NOBIS 95-2-11 RESTRISK; ASSESSMENT OF EFFECTIVENESS OF IN SITU REMEDIATION

Phase 2: Predicting fate & transport and future risks of organic contaminants

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Samenvatting

Het RestRisk stappenplan voorziet in een duidelijke, eenvoudige en betrouwbare aanpak voor het bepalen van risico's van restverontreinigingen op een willekeurig moment van een in situ sanering. Deze informatie is noodzakelijk als men wil beslissen over het stopzetten, extensiveren of voortzetten van een sanering. Het stappenplan is toegepast op pump & treat saneringen, persluchtinjectie en natuurlijke afbraak.

De bandbreedte van de voorspelde restrisico's bleek acceptabel en kan nog verder worden teruggebracht door concentratiemetingen te gebruiken voor modelkalibratie. Daarnaast is een alternatief concept ontwikkeld voor extensieve pump & treat als keuze naast stopzetten of doorgaan met de lopende sanering: het onttrekken van kleine volumes grondwater (1 - 10 m³/d) bleek voldoende te zijn om langzame desorptie en diffusie van verontreinigingen uit de bodem bij te houden. De saneringsduur kan niet worden versneld door grote volumes grondwater te onttrekken. Dit betekent, dat veel kleinere en daarmee goedkopere zuiveringsinstallaties kunnen worden ingezet, waarmee zowel grondwater als geld wordt bespaard.

Nazorgkosten kunnen ook drastisch worden teruggebracht door toepassing van het RestRisk stappenplan: toepassing hiervan voorziet in informatie die nodig is om een meetstrategie te ontwerpen, omdat de verspreiding van verontreinigingen in tijd en ruimte inzichtelijk wordt gemaakt.

Trefwoorden Gecontroleerde termen:

Vrije trefwoorden:

biosparging, decision support, natural attenuation

pump & treat, risks, spreading

Titel project

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Abstract

RestRisk is a guideline that aims at a straightforward, non-elaborate and reliable assessment of the risks of contamination still left in soil and groundwater at an arbitrary point during an in situ remediation - so-called restrisks. Assessment of restrisks is necessary to decide on ceasing or continuation of remedial actions. The guideline has been applied to pump & treat, biosparging and natural attenuation.

The a priori bandwidth of the predicted restrisks proved acceptable but can be drastically reduced by using concentration measurements to calibrate the key parameters.

A concept was developed of a less intensive pump & treat strategy as an additional option besides ceasing or continuation of remedial actions: very small groundwater extraction rates (1 - $10 \text{ m}^3/\text{d}$) proved sufficient to keep in pace with slow desorption/diffusion of contaminants out of the soil. The duration of a pump & treat remediation cannot be shortened by extracting large amounts of groundwater. Much smaller treatment systems can be used for the same remediation, saving money and groundwater.

Costs of after-care monitoring programs can be widely reduced by use of the RestRisk guideline: the guideline will provide information on the sample points and time scale for sampling as it shows the rate of spreading of the contaminants in space and time.

Keywords

Controlled terms: biosparging, decision support, natural attenuation, pump & treat, risks, spreading Uncontrolled terms:

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SAMENVATTING

RESTRISK; Assessment of effectiveness of in situ remediation

Het RestRisk zeven-stappenplan is bedoeld om op een eenvoudige en betrouwbare manier de risico's van een restverontreiniging te voorspellen op een willekeurige moment tijdens een in situ sanering.

Tijdens de uitvoering van een in situ sanering kan de vraag opkomen of het doorgaan met de sanering nog nodig is. Met name het voortzetten van een *stagnerende* grondwatersanering is vanuit het oogpunt van milieuverdienste niet aantrekkelijk, om nog maar over de enorme kosten te zwijgen. Op zo'n moment is het nodig om de risico's van het stopzetten van de sanering te bepalen, zodat een beslissing over stopzetting kan worden genomen.

Het stappenplan bestaat uit de volgende 7 stappen:

- 1. Analyse van de beschikbare data.
- 2. Formuleren van een hypothese over de sleutelprocessen.
- 3. Opzetten van een conceptueel model.
- 4. Controleren of het berekende gedrag van de verontreiniging overeenkomt met de metingen, zo ja dan kan worden vervolgd met stap 5, anders moeten stap 1 tot en met 4 opnieuw worden doorlopen, waarbij aanvullende gegevens worden gebruikt.
- 5. Formuleren van de saneringsalternatieven.
- 6. Voorspellen van het toekomstige gedrag van de verontreiniging.
- 7. Vaststellen van de toekomstige risico's.

Het stappenplan is toegepast op locaties waar saneringstechnieken zoals pump & treat, biosparging en natuurlijke afbraak werden ingezet.

De betrouwbaarheid van de voorspelde risico's kan worden geoptimaliseerd, wanneer het Rest-Risk zeven-stappenplan wordt gebruikt bij de voorspelling. Het stappenplan is naast betrouwbaarheid gericht op een zo eenvoudig mogelijke berekening: de complexiteit van de rekenmodellen wordt stapsgewijs aangepast aan de complexiteit van de processen. Bij toepassing van RestRisk op werkelijke saneringen is gebleken dat beschikbare rapportages, zoals nader bodemonderzoeken en saneringsplannen, voldoende informatie over de locatie bevatten om een modellering volgens RestRisk mogelijk te maken.

Hoewel het stappenplan voornamelijk door specialisten zal worden gebruikt, fungeert het voor beslissers als een kwaliteitscontrole op de modelleringsinspanning.

De a priori bandbreedte van het voorspelde verontreinigingsgedrag bleek acceptabel. De bandbreedte kan drastisch worden teruggebracht door concentratiemetingen te gebruiken om de modellen te ijken.

Een andere keuzemogelijkheid dan stoppen binnen het RestRisk-stramien is de sanering voortzetten op een minder intensieve wijze. Het stilzetten van de onttrekking en het volgen van de natuurlijke afbraak is zo'n extensieve saneringsstrategie. Een andere strategie is het reduceren van de debieten van grondwateronttrekkingen: zeer weinig grondwater onttrekken is even effectief om de verontreiniging uit de bodem te verwijderen. Weinig grondwater onttrekken of intermitterend grondwater onttrekken zijn dus kosteneffectieve alternatieven voor intensieve pump & treat. Het voorkomen van verspreidingsrisico's bij deze extensieve technieken vergt een zorgvuldig ontwerp.

In het kader van BEVER is geconcludeerd dat plaatselijk bevoegd gezag minder behoefte heeft aan nationale regulering met betrekking tot saneringsdoelstellingen. Sanering zouden dan ook gericht moeten zijn op een kosteneffectieve verwijdering van de verontreiniging met zo min mogelijk nazorg. De kosten van monitoringsprogramma's in het kader van nazorg kunnen met behulp van het RestRisk stappenplan worden gereduceerd: RestRisk geeft informatie over het gedrag van de verontreiniging in de tijd, waarop monitoring kan worden afgestemd. RestRisk is daarmee een instrument om de kosteneffectiviteit van saneringsoperatie in Nederland te verbeteren.

SUMMARY

RESTRISK; Assessment of effectiveness of in situ remediation

The RestRisk Seven Steps Guideline (SSG) aims at a straightforward, non-elaborate and reliable assessment of the risks of a contamination still left in soil and groundwater at an arbitrary point during an in situ remediation - so-called restrisk. At an arbitrary point during an in situ remediation will rise if continuation of remedial actions is still necessary. Especially continuation of a stagnant pump & treat remediation isn't beneficial from an environmental point of view, not to mention the enormous costs. At this point assessment of restrisks is necessary to decide on ceasing remedial actions at the site or continuation.

The guideline consists of the following 7 steps:

- 1. Analysis of available data.
- 2. Postulation of hypothesis for key processes.
- 3. Set up of preliminary conceptual model.
- 4. Check if predicted contaminant behaviour matches observed behaviour, if prediction matches observation proceed with step 5, otherwise step 1 to 4 have to be repeated using additional data.
- 5. Formulation of remediation alternatives.
- 6. Prediction of future contaminant behaviour.
- 7. Assessment of future risks.

The guideline has been applied to in situ remediations where techniques like pump & treat, biosparging and natural attenuation have been used.

The reliability of the assessment of the restrisks is optimised if the modelling procedure referred to as the RestRisk Seven Steps Guideline is used for prediction. Besides reliability the guideline aims at a straightforward, non-elaborate prediction: model complexity is adjusted to the complexity of the processes involved. Application to real world cases showed that ready available data like soil investigations and remediation research reports are sufficient for a reliable prediction. Although the RestRisk guideline will be mainly applied by specialists it provides decision makers with a quality check on the modelling effort.

The a priori bandwidth of the predicted contaminant behaviour during pump & treat, biosparging and natural attenuation proved acceptable. The bandwidth could be reduced to a large extent by using data on measured concentration to calibrate the parameters which govern the key processes.

RestRisk also allows to evaluate continuation of remedial actions in a less intensive way. Natural attenuation could be such an alternative. Another less intensive alternative was designed for a pump & treat remediation: extraction of very small volumes of groundwater proved to be as effective to remove contaminant mass from soil and groundwater as the common intensive pump & treat approach. Reduction of groundwater extraction rates or intermittent extraction are a cost effective alternative. Additional care should be taken to prevent unwanted spreading.

In the BEVER (the results of the evaluation of the Dutch policy of soil remediation of 1997) it was concluded that the local governmental authorities need for less national regulations on remedial target values and planning. The clean up of contaminated sites should aim at the most

cost effective solutions, with most restricted after-care. Costs of after-care monitoring programs can be widely reduced by use of the RestRisk approach. The RestRisk method will provide information on the sample points and time scale for sampling as it shows the rate of spreading of the contaminants in space and time. It can be concluded that RestRisk is a tool suited to improve the cost effectiveness of the remediation actions in The Netherlands now and in the near future.

CHAPTER 1

INTRODUCTION

1.1 Scope of RESTRISK

The RESTRISK project aims at providing a straightforward, non-elaborate tool for assessing the effectiveness of in situ remediations, in support of decisions on either continuation, discontinuation, or a change in method of the remediation.

In situ techniques are more and more used to remediate contaminated sites: contaminants are removed without excavation of soil by (enhanced) biodegradation, volatilization, mobilisation, or soil flushing (pump & treat), or a combination of these techniques (biosparging). A characteristic feature of in situ techniques - most clearly observed during pump & treat - is that, after a short period of rapid removal of contaminants, the mass removal rate decreases and the remediation becomes stagnant. In these situations questions arise like: *how will the contaminants behave* and *where will they spread once remediation is stopped*? or *what are the effects of changes in the remediation strategy on fate and transport of the contaminants*? and *what are the consequent human and ecotoxicological risks*? A reliable tool to help answer these questions would assist both regulators and problem owners in the evaluation of the remaining residual risks (so-called 'restrisks') of a stagnant remediation and the effect of a change of remediation strategy on these risks.

To this end an adequate description is required of the key mechanism(s) responsible for contaminant behaviour and the remediation effects (and hence for the stagnation). If fate and transport of contaminants can accurately be described, subsequent risk assessment based on predicted concentrations is possible. The RestRisk tool therefore consists of available models that describe contaminant behaviour affected by in situ remediation, directions on how to use these models and obtain reliable predictions (including guidelines on data acquisition by monitoring), a risk assessment model, and guidelines to promote acceptance of the predictions as decision support by regulators and problem owners.

While RestRisk is basically intended for the assessment of stagnant remediations, a side benefit of the approach lies in its application as a guideline for cost effective design of pump & treat remediations.

The scientific technical predictions provided by RestRisk usually will not be the sole criteria to decide on the measures to be taken at a given location. Other criteria (legal, economical, political, urban planning, etc.) have to be evaluated as well. This is considered to be outside the scope of RESTRISK. Other decision support tools are currently being developed that supplement RestRisk in this respect, such as REC: Risk reduction, Environmental merits and Costs [Nijboer et al., 1998] and CER: Cost Effective Removal [Beinat et al., 1998].

1.2 **Phase 1**

Phase 1 of RESTRISK mainly focussed on the evaluation of stagnant pump & treat remediations [Van Geer et al., 1997]. A well known transport model code (MODFLOW with MT3D) [McDonald and Harbaugh, 1988; Zheng, 1992] was adjusted to describe the key mechanisms causing stagnation of pump & treat remediation and was validated for four cases (two BTEX- and two VOCI-contaminated sites). It was then possible to use this model to predict the effect of shut down of the ground water extraction wells on the fate and transport of the

remaining contaminants. The consequent human and ecotoxicological risks were evaluated using the CSOIL computer code [Van den Berg, 1991], which proved to be straightforward. For one case the effectiveness of various alternative remediation scenarios was assessed, from which an optimal remediation strategy could be surmised. The methodology developed for the four cases was generalised in a 7-step guideline and presented to regulators and problem owners.

1.3 **Objectives of phase 2**

The main objective of phase 2 of the project was to further generalise the RestRisk approach to include other in situ techniques such as biosparging and natural attenuation, and to explore the bandwidth of the results. The combination of the results of fate and transport models with exposure models was not considered to require additional study.

A second objective was to gain insight into the risk perception of the different parties involved in a remediation project, to assist in the acceptance of RestRisk in practical situations.

As RestRisk had already been proven useful in cases where stagnancy asked for a change in remediation strategy, a first attempt was also made to use the methodology as an optimisation tool during the whole time span of remediation and not only in the end phase of a stagnant remediation.

1.4 **Reading guide**

This report summarizes the results of phase 2 of the RESTRISK project and - where necessary - also of phase 1. It is based on several other reports of which two are official NOBIS-reports and four others can be obtained from TNO and Tauw (see list below). The report consists of three main parts. Chapter 2 answers general questions like what is RestRisk, by whom, when and why is it going to be used and what kind of data is required to use it. Chapter 3 demonstrates the application of RestRisk in the fields of pump & treat, biosparging and natural attenuation and is of special interest to advisors/experts who want to use RestRisk in future. Being of a more 'technical' character, detailed understanding of this chapter may require some specialist knowledge. Section 3.5, however, which deals with uncertainties, is of interest to both regulators/problem owners and advisors/experts. Chapter 4 deals with the interaction between RestRisk and policy(makers). The conclusions are summarized in chapter 5.

Other RESTRISK reports are:

- RESTRISK; Spreading and risks of remaining contaminants in soil and groundwater, phase 1: *Development of a method to evaluate stagnant remediations* (in Dutch, NOBIS-report 95-2-11).
- RESTRISK; Spreading and risks of remaining contaminants in soil and groundwater, phase 2: *Smart pump & treat, uncertainties and concept* (in Dutch, NOBIS-report 95-2-11).
- RESTRISK; Spreading and risks of remaining contaminants in soil and groundwater, phase 2: *Natural attenuation and spreading* (in Dutch, TNO-report NITG-98-115A).
- RESTRISK; Spreading and risks of remaining contaminants in soil and groundwater, phase 2: *RESTRISK and sparging* (in Dutch, Tauw-report R3594777.D03).
- RESTRISK; Spreading and risks of remaining contaminants in soil and groundwater, phase
 Risk perception and soil contamination (in Dutch, Tauw-report R01-3594777-RCH-D01-D).
- RESTRISK; Spreading and risks of remaining contaminants in soil and groundwater, phase 2: Minutes of the RestRisk workshops (in Dutch, TNO-report).

CHAPTER 2

RESTRISK DECISION SUPPORT

2.1 Introduction

The motive for the project RESTRISK was the observation in the field that the commonly applied in situ remediation technique pump & treat wasn't as efficient as anticipated: an initial sharp decline of the contaminant concentration of extracted groundwater was followed by a period of slow mass removal rates indicated by tailing of the concentration-time curve (see fig. 1). Although the bulk of contaminants was removed, the contaminant concentration had to be continued. As can be seen from figure 1 it would take many years and a huge volume of extracted groundwater to reach the remediation target (if possible at all). Continuation of a stagnating pump & treat remediation is not beneficial from an environmental point of view because exhaust emission and resources outweight the benefit of remediation. The question to be answered is what the risks are when the pumps are shut down and when the contaminants left in soil and groundwater are free to spread? This was where RESTRISK phase 1 started.

Fig. 1. Contaminant concentration (µg/l) of groundwater extracted during a three year pump & treat remediation as indicator of stagnation.

The results of phase 1 are threefold. First a 'technical' result was achieved by successfully adjusting a common fate and transport computer code in order to describe the key mechanism responsible for stagnation of pump & treat.

A more important result is the acceptance of the concept of using predicted concentrations for assessment of future risks by exposure models such as CSOIL [Van den Berg, 1991] to decide on shut down of groundwater extraction wells. In this way RESTRISK contributes to the acceptance of the source-path-object approach in which dispersion of contaminants is regarded as a path to objects rather than as a criterion standing on its own like is the case in the Dutch 'Urgentiesystematiek'. The 'Urgentiesystematiek' is based on a stand still principle (spreading is not allowed), aspects like natural attenuation of contaminants and absence of human- and ecotoxicological risks or threatened objects are not taken into account. RestRisk does allow for those aspects to be taken into account. Groundwater volumes assigned for (future) drinking water purposes, can be protected by marking them as threatened objects in the RestRisk approach.

In order to facilitate a wide application of the approach formulated in the RESTRISK project, it is described in a Seven Steps Guideline (SSG). In phase 1 this guideline was applied to four cases of stagnating pump & treat remediations, in phase 2 the guideline was applied to the in situ techniques biosparging and natural attenuation and was slightly adjusted.

2.2 **Decision support tool**

As mentioned in section 2.1 the project RESTRISK developed a *methodology* to predict (future) dispersion and risks. To make these predictions for pump & treat scenarios a computer model (*MT3D*+) is used which describes non-equilibrium sorption of contaminants to soil. In case of biosparging and natural attenuation, public domain model codes like RT3D [Clement, 1998] are implemented. The RestRisk Seven Steps Guideline (SSG) describes how to apply those models to sparging and natural attenuation.

During the development of the SSG in the first phase of the RESTRISK project, emphasise has been put on stagnation that occurs at sites where pump & treat is used as remedial measure. In this second phase the RestRisk SSG has been adapted to be of use for other remedial strategies such as biosparging and natural attenuation. The SSG presented here (see fig. 2) is applicable for:

- evaluation of remedial actions at sites that are currently treated and where stagnation occurs;
- evaluation of the efficiency of various remedial strategies at sites that are to be remediated.

The outcome of the SSG provides the scientific technical information on future behaviour of a contaminant plume. However, besides this scientific technical information other criteria are important to be evaluated such as legal, urban planning, economical, political, changed use of the site etc. The evaluation of these aspects is beyond the RESTRISK project. The outcome of the SSG gives the scientific technical support for the decision to either:

- 1. stop the remedial actions;
- 2. reduce the intensity of remedial actions;
- 3. continue remedial actions;
- 4. intensify remedial actions.

Ad 1. Stopping of the remedial actions

It can be decided to cease all remedial actions when the modelling efforts demonstrate that the future development of the plume will be within the constraint agreed upon by regulators and problem owners. An important factor is the evaluation of costs versus expected environmental benefits. It is considered logical to stop the remediation when the costs are 'unreasonably' high with respect to the further (minimal) decrease in residual risks and concentrations of contaminant. In regulatory terms this is called 'ALARA', As Low As Reasonably Achievable. In the Netherlands several models are currently being developed to assist these evaluations like REC: Risk reduction, Environmental merits and Costs [Nijboer et al., 1998] and CER: Cost Effective Removal [Beinat et al., 1998].

When it is decided to cease remedial actions, monitoring of the *actual* development of the plume should guarantee that the development of the contaminant plume remains within its constraint. Monitoring should be done according to a specific strategy. Such monitoring strategies have been developed within different NOBIS projects such as 'Monitored natural attenuation' [Sinke et al., 1998], and 'Flexible Emission Control' [Heijer and Schurink, 1998]. These strategies aim at validation of hydrological and biochemical models and verification of protection of the downstream receptors from contamination.

Ad 2. Reduce the intensity of the remedial actions

It can be decided to continue the remedial actions in a less intensive way when the modelling shows that a less intensive approach is sufficient to control or reduce the contaminant in an acceptable manner.

As part of a reduction of intensity it is also possible to take other remedial actions into consideration. The modelling effort in the SSG provides enough information to compare different remedial strategies. For instance monitored natural attenuation can be an effective strategy when degradation keeps pace with plume spreading. In some cases a 'maintenance' regime of slow pump & treat is sufficient to keep the plume in place.

Ad 3. Continuation of remedial actions

This decision has to be taken when the modelling efforts indicate that the plume will spread outside the negotiated perimeter of the contaminant if the current remedial actions would be reduced in intensity. The decision on the exact constraint for continuation of remedial action can be further detailed on basis of the modelling effort in the SSG. With the model applied in the SSG, different scenarios and their expected effectiveness, can be compared such as:

- unchanged continuation of ongoing measures;
- switching to another type of remedial action;
- using a combination of different remedial actions.

Ad 4. Intensifying the remedial actions

This decision has to be taken when the current remedial activities do not succeed in controlling the plume.

2.3 Seven Steps Guideline

In the first phase of the RESTRISK project, a SSG has been formulated to evaluate the plume development at a contaminated site and the future (human) risks. The SSG gives information on what data to collect and how to set up and validate fate and transport models. The guideline aims at making reliable predictions on future plume behaviour with the use of as little information as possible: the modelling procedure of the SSG involves gradually increasing model complexity until the model describes observed contaminant behaviour satisfactorily.

The Seven Steps Guideline consists of the steps as shown in figure 2.

Step 1: Analysis of existing data

The first step is the analysis of existing data. This is necessary to pose an hypothesis about the key mechanisms affecting fate and transport of contaminants due to the in situ remediation. The key mechanisms determine which model will be chosen to describe the in situ remediation. In step 3 the data will be used again to schematize and to design the model.

7-steps guideline



Fig. 2. RESTRISK's Seven Steps Guideline.

The type of data to be collected to characterize a site can be divided in three categories (see table 1):

- geohydrological aspects (determine transport of the contaminants and exposure paths);
- chemical and biological aspects (determine the fate of the contaminant);

- concentrations in source and plume of *contaminants* and metabolites (to estimate initial mass and to estimate model parameters like sorption and degradation rates).

The geohydrological parameters determine at which velocity and in what direction the contaminants may spread. The chemical and biological conditions in the system determine which reactions may proceed: sorption, degradation, chemical transformation, etc. The measurement of the contaminants and the degradation products is important to characterize the current extent of the pollution and the occurrence of degradation (see section 2.4 and table 1 for a more extensive discussion on data requirement). Furthermore potential receptor exposure points (e.g. drinking water wells, surface or groundwater discharge points) should be identified at this time.

When the SSG is applied to the execution phase of a remediation, available data will usually consist of:

- soil surveys in which geohydrology and the contamination are described;
- a scan of remediation alternatives and remediation plans in which the design of soil and groundwater remediation are described in detail;
- an evaluation of the soil excavation, which includes information on the amount of contamination left in the soil and on the groundwater extraction rates during excavation;
- monitoring of the remediation from which information about the progress of the remediation can be deduced (data for validation!).

Step 2: Hypothesis for key processes

In step 2 key processes affecting the contaminants should be identified. Sorption of contaminants to the soil matrix and biological degradation are the key processes affecting pump & treat, sparging and natural attenuation. Non-equilibrium processes like sorption or Non Aqueous Phase Liquid (NAPL)-dissolution seem to be *the* limiting process affecting the progress of pump & treat, although biodegradation can greatly affect the maximum observed concentration in groundwater. Biodegradation is a key process affecting contaminant behaviour during biosparging, although volatilization becomes more important when the contamination mainly consists of light, volatile compounds. Biodegradation is *the* key process affecting behaviour of contaminants during natural attenuation. Although those key processes could cause stagnation of the in situ techniques, site specific circumstances like hydraulic heterogeneity can also affect contaminants behaviour to large extend, so a careful analysis of available data should always proceed the formulation of a hypothesis and model choice.

The key processes that govern the transport and fate of the studied contaminant should be formulated and described as simple as possible. The modelling procedure of the SSG involves gradually increasing model complexity until the model describes observed contaminant behaviour satisfactorily. This is checked by comparing model results with historical data. *Note: the data used to design the model are not used to check the validity of the model.*

In case of a stagnant pump & treat remediation such a sequential refining of the model would be the following:

- presence of low permeability zones and preferential flow-paths;
- linear equilibrium sorption;
- non-linear equilibrium sorption;
- non-equilibrium sorption;
- biological degradation.

Step 2a: In depth analysis of data

In case the available data do not allow to formulate an adequate hypothesis for the key processes, additional data have to be collected. These data most likely refer to a more complex geohydrology, more complex sorption or degradation processes, detailed insight in the contaminant mass distribution in the plume (lateral spreading).

Step 3: Preliminary conceptual model

The site conceptual model is a representation of the site-specific groundwater flow and contaminant fate and transport. This model is typically used to predict future contaminant distributions in the soil and groundwater at the site in relation to groundwater flow and fate and transport processes. The conceptual model can be used to identify:

- movement of the centre of mass of the contaminants in relation to groundwater flow and transport;
- mass loss due to degradation;
- fate and transport of degradation products;
- locations at the site where additional data are required.

Ready available public domain model codes like MODFLOW [McDonald and Harbaugh, 1988], MT3D [Zheng, 1992] and RT3D [Clement, 1998] have proven to be successful in describing the key processes occurring during in situ techniques like pump & treat, biosparging and natural or enhanced attenuation (the code MT3D was adjusted by TNO to incorporate the mechanism of non-equilibrium sorption).

This step comprises the choice of a model like a combination of MODFLOW and the MT3D+ or RT3D code depending on the in situ technique and the nature and complexity of the key processes. Parameters which affect sorption processes can be obtained from literature, biodegradation rates are mostly obtained by a fitting procedure (see chapter 3 for details).

Step 4: Description of contaminant behaviour

In this step the selected fate and transport model is tested. It should adequately describe the already available data on concentration development in time or space. These are the data generally obtained as concentration measurements during the executional phase of a remediation. The measurements are used to validate the hypothesis for the key mechanisms affecting fate and transport of contaminants during and after remediation and to estimate model parameters. If the data fit to the model, it can subsequently be used to compare different remedial scenarios (step 5) and to make estimations on the future behaviour of the plume (step 6).

Step 4a: More complex modelling

If the fate and transport model does not describe the available field data adequately the hypothesis and the model have to be adapted. In some cases a technical adaptation of the model can be carried out but in other cases a more detailed measuring of specific parameters in the field is inevitable (step 4b).

Step 4b: Extended data analysis

In case that the hydrological processes are not the key processes that determine the behaviour of the contaminant and the development of the plume also other processes need to be considered. Especially biological degradation of the contaminants can contribute to a restriction of the spreading of the plume. At first the modeller can start using literature values for degradation rates but might need in more detail real data on the degradation rates and the production of metabolites. Also data on the redox conditions and the presence of natural organic matter are helpful to adequately model the (future) behaviour of the plume.

Step 4c: 'Worst case' scenario

In case that there is no common opinion on the key processes and the data give no straightforward information, a worst case scenario should be used. In this model all parameters are set at the most 'pessimistic' value (e.g. high value for velocity; low value for sorption and degradation). This more or less implies predicting the transport of a conservative, non-reacting contaminant. This model is than used to estimate a 'worst case' behaviour of the plume. Of course new field information, collected in a later stage, can be used to adapt this scenario to a more realistic version.

Step 5: Formulation of alternatives

Depending on the intended future usage of the site, the costs development and the possible stagnation of the remediation, alternative scenarios can be formulated:

- switching off the existing remedial measure;
- reducing the intensity of on-going measures;
- unchanged continuation of on-going measures;
- intensifying on-going measures;
- switching to another type of remedial action;
- using a combination of different remedial actions.

The future behaviour of the contaminants in the different scenarios can be estimated (step 6).

Step 6: Prediction of future contaminant behaviour

This step is aimed at providing the future concentration of contaminants in soil and groundwater as a result of the implementation of the alternatives formulated in step 5. To give a good insight in the results, concentration contours for the specific location should be given. Predictions should cover a period of more than twenty years.

The validated model (step 4) has to be used with care here because there are some restrictions. As the model has been validated with data that were obtained during a specific type of remedial treatment, its reliability is only certified for predictions that refer to small changes in the on-going remedial measure. For instance for pump & treat remediations the effects of shutting down or reducing the groundwater extraction rates, can be predicted sufficiently reliable. Also in case of sparging, an adaptation of the sparging frequency can be well predicted. However, the computer model has to be thoroughly reviewed and adjustments have to be made when there are major changes in the remediation technique. Still, the obtained information on the key processes can be used to make a rough estimation on the effects of different remedial scenarios.

Step 7: Estimation of future risks

The last step involves the prediction of the (future) actual risks using common risk assessment models like CSOIL [Van den Berg, 1991] or HESP [ECETOC, 1990], based on the predicted future contaminant concentrations in soil and groundwater.

To give a good insight in the results that are used as the basis for the calculations of the risks, the concentration contours can be used (step 6). These concentration contours visualise how the plume will develop during the forthcoming decades. The assumption underlying the estimations of future risks is that the usage of the site does not change or that information on present and future usage of the soil and groundwater are available. Factors that may drastically affect the future risks are:

- changes in the hydrological regime (e.g. new groundwater extraction sites);

- changes in the usage of the site (receptors);
- changes in the biological processes (bacteria become less active).

Changes in the hydrological regime such as increased pumping of (drinking)water or building of underground constructions, result in a deviation of the groundwater flow direction and magnitude and thereby render the initial model predictions on plume development useless (however not the model itself, often the model can be easily adjusted to describe a new flow regime).

Changes in the usage of a site have implications for the outcome of the risk assessment models. When a former industrial site is redeveloped (e.g. housing) the exposure pathways are very different than before and have to be re-evaluated. In this case the modelled original concentration contours can be used unchanged but the assumptions on pathways in the risk assessment model have to be adapted.

2.4 **Data requirements and monitoring**

The residual risks during and after a remediation can be assessed using the SSG. The guideline consists of a modelling procedure for prediction of fate and transport during and after an in situ remediation. Data collection and analysis are an important part of the procedure. This section describes what data are required in the SSG and where these data can be obtained. Table 1 gives an overview of the data requirements at several steps of the guideline.

parameter		step		
	1	2a	4b	
transport: groundwater flow				
definition of site geology	Х			
permeability and porosity of aquifers and aquitards	Х			
regional groundwater flow regime	Х			
groundwater head measurements		Х		
groundwater extraction and infiltration locations, plus amounts		Х		
natural and artificial drainage systems		Х		
groundwater velocity measurements			Х	
fate: chemical and biological processes				
sorption: influent concentration-time curve	Х			
sorption: organic carbon content of soil		Х		
sorption: partition coefficient of contaminant between soil and water		Х		
sorption: kinetic sorption rates			Х	
degradation: degradation rates		Х		
degradation: concentration of contaminant and degradation products in space and time		х		
degradation: availability of electron acceptors or -donors		Х		
degradation: additional evidence like redox, inhibitors etc			Х	
characterization of initial contaminant situation				
concentration contours of contaminant		Х		
total initial mass of contaminant in plume		Х	Х	

Table 1. Parameters that are advised to be collected (or measured) in the sequential steps to assess the risks at a site.

total initial mass of contaminant in source and location	Х	Х
metabolites of contaminant	Х	Х

The parameters mentioned in table 1 are explained below:

Transport: groundwater flow

Advective transport of contaminants dissolved in groundwater due to groundwater flow is one of the most important mechanisms causing migration of contaminants during and after in situ remediation. Diffusion of contaminants is rather slow and can mostly be neglected compared to advective transport due to groundwater flow (except for transport in impermeable layers). Density driven transport of contaminants (dissolved or as a separate liquid like Dense Non Aqueous Phase Liquids) can cause considerable downward migration of contaminants. This transport mechanism is not considered here, because none of the considered in situ remediation techniques involves removal of contaminants by density driven flow mechanisms. Transport of contaminants as a vapour phase can also cause considerable migration. This would be the case during biosparging and bioventing remediations. However, vapour transport is not considered here, although RestRisk was applied to a biosparging remediation (see section 3.3 for justification). Vapour transport is implicitly considered when human and ecotoxicological risks are assessed using exposure models like CSOIL.

The effect of groundwater flow on advective transport of dissolved contaminants can be quantified if a schematization of the geohydrology, generally in terms of an alternating sequence of aquifers and aquitards and its permeability and porosity, are known. This information can be derived at a regional scale from geological maps or the regional, geohydrological on-line database of TNO (REGIS), and at a local scale from soil investigations at the site. Furthermore 'driving' forces should be identified like the amount of groundwater recharge, groundwater extraction in the neighbourhood of the site and natural and artificial drainage systems. All these factors influence the groundwater flow direction and velocity at the site. A groundwater model incorporating these factors will predict the groundwater flow at the site. Predictions can be verified by comparing model results to groundwater head measurements. Sometimes local scale groundwater velocity measurements are available, but these are of limited use due to their local scale character. Head measurements can also be used to calibrate the permeability of aquifers and aquitards. If the groundwater flow is known, the advective transport of dissolved contaminants can be predicted by a transport model.

Fate: chemical and biological processes

Besides advective transport other processes control the fate of the contaminants. Chemical processes like sorption of contaminants to the soil retard the transport of contaminants towards receptors or to a remediation well. Biological processes like degradation of contaminants cause removal of contaminant mass and can greatly contribute to a reduction of risks. Chemical and biological processes may transform the initial contaminant into reaction products that may be less or more harmful than the parent compound.

The effect of chemical and biological processes on the fate of dissolved contaminants can be predicted by a transport model as well. To describe the sorption of contaminants to the soil in its simplest form (linear equilibrium sorption) only the organic carbon content of the soil and the partition coefficient, a compound specific attribute, are needed. These parameters can be obtained from literature or soil investigations. More complex sorption models like non-equilibrium sorption require the estimation of additional sorption parameters like sorption *rates* which can be obtained from literature as well (see section 3.2.2).

In phase 1 of RESTRISK concentration measurements of the contaminant in the extracted groundwater during a pump & treat remediation (so-called influent concentration) proved to be very useful to validate the choice of the sorption module of the transport model and to estimate sorption parameters like the partition coefficient and the sorption rates [Van Geer et al., 1997].

Effluent concentrations are normally measured during a pump & treat remediation, so data are available for calibration and validation of transport model.

Biodegradation of dissolved contaminants is generally one of the key processes which should be described if the residual risks during or after an in situ remediation have to be accurately assessed. Degradation can be described by transport models if the degradation *rates* are known. Literature values are of limited use here, because a very wide range of values, ranging from no degradation at all to half life times of a day, have been reported. The rates should be estimated for the site specific conditions. This could be done by laboratory experiments but the up-scaling to site scale has to be done with care.

Usually, time *history matching* using measured contaminant- and degradation product concentrations, is used to derive the rates indirectly. A simple mass balance can be used (see section 3.4) or transport models may be used for this purpose [Hetterschijt et al., 1998b].

In case of a contamination with petroleum hydrocarbons (like BTEX) the oxidative capacity is important besides the degradation rates. Therefore the availability of electron acceptors like oxygen, nitrate, iron oxides, sulphate and methane should be quantified, with site specific measurements.

Additional evidence for the occurrence of biodegradation could justify the hypothesis that biodegradation is a key process. This additional evidence consists of a characterization of the redox conditions, because the redox conditions determine the type of degradation process that might proceed in the aquifer. In case of a contamination with petroleum hydrocarbons (BTEX) the oxidative capacity is important. In case of a contamination with chlorinated solvents a low redox potential stimulates the reductive dechlorination (e.g. sulphate reducing or methanogenic conditions). Aerobic conditions favour the degradation of lower chlorinated solvents such as DCE and VC but inhibit the degradation of the higher chlorinated solvents such as PCE. Other parameters such as alkalinity, pH, temperature, conductivity, chloride, toxic metals provide additional evidence for occurrence of biodegradation:

- when the pH is too low (< 5) or too high (> 9) the bacterial activity might be suppressed;
- the presence of large amounts of heavy metals might inhibit the bacterial activity;
- temperature directly influences the rate of chemical, physical and biological processes;
- 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 of chlorine form chlorinated solvents.

Characterization of initial contaminant situation

The (change of) the contaminant situation at a site over time is used to derive a hypothesis of the key processes, to validate the fate (sorption and degradation) module of a transport model and to estimate parameters of the fate module (sorption and degradation rates). Beside this, fate and transport models simply need an initial contaminant situation for the prediction of fate and transport of the contaminants in the future. Dependent on the dimensions of the fate and transport model (two or three dimensional) a two or three dimensional image of the soil and groundwater contamination is required. Important is the identification of so-called secondary sources of groundwater contamination. These source zones or -layers consist of contamination in the form of a separate liquid, or NAPLs (Non Aqueous Phase Liquids like perchloroethylene, trichloroethylene, PCB or mineral oil). A high amount of contaminant present as a secondary source takes more time and effort to be removed.

2.5 **Applicability of RestRisk**

If the outcomes of the SSG of RestRisk is used as decision support on discontinuation of a remediation, the uncertainty of the predicted restrisks has to be acceptable by all parties involved (including the public). For such decisions a successful completion of step 4, meaning matching of predicted and measured concentrations, is an absolute prerequisite.

If RestRisk is applied at the planning phase of a remediation, which means no information is available to validate the hypothesis about the key mechanisms and to estimate parameters, step 4 and 5 are omitted. Application of RestRisk at the planning phase can be useful for a first quick scan of the spreading and risks of remediation alternatives. The results could be used as input for a REC (Risk reduction, Environmental merit and Costs) analysis [Nijboer et al., 1998]. Such a quick scan should always be accompanied with an uncertainty assessment. The bandwidth of the predicted concentrations can be quite large. Uncertainty analysis can be done through a sensitivity analysis for the key parameters.

An a priori uncertainty analysis was made for prediction of fate and transport as a result of pump & treat-, biosparging- and natural attenuation cases (see chapter 3). If those uncertainties are considered acceptable for choosing between alternatives at the planning phase, RestRisk can be applied.

2.6 Why and when to use RestRisk and by whom?

The main benefit of RestRisk is that the consequences of shutting down a remediation or a change towards a less intensive remediation are made explicit in predicted spreading of the contaminants in soil and groundwater in relation to the exposure of threatened objects. Furthermore the reliability of those predictions is made clear to all parties involved. In this way RestRisk supports objective decision making on remedial actions.

The RestRisk SSG can be applied in situations where during an in situ remediation, an involved party wants to have permission to reduce the intensity of remedial measurements before the remediation target has been achieved. This point will arise when the bulk of contaminants has been removed and continuation in an intensive way is not preferred from an environmental merit and economical point of view. This point can be situated just after the '*check*' of the 'plando-check' cycle, which refers to the cyclic character of the decision procedures before, during and after an in situ remediation (see fig. 3). At this point other decision support tools developed in 'Flexible Emission Control' [Heijer and Schurink, 1998] and 'Natural attenuation' [Sinke et al., 1998] provide decision support as well on the matter of how to proceed with a 'stagnant' remediation.

As stated before RestRisk can also be used in the *plan*ning phase of a remediation as a quick scan on dispersion patterns and risks of several remediation alternatives. In this phase results of RestRisk will be less accurate than in the check phase but results may be useful input as REC input, the decision support tool for choosing between remediation alternatives (Risk reduction, Environmental merit and Costs).

RestRisk involves usage of computer codes which are not easily accessible for a layman, which means that the actual restrisk assessment is done by advisors/experts. However the SSG provides other parties involved a framework to asses the quality and reliability of the predictions (step 4 of the guideline).



Fig. 3. Plan-do-check cycle and position of several 'NOBIS' decision support tools.

CHAPTER 3

RESTRISK ON SITE(S)

3.1 Introduction

To guarantee the applicability of the RestRisk methodology to the field, the decision support tool for evaluation of in situ remediations was developed by applying it to real world cases. One of the aims of phase 2 was to generalise the guideline for application to other in situ techniques and to quantify the bandwidth of the results. This was also done by applying the Seven Steps Guideline to real world cases. This chapter presents the application of RestRisk to a pump & treat remediation of a BTEX contaminated site (see section 3.2), a biosparging remediation of a hydrocarbon contaminated site (see section 3.3) and natural attenuation of a chlorinated solvent contaminated site (see section 3.4). This chapter only presents a short overview to demonstrate how RestRisk is applied to those cases. A full discussion on the sites can be found in Hetterschijt and te Stroet [1998a], Hanneman [1998] and Hetterschijt and te Stroet [1998c].

In phase 2 the prediction of the restrisks of the cases did not incorporate prediction of human and ecotoxicological risks, only risks of spreading were assessed. Phase 1 proved the assessment of human and ecotoxicological risks based on future concentration contours to be straightforward. Application of the combination of fate and transport models with exposure models was dealt with in phase 1 [Van Geer et al., 1997].

3.2 Pump & treat

3.2.1 *Key mechanism (step 2): rate limited kinetic processes*

The slow exchange of contaminants between 'mobile' and 'immobile' zones within the subsurface seems to be the key process towards stagnancy of pump & treat. Immobile zones physically represent layers of low hydraulic conductivity, organic carbon particles or clay minerals to which contaminants are sorbed or otherwise the less mobile phase of the contaminant like e.g. pure product. Mobile zones represent the fraction of contaminants dissolved in groundwater in the layers of high conductivity. The removal of contaminants from the mobile zones is largely affected by the groundwater extraction system, while the removal of contaminants from immobile zones isn't. Contaminants first have to be transported out of the immobile zones towards the mobile zones, before they can be extracted with the groundwater. The transport of contaminants out of immobile zones due to natural processes like diffusion, desorption or dissolution tends to be rather slow compared to the average duration of a pump & treat remediation.

The effect of slow exchange between mobile and immobile zones is illustrated in figure 4, where in this case the mobile zone is represented by a highly permeable sandy layer and the immobile zones are represented by clayey layers of low conductivity. If this two phase system is remediated by pump & treat, the contaminant is quickly removed from the mobile zone by ground-water extraction, whereas removal of the contaminant out of the immobile zone is largely dependent on the exchange rate between immobile and mobile zone, causing the tailing of the break through curve. This rate can be physically represented by the diffusion coefficient in case of layers of low permeability, the dissolution rate in case of the presence of pure product, or sorption kinetics in case of sorption to organic carbon. The rate of processes like diffusion, dissolution and desorption is much smaller than the rate of removal by a groundwater extraction. Those processes therefore limit the progress of pump & treat and determine the restrisks.

Fig. 4. Slow decontamination of a two phase system during pump & treat.

The slow exchange of contaminants between immobile and mobile zones can be described with many different conceptual models like hydraulic heterogeneity, non-linear sorption, sorption hysteresis, and non-equilibrium sorption [Hetterschijt and te Stroet, 1998a], that mathematically have much in common.

A non-equilibrium model proved to be very successful to describe the non-equilibrium *sorption* behaviour of contaminants during pump & treat of a two phase system (see fig. 5). The term non-equilibrium refers to the fact that the contaminant concentration in the immobile zone (the soil) is not in equilibrium with the contaminant concentration of the mobile zone (groundwater): the contaminant removal from the groundwater by the extraction system is much faster than the removal of contaminant from the soil by diffusion. Therefore much more contaminant mass is present in the soil as would be expected under equilibrium conditions. It also takes much more time to remove this mass from the soil than would be expected under equilibrium conditions.

The parameters of the non-equilibrium model are, in the case of sorption, related to physical entities like porosity, diffusion coefficient and the partition coefficient unlike other models like non-linear sorption or hysteresis. A main advantage of the non-equilibrium model above modelling immobile and mobile zones explicitly is that the spatial variation of the mobile and immobile zones hasn't to be known. The non-equilibrium model enables modelling two phase systems at microscale (like organic carbon particles) which simply isn't possible to do explicitly.

If immobile zones can be discriminated explicitly (e.g. as clay layers) the expert should choose between the non-equilibrium model and explicit modelling.

Fig. 5. Comparison of different sorption models.

3.2.2 Parameter estimation (step 3): rate coefficients

Non-equilibrium sorption is described using the formula:

$$\frac{r}{q}\frac{\partial S}{\partial t} = a\left(C - \frac{S}{\frac{\partial}{r}}_{K_{d}}\right) \quad \text{or} \quad \frac{r}{q}\frac{\partial S}{\partial t} = k_{f}C - k_{b}S \quad (3.1)$$

in which *S* is the contaminant concentration sorbed to the soil, *C* is the dissolved concentration, *è* is the porosity, \tilde{n} is the bulk density, K_d is the partitioning coefficient and \dot{a} is the *exchange rate* or coefficient. The exchange rate \dot{a} - or forward sorption rate k_f - has been estimated by laboratory experiments for several chemical compounds like BTEX [e.g. Roth and Jury, 1993]. The backward rate k_b is simply calculated from k_f .

The exchange rate \dot{a} can also be estimated from the porosity of the immobile (\dot{e}_a) and mobile (\dot{e}_m) zones, a shape factor for immobile zones (*a*) and the effective diffusion coefficient (D_e) by the formula [Rao et al., 1980]:

$$a = \frac{D_{\rm e} q_{\rm a} j q_{\rm h}}{a^2} \qquad \text{where} \qquad j = \frac{q_{\rm m}}{q_{\rm m} + q_{\rm a}} \tag{3.2}$$

Values for q_1 as a function of \ddot{o} can be found in Rao et al. [1980].

The mobile and immobile zones porosity depend on the nature of the zones. In case of a porous medium in which the mobile zone is a homogeneous sandy aquifer and the immobile zones are microscopic organic carbon particles, the mobile zone porosity ranges typically between 0.15 - 0.35 and the immobile porosity would be 0.001. The shape factor (*a*) - or the average diffusion length - is very small in the range of 10^{-4} m (dimension of the carbon particles). If immobile zones consists of small clay lenses, the immobile porosity and the shape factor would be quite larger (porosity 0.35 - 0.65 and shape factor $10^{-2} - 10^{0}$ m). Values for D_{e} , \dot{e}_{m} , \dot{e}_{a} and *a* for several porous media can be found in Wu and Schwend (1986), Rowe et al. (1988), Barone et al. (1989), Rijnaarts et al. (1990), Yanful and Quigley (1990), Ball and Roberts (1991), Myrand et al. (1992), Grathwohl (1992), Grathwohl and Reinhard (1993) and Harmond and Roberts (1994) [references from Griffioen, 1998].

The effective diffusion coefficient is dependent on the diffusion coefficient which is in the order of magnitude of 10^{-5} cm²/s and the contaminant specific retardation factor (*R*) (see equation (3.4) in section 3.3.2.

3.2.3 Design of less intensity pump & treat strategies

The application of the Seven Steps Guideline to real world pump & treat cases was dealt with in phase 1 and is not described here [Van Geer et al., 1997]. In this section the results of research on more cost effective pump & treat alternatives using the non-equilibrium model will be briefly discussed. For extended discussion on this subject see Hetterschijt and te Stroet [1998a].

Pump & treat is applied at a large scale since the 1980's. At the beginning of the 90's the performance of pump & treat was questioned by Keeley [1989], Haley et al. [1991], Freeze and Cherry [1989] and Mackey and Cherry [1989]. The main disadvantage of pump & treat seemed the impossibility to achieve the remediation target within a few years. Phase 1 of RESTRISK partially focussed on a more cost effective pump & treat strategy as an alternative to common pump & treat.

Intermittent pumping seemed to be more cost effective: although a much smaller volume of groundwater was extracted in this way, the contaminants spreaded as little over a 30 years period of intermittent pumping as over a 30 years period of 3 years continuously pumping (with high extraction rates) followed by 27 years of doing nothing. These results agree well with the theoretical discussion about remediation of a two phase system (see section 3.2.1): a short period of rapid removal of mass out of mobile zones will be followed by a period of slow mass removal out of immobile zones. Groundwater extraction can be stopped in this second phase to allow transfer of mass out of immobile zones by natural processes like diffusion. When mobile zones are contaminated to significant levels again by diffusion, groundwater extraction should be resumed. In this way the overall mass removal rate is the same as when groundwater is extracted continuously, but the volume of extracted groundwater is enormously reduced.

Phase 2 of RESTRISK partially focussed on the design of intermittent pump & treat, especially on issues like the duration of the extraction period in relation to the duration of the pause and the extraction rates. An optimisation procedure was carried out using the non-equilibrium model to describe the slow exchange of contaminants between mobile and immobile zones for a real world case [case 2; Van Geer et al., 1997].

Continuous extraction of a minimum volume of groundwater by a network of extraction wells proved to be the most efficient pump & treat strategy (see fig. 6). In this way the rate of mass removal from the mobile zone is just in pace with the slow process of desorption of contaminants from the immobile zones, while the least amount of groundwater is extracted. Extraction of 0.8 m^3 groundwater per day by a network of wells is as effective as extracting $80 \text{ m}^3/d$ or even $800 \text{ m}^3/d$. In order to prevent prolonged duration of the remediation, groundwater had to be extracted at several points in the contaminants to the well becomes a limiting factor. The distance of the contaminant to the well can be shortened by extracting groundwater from several wells.

Fig. 6. Mass removal under several groundwater extraction rates.

The main conclusion is that extraction of large volumes of groundwater doesn't accelerate the duration of the remediation, even extraction of very small volumes of groundwater is as effective in removing contaminant mass as extraction of hundred cubic meters groundwater per day.

This 'smart pump & treat' should be designed carefully; An other reason for the extraction of large volumes of groundwater is that the spreading of the contaminant should be controlled by the extraction system. When natural groundwater flow velocity is high, more groundwater should be extracted to control the contamination (see fig. 7a).

A solution for this case is the separation of the controlling- and remediation function of the extraction system. This can be done by installing two separate extraction systems, one for controlling the dispersion of the contamination by dividing natural groundwater flow and creation of a stagnant zone and one smart pump & treat system for remediation (see fig. 7b). The advantage is that only groundwater extracted by the system meant for remediation has to be treated, the groundwater extracted and injected by the system for controlling dispersion is

clean groundwater. In this way the volume of groundwater which has to be treated can be reduced to 5 - 20 %. This has an enormous impact on the treatment costs and thus on the overall costs of the in situ remediation.

Fig. 7a. Dependency of capture zone on natural groundwater flow and extraction rate.

Fig. 7b. Separation of controlling and remediation function of the grondwater extraction system.

3.3 Biosparging

3.3.1 Key processes (step 2): biodegradation

One of the key processes affecting fate and transport of contaminants during biosparging is enhanced biodegradation due to oxygen/air injection. Another important process responsible for mass removal is the volatilisation of light and volatile compounds of the contamination. A complete description of the effect of a biosparging remediation on fate and transport of contaminants would require a model which incorporates these two processes. Moreover the model should be able to predict the oxygen concentration as a result of erratic distribution of air channels occurring during sparging. Multi phase flow models can handle those processes simultaneously, because they describe each phase (air, water, soil, pure product) and the interaction between phases. Current multi phase flow models don't describe the irregular distribution of air channels during sparging. Instead a uniform distribution of oxygen/air will be predicted, because no data about heterogeneity of the subsurface is available at a scale relevant to air flow (grain scale).

Therefore and for reasons of simplification, the process of enhanced biodegradation has been modelled by describing the increased oxygen concentration explicitly based on expert knowledge of sparging systems (radius of influence). The process of volatilisation is neglected in this way, which is justified if biodegradation of non- or less volatile compounds is regarded. Those compounds are generally characterized by molecules which consists of more than 10 carbon atoms (e.g. n-dodecane $C_{12}H_{26}$). When modelling of volatilisation of organic compounds due to sparging becomes a straightforward procedure, it can be incorporated in the RestRisk Seven Steps Guideline.

Fate and transport of the contaminant during sparging and after shut down of the sparging wells can be estimated using the groundwater model code MODFLOW and the fate and transport model code RT3D.

3.3.2 Model set up and parameter estimation (step 3)

As mentioned in section 3.3.1 the degradation rate is an important parameter affecting fate and transport of contaminants during biosparging. Modelling biosparging involves estimation of this parameter. This section deals with the parameter estimation.

No measurements with a large support scale are available which describe the overall sparging remediation, like effluent concentration measurements in case of pump & treat. Instead point measurements at monitoring wells describe the processes occurring during remediation. The support scale of those measurements is small and is affected by local scale heterogeneities. Unless other measurements become available we have to use these local scale measurements to derive biodegradation rates which are valid for the whole area affected by sparging.

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \mathbf{m}c - \frac{\mathrm{d}s}{\mathrm{d}t}$$

Formula (3.3) describes the change of contaminant concentration at a monitoring well due to biodegradation and sorption only (no supply or discharge of contaminants as a result of groundwater flow is considered) of which c and s are the dissolved and sorbed contaminant concentration, t is time and μ is degradation rate.

(3.3)

If first order degradation and linear equilibrium sorption are assumed, formula (3.3) can be rewritten in the form of (3.4):

$$c(t) = c(t_0) e^{\frac{m}{R}t}$$
(3.4)

in which the retardation factor $R = 1 + \tilde{n}K_d/J$ (\tilde{n} is bulk density, K_d is distribution coefficient, J is porosity).

If the change of contaminant concentration of monitoring wells is smooth, i.e without considerable noise, these measurements can be used to derive the quotient of μ over R. Fitting of μ/R using measured concentrations at monitoring wells doesn't provide independent estimation of the degradation rate (μ) and the retardation due to sorption to the soil (R). One of the two has to be derived independently for instance from literature. The bandwidth of literature values of sorption characteristics is in general much smaller than the bandwidth of degradation rates. It is therefore recommended to derive sorption parameters like the distribution coefficient (K_d) from literature values for octanol-water partition coefficients (K_{ow}) instead of using literature values of degradation rates.

Another important model parameter is the dissolved oxygen concentration. The oxygen concentration determines how much contaminant mass in the soil can be degraded during and after biosparging. It is primary dependent on the radius of influence of the sparging wells. This radius can be determined independently using expert knowledge, tracer test studies or multi phase flow numerical or analytical models. The concentration of oxygen within the area of influence is set at 12 mg/l if air is injected.

3.3.3 Case 'Nijmegen'

In this section the application of the Seven Steps Guideline to a gasoline and diesel contaminated site in Nijmegen is briefly discussed. A more detailed description is given by Hanneman [1998].

The soil and groundwater of the site are contaminated with gasoline and diesel down to a depth of 17 meters below surface. A biosparging system was installed in order to remediate the saturated zone, after a floating layer of gasoline had been nearly completely removed by soil vapour extraction. The biosparging system had been operated for three years and the contaminant concentration decreased to low levels, except for two spots where the concentration remained high, due to inefficient sparging. The sparging system is to be adjusted at those two spots. The RestRisk Seven Steps Guideline will be used to assess the restrisks of the low level concentration areas during biosparging. The same approach could be used to assess the restrisks after biosparging has been stopped.

Steps 2 and 3 - 'definition of key processes' and 'parameter estimation' - have already been discussed to some extent in section 3.3.1 and 3.3.2. As mentioned before only key processes like sorption and biodegradation will be taken into account, not volatilisation. The assessment of the restrisks in this case will therefore be focussed on the less or non-volatile compounds (the C_{10} - C_{20} fraction).

Modelling biosparging at the Nijmegen site involved the following activities:

- 1. Estimation of sorption and biodegradation parameters.
- 2. Estimation of oxygen distribution.
- 3. Prediction of fate and transport of contaminants during sparging.

The geohydrology at the Nijmegen site is very complex. A full characterization of the geohydrology was beyond the scope of this project, so only a simplified model was used to demonstrate the validity of the RestRisk procedure. Therefore fate and transport of contaminants were predicted using the estimated '*real world*' sorption and biodegradation parameters and a *best estimation* of the oxygen distribution at the site. A *simulated* groundwater flow field (strongly simplified) was used to demonstrate the use of the RestRisk procedure to assess risks of contaminants during sparging.

The estimation of the sorption and biodegradation parameters was done by fitting formula (3.4) to the contaminant concentration decrease observed in monitoring wells during sparging. Measurements are suitable for this purpose if the observations show a smooth decrease like figure 8a. Irregular concentration measurements like those observed in monitoring well T111 (see fig. 8b) are not suitable to estimate the sorption and biodegradation parameters.

Fig. 8. Observed contaminant concentration decrease at two monitoring wells GT304 (a) and T111 (b). Measurements of GT304 are used to fit formula (3.4) to obtain μ and R.

The change of contaminant concentration observed at monitoring well T111 is very irregular and cannot be explained by processes like desorption and biodegradation. Factors like an irregular oxygen distribution due to heterogeneity of the soil probably control the change of concentration here. The heterogeneity is not known, and therefore cannot be modelled explicitly. Therefore those monitoring wells are excluded from the parameter estimation. If all available monitoring wells show a very erratic change of contaminant concentration over time, estimation of sorption and degradation parameters by fitting isn't possible and the sparging process cannot be described. This limits the applicability of the RestRisk approach to sparging. Based on a fit of formula (3.4) on the contaminant concentration decrease observed in monitoring well GT304, a value of 0.0036 could be derived for the ratio of the biodegradation rate (μ) and the retardation (R) of the contaminant due to sorption. A value for μ could be derived if R could be estimated independently for instance from literature.

In this case a mixture of contaminant compounds ($C_{10} - C_{20}$) was regarded, which hindered a very accurate estimation of *R*: a range of octanol-carbon partition coefficient values (K_{oc}) - a measure for sorption to the soil - of 100 till 1000 could be obtained from literature for $C_{10} - C_{20}$ compunds.

The retardation could be calculated by formula (3.5):

$$R = 1 + \frac{K_{\rm oc} \cdot f_{\rm oc}}{q} r_{\rm b}$$
(3.5)

in which *R* is the retardation factor, K_{oc} is the ocatanol-carbon partion coefficient, f_{oc} is the organic carbon content in the soil, \dot{e} is the soil porosity and \tilde{n}_{b} is the soil bulk density.

In this case an average value of 15 was chosen for the retardation of non-volatile compounds, the degradation rate would be 0.06 d^{-1} . Due to the dynamics of the real world subsurface (groundwater flow wasn't taken into account) biodegradation will be faster than the estimated rate of 0.06 d^{-1} . Therefore the contaminant concentration decrease observed in monitoring well GT304 was compared with concentration predicted using a slightly higher biodegradation rate of 0.068 d^{-1} .

The estimated retardation and biodegradation rate are combined with the estimated oxygen distribution and the groundwater flow in order to assess the fate and transport of the non-volatile contaminant compounds during sparging. A single well biosparging system is schematized as depicted in figure 9.

Fig. 9. Schematization biosparging.

Three separate zones can be identified (see fig. 9, profile (a) and planar (b)): a small zone (1) upstream of the radius of influence of the sparging well characterized by low oxygen concentration levels. Oxygen is supplied to this zone by diffusion from the well aerated zone (2), where the oxygen concentration amounts to 12 mg/l (due to air injection). Diffusion and advective transport of dissolved oxygen create a large zone (3) down stream of the aerated area with low to intermediate oxygen concentration.

As mentioned before a geohydrological characterization of the site at Nijmegen wasn't part of the scope of the project. The distribution between well aerated areas like zone 2 in figure 9 and areas characterized by low to intermediate oxygen concentration levels like zones 1 and 3 in relation to the monitoring wells could not be assessed at the site. Therefore the predicted concentration at all three zones are compared to the observed concentration at monitoring well GT304 (see fig. 10).

Fig. 10. Predicted (lines) and observed (•) contaminant concentration decrease due to biosparging.

Figure 10 shows that the at monitoring well GT304 the observed decrease of the contaminant concentration is reasonably accurately predicted by the model.

3.4 **Natural attenuation**

3.4.1 *Introduction*

Natural attenuation can reduce restrisks to a large extend. Within the RESTRISK project natural attenuation is defined as the in situ biodegradation of contaminants in soil and groundwater without application of external stimuli. The degree of natural attenuation should be assessed if restrisks have to be accurately estimated.

Several other initiatives focus on the assessment of the potential of natural attenuation at contaminated sites [Sinke et al., 1998] especially for contamination with chlorinated solvents and aromatic hydrocarbons.

One of the most convincing pieces of evidence of natural attenuation is the observation of degradation products in soil and groundwater (if those products can be uniquely assigned to

degradation processes and not to spilling). Time series of concentration measurements of mother compounds and degradation products in soil and groundwater provide evidence about the rate of natural attenuation processes: does biodegradation keeps pace with the supply from hot spots and is the plume of contaminated groundwater stable in time? Natural degradation is a slow process, it can take years for contamination to reach acceptable levels. Therefore time series over a couple of years are needed to 'prove' the success of biodegradation and those time series of concentration measurements are not commonly available.

Another option for degradation rates estimation is *history matching*. If the degradation path can be clearly defined like is the case with chlorinated solvents like perchloroethylene and trichloroethylene, history matching using a fate and transport model can be a powerful tool to estimate sequential degradation rates [Schippers et al., 1998; Hetterschijt et al., 1998b]. Concentration of the contaminant and its degradation products have to be measured within the groundwater contaminated area (further called *plume*) along the direction of the groundwater flow. The supply of contaminants out of the source zone towards the contaminant plume has to be known and the age of the contamination as well.

3.4.2 Case 'Weert'

For one of the cases, which was dealt with in phase 2 of the project RESTRISK, natural attenuation was the key process affecting the 'restrisks'. One of the remediation alternatives for a large scale chlorinated solvent contaminated site at Weert, consisted of a geohydrological isolation system to prevent further spreading of the contaminants: groundwater was extracted downstream of the contaminant plume and injected upstream after treatment. Half of the volume of extracted groundwater could not be injected in order to contain the complete plume. An option to consider was downstream injection of this volume of groundwater after treatment. This volume of groundwater still containing 2 - 20 micrograms per litre chlorinated solvents would spread in time. Natural attenuation of the chlorinated solvents could reduce the rate and amount of spreading and therefore reduce the 'restrisks' to a large extend.

The RestRisk approach was applied to this case to assess the restrisks. An important step in assessing the restrisks of this case is step 3 of the Seven Steps Guideline: model set-up and parameter estimation. The biodegradation rate of the contaminants should be estimated. However no series of adequate concentration measurements were available at the site. Measurements were carried out to delineate the contaminant plume and not to quantify the degradation process. History matching as described in the section above was therefore not an option.

However a lucky feature of this case is the fact that chloroform, a degradation product of one of the contaminants (carbon tetrachloride or *tetra*), was observed and delineated at the site. Chloroform hasn't been used in the production operations and the abundance of chloroform can uniquely be assigned to degradation of tetra. A tetra/chloroform mass balance was set up to estimate the degradation rate using formula (3.6):

$$C_{\rm t} = C_0 \mathrm{e}^{-\mathrm{k}\mathrm{t}} \tag{3.6}$$

In which C_t is the mass of tetra (kg) at time t, C_0 is the initial mass of tetra (kg), t is time (days) and k is the degradation rate (d⁻¹). Formula (3.6) can be rewritten in the form:

$$k = \ln \left[C_0 / C_t \right] / t \tag{3.7}$$

to estimate k out of the initial and present day mass of tetra and the 'age' of the contamination. Based on data gathered during several soil investigations [Bakker, 1996; Boode en Bakker, 1997] the mass of tetra today at 1996 present in soil and groundwater was estimated at $4.1 \cdot 10^3$ kg, the mass of chloroform was estimated at $2.8 \cdot 10^3$ kg. This amount of chloroform corresponds to an amount of $3.6 \cdot 10^3$ kg tetra degraded over the pas 20 - 30 years. The total amount of tetra which dissolved from layers of pure product over the past 20 - 30 years is therefore estimated at $7.7 \cdot 10^3$ kg.

If we assume that only dissolved tetra can be degraded, the half time of tetra can be derived by estimation of the yearly flux of tetra from the layers of pure product towards the groundwater. The first year after spillage the flux would be 7700 kg tetra divided by 30 years is 257 kg. If the half life of tetra would be 14 years, then 13 kg of tetra would be degraded into chloroform. The amount of dissolved tetra to be degraded next year would be equal to the yearly flux of 257 kg tetra plus 244 kg tetra which hasn't been degraded the year before. Again according to the half life of 14 years, 24 kg of this amount of tetra would be degraded in to chloroform and so on. Using a simple spreadsheet program the amount of tetra left after 30 years of dissolution and degradation and the amount of chloroform produced are estimated. These calculated values were compared with the estimated values based on measurements. The half life of 14 years or a degradation rate of 0.00014 d¹. The age of the contamination isn't known exactly. It could be between 20 and 30 years. If the contamination would be 20 years old, the half life time should be 10 years or k would be 0.00019 d¹ in order to correspond to the mass values estimated using field measurements.

The degradation rates derived by the mass balance were used to predict the spreading of tetra as a result of uncontrolled injection. Further degradation of the metabolite chloroform was not predicted, because in this case no evidence could be found to justify ongoing degradation. Figure 11 shows the migration of tetra from the injection point over 200 years as a result of a half life of 14 (a) or 10 years (b).

For both cases (half life 10 or 14 years) the contour of 1 μ g/l tetra at 20 years coincides with the contour at 50 years. The contour of 0.01 μ g/l at 100 years coincides with the contour at 200 years. This implies that after 100 years the degradation keeps pace with the flux of contaminant and a further migration of the contaminant plume stops. This situation occurs after 20 years for the 1 μ g/l contour.

The difference between the half life of 10 and 14 years is obvious from the length of the plumes: a half life of 10 years results in a plume of 470 meters length, the half life of 14 years results in a stable plume of 625 meters length.

Fate and transport of tetra was predicted before the planned injection strategy was carried out. No data were available to validate the model prediction and step 4 of the guideline was skipped. The predictions should be treated with caution and verification of the model predictions by monitoring is a must. However, due to the very slow degradation of tetra, only monitoring over period of many years would be useful for calibration and validation purposes.

Fig. 11. Concentration tetrachloromethane in groundwater over a period of 200 years using a half life of 14 (a) and 10 years (b). Red line = $1 \mu g/I$, blue line = 0.01 $\mu g/I$ and contour value = years.

3.5 Uncertainty

The accuracy of the assessment of the restrisks during or after an in situ remediation is largely dependent on the reliability of the predicted contaminant concentration in soil and groundwater as a function of time and space. The accuracy of those predictions is determined by the uncertainty with which the input parameters of the predictive models could be estimated.

Moreover the reliability of the prediction can only be assured if all the key processes are incorporated into the model and are accurately described. Step 4 of the Seven Steps Guideline - matching predicted versus measured concentration - provides an indication of the validity of the model.

This section will focus on the effect of uncertainty of the model parameters on the bandwidth of the model predictions and the assessment of the restrisks. This is done by varying some parameters of key processes and evaluating the effect on predicted contaminant concentration. Under natural conditions, when a remediation has been stopped, the uncertainty of the direction and magnitude of the groundwater flow has a large impact on the reliability of the prediction of fate and transport of the rest contamination. At many sites little or no information is available on the local scale natural groundwater flow. The uncertainty of the natural groundwater flow can be assessed by a hydraulic sensitivity analysis, which is straightforward and not addressed in this section.

Section 3.5.1 focuses on the uncertainty in the sorption parameters and its effect on the bandwidth of the predicted break through of the contaminant at a groundwater extraction well (duration of remediation). Section 3.5.2. focuses on the effect of the uncertainty of sorption and biodegradation rate on the bandwidth of the predicted contaminant concentration over time at monitoring wells due to biosparging. Section 3.5.2 also deals with the effect of the magnitude of the groundwater flow on the predicted concentration, because the contaminant concentration during biosparging is clearly influenced by the natural groundwater flow regime which is not the case for a stressed system like a pump & treat system. The uncertainty of degradation rates and its effect on spreading of contaminants is also discussed in section 3.4.2.

3.5.1 Pump & treat

Slow desorption of contaminants from less permeable zones within the soil limits the progress of a pump & treat remediation. Hetterschijt and te Stroet [1998a] have shown that slow exchange of contaminants between the less permeable zones within the soil and groundwater can either be modelled by defining the less permeable zones explicitly or by a more average description using a non-equilibrium model. The advantage of using the non-equilibrium model is that the soil heterogeneity doesn't have to be defined exactly at micro scale. The non-equilibrium model neglects the second order diffusive effects, but these effects are only important at a time scale of tens of years or more. The non-equilibrium model therefore provides a sufficient description of kinetic processes like non-equilibrium sorption.

Non-equilibrium sorption is described by a model that contains three parameters: the soprtion or *forward* rate (k_f), the desorption or *backward* rate (k_b) and the partition coefficient (K_d) all combined in the *exchange coefficient* \dot{a} (see formula (3.1)). The exchange coefficient can be obtained from literature [Roth and Jury, 1993] but can also be derived from the porosity of mobile and immobile zones, a shape factor for immobile zones, the diffusion coefficient and the partition coefficient (see section 3.2.2). The effect of the uncertainty of the exchange parameter \dot{a} on the prediction of the influent concentration is assessed by varying the porosity of mobile and immobile zones, the shape factor for immobile zones, the diffusion coefficient and the partition coefficient between 0.1 and 1 times of its original values. This resulted in a range of the exchange coefficient \dot{a} of 2 - 3. The variation of the exchange coeffient (2 - 3) is smaller than the variation of the individual parameters (1 - 10) due to the fact that \dot{a} is the product of D_e , \dot{e}_m , \dot{e}_a and a (see section 3.2.2.) and that the values of D_e , \dot{e}_m , \dot{e}_a and a are smaller than 1: the variance of the product of variables x and y is more or less equal to the sum of the product of the variance of x and the square of its value and the product of the variance of y and the square of its value (see [Mood et al., 1963] for a discussion on estimation of the variance of the Figure 12 shows the effect of uncertainty of the exchange coefficient (range 2 - 3) on the predicted concentration of contaminants in groundwater to be acceptable. The bandwidth of the predicted concentration of contaminant sorbed to the soil is rather large. The bandwidth can be narrowed to a great extend if concentration measurements in groundwater and soil are available to calibrate the exchange coefficient. Concentration measurements in groundwater are commonly available during a remediation, concentration measurements in soil are less common.

Fig. 12. Bandwidth of predicted concentration of contaminant of extracted groundwater and soil at extraction point as a results of a priori uncertainty of the exchange coefficient (sorption parameter).

3.5.2 Biosparging

Figure 13 shows the effect of the variation of the retardation factor (a), the biodegradation rate (b) and the magnitude of the natural groundwater flow (c) on the predicted contaminant concentration at a well in the aerated zone and a well downstream of this zone. The sensitivity analysis is based on the Nijmegen case. Biosparging of compounds C_{10} - C_{20} is depicted.

The bandwidth shown by figures 13a, b and c is based on the following values:

	low value	high value
sorption R	3 l/kg	6 l/kg
degradation (d ⁻¹)	0.065	0.13
groundwater flow (m/d)	0.14	0.29

Fig. 13. Sensitivity of predicted contaminant concentration in different monitoring wells to uncertainty of retardation factor (a), biodegradation rate (b) and groundwater flow (c).

Uncertainty in the retardation factor and the biodegradation rate has a large impact on the bandwidth of the predicted concentration. An increase of the sorption of the contaminant to the soil causes a slower decrease of the contaminant concentration over time: contaminants sorbed to the soil are not available for biodegradation. The impact of uncertainty with respect to the magnitude of the groundwater flow on the predicted concentration is less significant but clear: more dissolved oxygen will be advectively transported downstream, the oxygen concentration downstream will approach the level in the well aerated zone and biodegradation will be almost as fast in the downstream zone (see zone 3 in fig. 9) as in the aerated zone (see zone 2 in fig. 9).

CHAPTER 4

THE RESTRISK CONCEPT IN THE FRAMEWORK OF THE DUTCH POLICY

At a workshop in the first phase of the RestRisk project, the spreading of contaminants at four different sites with stagnant groundwater remediations was presented. In the presentation of the results the conclusion put forward was that a continuation of remedial activities was not needed, as the results indicated no future exposure risks for humans and ecosystems due to spreading of the contaminants. Many participants of the meeting disagreed with this conclusion. They stated that the 'risks' of soil contamination are not restricted to the exposure risks solely. Other types of risks such as financial risks and aspects of liability were said to be also important for the decision whether or not to stop a stagnant groundwater remediation.

At that time the RestRisk concept was meant to be used to support the decision whether or not it is allowed to stop the remediation, even if the Dutch Target Values have not been reached. In response to the statements in the workshop it was decided to investigate how the risk perception of different parties may influence the decision-making. This was done by means of interviews with people involved, and on the basis of reactions of persons participating in the workshop of the RestRisk project. The information was evaluated for differences in risk perception of different parties, and its consequences.

Risk perception is driven by the human psychological nature. It is easily influenced by external opinions. Humans are mainly focused on short-term response. Potential risks on a longer term are perceived as less risky. As a result, people may have a different attitude towards a risky situation, which depends on aspects such as the time scale and effects to occur, the number of persons affected, the severity of adverse effects, and the rate of active control of the situation.

Three parties are generally involved in a soil remediation, with each clear differences in risk perception:

- The first party is the 'owner' of the contaminated soil. As he is often not in direct contact with the contamination, his perception will not be focused on the immediate consequences of exposure. For this party, exposure risks are not acceptable if the risks exceed the maximal permissible levels that are defined by society. If a soil remediation is needed, it must reduce the exposure risks down to the acceptable level (i.e. below a risk-based standard).

The 'owner' is thinking in terms of financial risks. These include the decreased value of the contaminated site and the costs of remedial activities. It is in his interest to reduce his immediate costs, for example by a remediation in combination with other activities.

Additionally there is the risk of liability: 'his' contamination may affect the properties of neighbours. If it can be proven that the contamination will spread outside the boundaries of his property only on the longer term, a remediation to prevent spreading will not be urgent from his point of view.

 The 'public authority' is the second party. He is also not in direct contact with the contamination. His primary objective is to protect society from unexpected consequences of a soil contamination. He will plea for remedial target values down to clean soil levels, as these guarantee against possible unwanted situations.

His perception is focused on the legal consequences of agreements that are made in the remedial plans.

- The third party involved are the people living at the contaminated site. According to their perception they are directly exposed to someone elses contamination. Besides, their perception is that they cannot actively control the situation. Consequently, the public will

experience the exposure risks as far more critical than the owner and the public authorities. The general feeling will be that they may be let down when remedial plans are changed.

Due to these differences in risk perception the three parties will react differently on the remedial objectives and changes in plans. Some solutions for improvement of the remedial plans can be proposed. It is in the interest of the owner to remedy the contaminated site at a moment that offers the best cost-benefit ratio (i.e. with highest interest of investment). So, the moment of remediation should be defined by the public authorities in close consultation with the owner.

For the public authorities it is essential to make the remedial objective as realistic as possible. It should aim at the lowest level that is technically and financially feasible, but the goal should be achieved. Then it is possible to make agreements with parties that can easily be kept, with low legal risks.

For the people living at the contaminated site it is essential that they are involved in the total process of planning and execution. If they feel in control, larger residual exposure risks are far more acceptable for them.

In the evaluation project of the Dutch policy of soil remediation of 1997 (BEVER) it was concluded that the local governmental authorities need less national regulations on remedial target values and planning. The aim of restoration of the soil down to 'multifunctional' values is now to be evaluated on the cost effectiveness of the action for mobile contaminants, with minimal aftercare. Cost effectiveness of various remedial alternatives, and the design of after-care monitoring programs can be improved by the use of the RestRisk approach. The RestRisk method will provide information on future contours of various alternatives, and on the most suitable sample points, and timing for monitoring. It can be concluded that RestRisk is a tool well suited to evaluate the cost effectiveness of the remediation actions in The Netherlands now and in the near future, as asked for in the outcome of the BEVER project.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

RestRisk is a guideline that aims at a straightforward, non-elaborate prediction of fate & transport of contaminants and future risks.

At some moment in time during an in situ remediation, the question will rise whether or not continuation of remedial actions is still necessary. Currently this question can only be answered by comparing the amount of contaminant still left in soil and groundwater to the remediation target, which is normally set to the Dutch Target Value.

However, this approach implies that many ongoing in situ remediations should be continued for ever, while only slightly more contaminant mass is removed and the risks have already been reduced to agreed levels.

RestRisk showed that an intelligent use of fate and transport models in combination with exposure models provides evaluation criteria which allow subsequent incorporation of other aspects too. These include costs and environmental merit: spreading rates of contaminants in groundwater after ceasing all remedial actions and possible exposure paths towards receptors can be reliably predicted. RestRisk can also be used to predict the risk reduction at the planning phase of a remediation to compare several alternatives with a REC-analysis, although predictions will be less reliable in this phase.

RestRisk provides the technical information necessary to decide on continuation of an in situ remediation before target levels have been achieved by predicting the effect of this action on the risks of the remaining contamination. The urge to decide on discontinuation of a remediation before target levels have been achieved can originate from many motives, but the observation that target levels will never be achieved is one of the main motives. Due to heterogeneity of the soil, zones within the subsurface of any site exists which are not or to a lesser extent affected by an in situ remediation. Removal of the contamination from these zones will cost an enormous effort and might have an overall negative environmental merit, while the restrisks might be acceptable to all parties involved.

The reliability of the assessment of the restrisks is optimised if the modelling procedure referred to as the RestRisk Seven Steps Guideline is used for prediction. Besides reliability the guideline aims at a straightforward, non-elaborate prediction: model complexity is adjusted to the complexity of the processes involved. Application to real world cases showed that readily available sources of data like soil investigations and remediation research reports are sufficient for a reliable prediction. The data requirement is not the limiting factor: most of the required data is already available. Although the RestRisk guideline will be mainly applied by specialist it provides decision makers with a quality check on the modelling effort.

RestRisk also allows to evaluate continuation of remedial actions in a less intensive way. Natural attenuation could be such an alternative. Another less intensive alternative was designed for a pump & treat remediation: extraction of very small volumes of groundwater proved to be as effective to remove contaminant mass from soil and groundwater as the common intensive pump & treat approach. Reduction of groundwater extraction rates or intermittent extraction are a cost-effective alternative. Additional care should be taken to prevent unwanted spreading.

In the BEVER (the results of the evaluation of the Dutch policy of soil remediation of 1997) it was concluded that the local governmental authorities need for less national regulations on remedial target values and planning. The clean up of contaminated sites should aim at the most cost effective solutions, with most restricted after-care. Costs of after-care monitoring programs can be widely reduced by use of the RestRisk approach. The RestRisk method will provide information on the sample points and time scale for sampling as it shows the rate of spreading of the contaminants in space and time. It can be concluded that RestRisk is a tool suited to improve the cost effectiveness of the remediation actions in The Netherlands now and in the near future.

REFERENCES

Bakker, L.M.M, 1996. Aanvullend nader onderzoek voormalig bedrijfsterrein Akzo Nobel te Weert. Tauw by, report R3447073.T02/LMB, Deventer, 1996.

Beinat, E., C. van den Brink, J.G.M. Koolenbrander, M. in 't Veld, and H. Vermeulen, 1998. Kosteneffectiviteit van bodemsanering - Een afwegingsystematiek voor verontreinigingen in het mobiele regime.

Editors: M. van Drunen and E. Beinat, Instituut voor Milieuvraagstukken, Amsterdam, 1998.

Berg, R. van den, 1991.

Blootstelling van de mens aan bodemverontreiniging. Een kwalitatieve en kwantitative analyse leidend tot voorstellen voor humaan toxicologische C-toetingswaarden. RIVM report 725201.006. RIVM, Bilthoven, 1991.

Boode, J., and L.M.M. Bakker, 1997. Akzo Nobel, voormalig bedrijfsterrein Weert: saneringsplan. Tauw bv, report R3447030.T02, Deventer, 1997.

Clement, T.P., 1998. A modular computer code for simulating reactive multicomponent species transport in 3-dimensional groundwater systems. Pacific Nortwest National Laboratory, Richland, Washington, U.S.A., 1998.

European Chemical Industry Ecology and Toxicology Centre, 1990. Hazard assessment of chemical contaminants in soil. Technical report No. 40, ECETOC, Brussel, 1990.

Freeze, R.A., and J.A. Cherry, 1989. What has gone wrong? Ground Water, Vol. 27 (4): pp 458-464, 1989.

McDonald, M.G., and A.W. Harbaugh, 1998. A modular three-dimensional finite difference groundwater flow model. U.S. Geological Survey, 1998.

Griffioen, J., 1998. Suitability of the first-order mass transfer concept for describing cyclic diffusive mass transfer in stagnant zones. J. of Cont. Hydrol., Vol. 34: pp 155-165, 1998.

Haley, J.L., B. Hanson, C. Enfiedl, and J. Glass, 1991. Evaluating the effectiveness of groundwater extraction systems. Groundwater Monitoring Rev., Vol. 11 (1): pp 119-124, 1991.

Hanneman, F.A., 1998. RESTRISK; Verspreiding en risico's van restconcentraties in bodem en grondwater, fase 2, deelrapport IV, RESTRISK en persluchtinjectie. Tauw bv, report R3594777.D03, Deventer, 1998. Hetterschijt, R.A.A., and C.B.M. te Stroet, 1998.

RESTRISK; Verspreiding en risico's van restconcentraties in bodem en grondwater - Fase 2: Deelrapport 1: Slimmer saneren met pump & treat; onzekerheden en pompstrategieën. CUR/NOBIS report 95-2-11, Gouda, October 1998.

Hetterschijt, R.A.A., C.B.M. te Stroet, and T.N.P. Bosma, 1998. Neproma PCW remediation study. Model study on effectivity and duration of several remediation alternatives. TNO NITG 98-82-C, Delft, 1998.

Hetterschijt, R.A.A., and C.B.M. te Stroet, 1998. RESTRISK; Verspreiding en risico's van restconcentraties in bodem en grondwater, fase 2, deelrapport III, Natuurlijke afbraak en verspreiding. TNO NITG 98-115-A, Delft, 1998.

Heijer, R., and E. Schurink, 1998. IBC en nazorg door Flexibele Emissie Beheersing. CUR/NOBIS report 96.930, Gouda, October 1998.

Keeley, J.F., 1989. Performance evaluation of pump & treat remediations. Superfund Issue Paper, EPA/540/8-89/005, R.S. Kerr Environmental Research Lab., Ada OK, 14 pp, 1989.

Mackey, D.M., and J.A. Cherry, 1989. Groundwater contamination: pump-and-treat remediation. Environ. Sci. Technol., 23 (6): pp 630-636, 1989.

Mood, A.M., F.A. Graybill, and D.C. Boes, 1963. Introduction to the theory of statistics. McGraw-Hill Int. Book Comp., Singapore, pp 180, 1963.

Nijboer, M.H., M.A. van Drunen, A.R. Schütte, E. Beinat, J.G.M. Koolenbrander, and J.P. Okx, 1998.

Het beslissingsondersteunende systeem RMK voor het beoordelen van varianten voor bodemsanering - Fase 2: Een methodiek gebaseerd op Risicoreductie, Milieuverdiensten en Kosten. CUR/NOBIS report 95-1-03, Gouda, March 1998.

Rao, P.S.C., R.E. Jessup, D.E. Rolston, and J.M. Davidson, 1980. Solute transport in aggregated porous media: theoretical and experimental evaluation. Soil Sci. Soc., Am. J., Vol. 44, pp 1139-1146, 1980.

Roth, K., and W.A. Jury, 1993. Linear transport models for adsorbing solutes. Wat. Res. Res., Vol. 29 (4): pp. 1195-1203, 1993.

Schippers, B.P.A., J.H. van den Berg, T.N.P. Bosma, L.A. Hamerlinck, P.C.J. Leijten, H.C. van Liere, T.F. Praamstra, L. Schipper, and C.B.M. te Stroet, 1998.

Intrinsieke biodegradatie en bioreactieve schermen bij bodemverontreiniging bij textielbedrijven - Fase 2 en 3.

CUR/NOBIS report 96-2-01, Gouda, July 1998.

Sinke, A.J.C., T.J. Heimovaara, H. Tonnaer, and H.J. van Veen, 1998.

Beslissingsondersteunend model natuurlijke afbraak - Fase 1: Deelresultaat 1: Ontwikkeling van een beslissingsondersteunend model ten behoeve van de acceptatie van natuurlijke afbraak als saneringsvariant.

CUR/NOBIS report 97-1-02, Gouda, November 1998.

Van Geer, F.C., F.A. Hanneman, A.J. Palsma, A.J.C. Sinke, C.B.M. te Stroet, R.M.C. Theelen, J.C.M. de Wit, 1997.

RESTRISK; Verspreiding en risico's van restconcentraties in bodem en grondwater - Fase 1: Ontwikkeling van een beoordelingsmethodiek voor locaties met stagnerende grondwatersanering.

CUR/NOBIS report 95-2-11, Gouda, June 1997.

Zheng, C., 1992. MT3D Documentation and User's Guide. S.S. Papadopulos & Associates Inc., Maryland, U.S.A., 1992.