stable plume
- Whether the stable plume reaches a vulnerable object downstream.

A5.4 Uncertainties

The risks mentioned are given by a 'risk bar'.

The 'risk bar' indicates the uncertainty of the results. If for example the time reaching a stable plume is less than three-quarter (0.75) of the time that is required by law, 30 years, it can be concluded that it is likely for the plume to reach a stable situation within the mentioned timeframe. This is indicated with a green colour. However, if the time necessary for reaching stability of the plume exceeds the required time of 30 years by a factor of 1.25, it is most likely that the plume will not reach stability within the mentioned time. This is indicated with a red colour. In the time frame in-between these two margins, it is uncertain what will happen in practice. Further research may lead to results that are more reliable.

A5.5 Connection WebPlume and Sanscrit: additional demands

Reaching a stable situation is not important for Sanscrit for this moment. Sanscrit focuses on the (increase in) volume of the plume. Webplume does not present this result at this moment, although it is actually used in the calculation. The increase in volume for a given concentration level (not necessarily the Intervention Value), can be presented. It is also possible to calculate the volume of the stationary plume. It can be an option to present this volume within a range of uncertainties. The increase in volume will also be given.