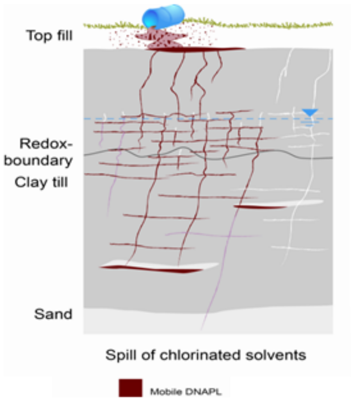
Practical Tool for Enhanced Reductive Dechlorination Design in Clay till

Chlorinated solvent in clay till
The problem
The processes



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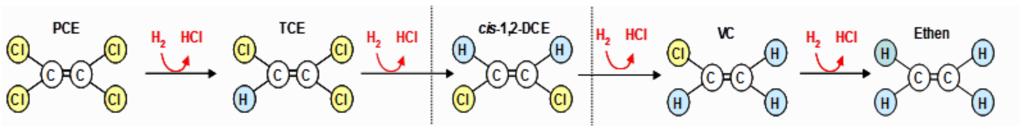

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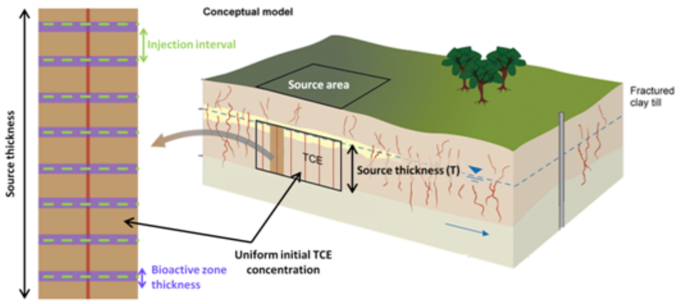

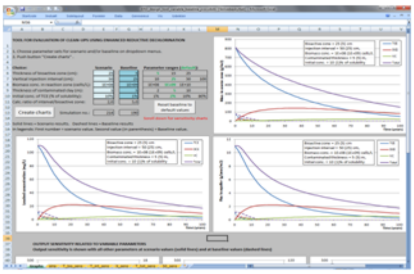

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Technical University of Denmark DTU

REMTEC
Innovative REMediation and assessment TECHnologies

ORBICON

Practical tool for enhanced reductive dechlorination design in clay till

A collaboration project between
Orbicon A/S and DTU Environment

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PREFACE

This work has been carried out in collaboration between DTU Environment and Orbicon A/S, as part of the REMTEC project (Innovative REMediation and assessment TEChnologies for contaminated soil and groundwater) www.remtec.dk

Recent studies have shown that enhanced reductive dechlorination (ERD) in clay tills is challenging and its success depends on both site specific and design parameters. Therefore a practical tool has been developed in order to assess mass removal and contaminant mass flux to the aquifer during ERD in clay tills, depending on these controlling parameters. This Excel-based tool can be used by consultants and authorities for several purposes:

- Decision-making support to select remediation technology
- Optimization of remediation design
- Planning of risk management during remediation
- Input for other decision-support tools (LCA, environmental economics)

This work consists of the Excel based practical tool and the present technical note. The technical note provides a brief introduction to the main concepts regarding enhanced reductive dechlorination in clay till as well as a brief description of the framework for developing the practical tool. The Excel based practical tool has been developed by Orbicon A/S based on data generated by a numerical model developed by DTU Environment.

Acknowledgements

This work was supported by REMTEC, Innovative REMediation and assessment TEChnologies for contaminated soil and groundwater, Danish Council for Strategic Research. We also wish to acknowledge the Capital Region of Denmark and the Region of Southern Denmark for collaboration on different projects that were used as input for the developed practical tool. We also thank Dr. Neil Durant of Geosyntec Consultants who provided constructive feedback on this document. Finally, we wish to thank the Information Center on Contaminated Sites / Danish Regions for accommodating this work on their website and providing technical support.

1 BACKGROUND AND PROBLEM DESCRIPTION

Chlorinated solvents in the subsurface are sparingly soluble dense non aqueous phase liquids (DNAPLs) that can be long term sources of contamination to groundwater. Many contaminated sites occur in areas with fractured clay geology at the land surface (Chapman and Parker, 2005), where the released DNAPLs penetrate into preferential flow pathways formed by fractures and can then rapidly dissolve and diffuse from the fractures into the matrix (Falta, 2005). Even after the removal of the physical source from the site, the contaminant can diffuse back and from the fracture network for hundreds of years, causing **long-term leaching** to an underlying aquifer (Harrison et al., 1992; Parker et al., 1997; Reynolds and Kueper, 2002). Typical migration processes for chlorinated ethenes in fractured low-permeability media are illustrated in Figure 1. Figure 2 shows an example of fractured clay geology from a Danish site.

Such sites are **challenging to remediate** because most of the contaminated **mass is located in the low-permeability matrix**, which is difficult to access due to the **mass transfer limitations** caused by slow diffusion processes (Chambon et al., 2010). Biological Enhanced Reductive Dechlorination (ERD), which has been successfully applied to sandy aquifers, is a promising technology for *in situ* remediation of such contaminated sites. At clay till sites, several conditions are decisive when choosing ERD as the remediation technology (cf. chapter 1.1).

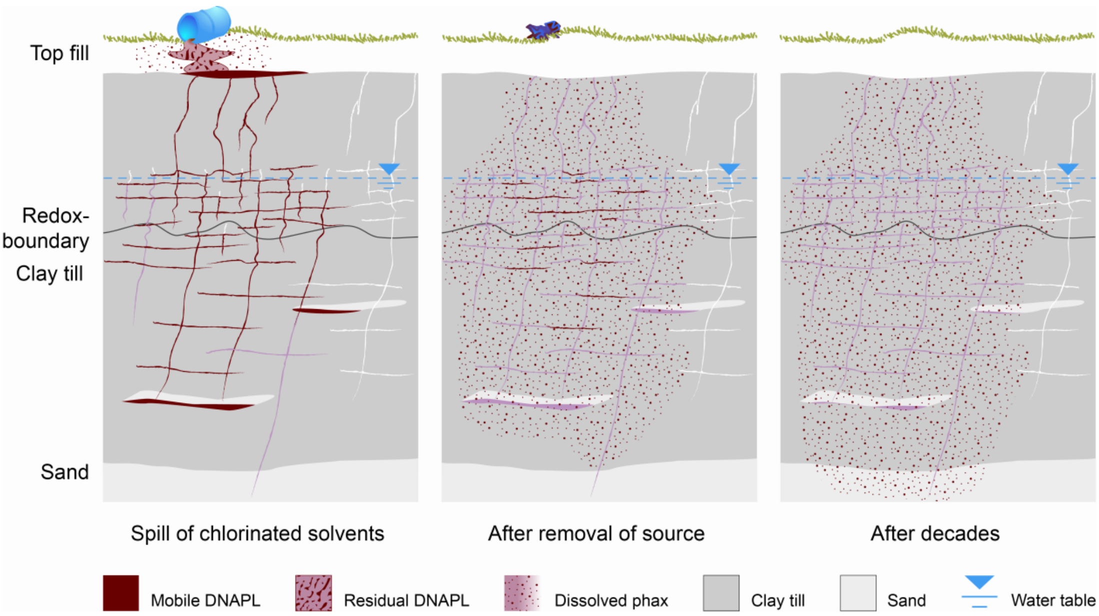

Figure 1 – Typical migration process for chlorinated ethenes in fractured low-permeability media (DTU Miljø & Region Hovedstaden, 2010)

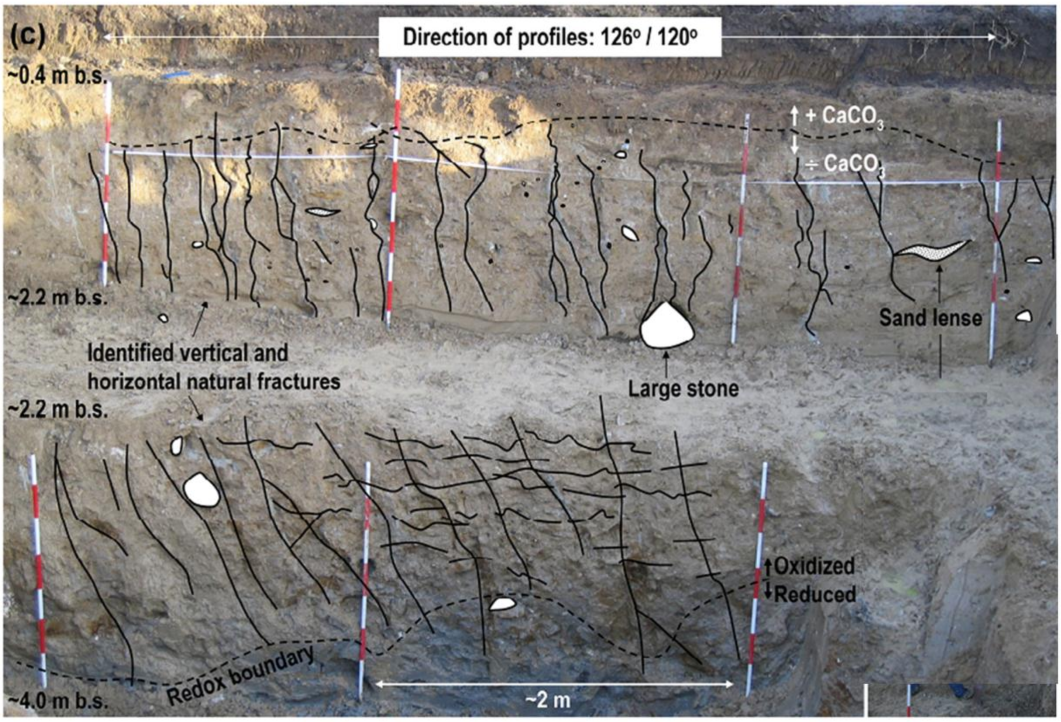

Figure 2 – Illustration of fractured clay till geology with fractures and low-permeability matrix (modified from Christiansen, 2010)

1.1 Pros and cons for ERD selection

Several technologies can be considered for the remediation of clay till sites contaminated with chlorinated solvents. Typical options include: Excavation, mass transfer technologies (mainly thermally based), and mass destruction technologies that rely on the introduction of chemical or biological amendments in the soil.

When choosing a remediation technology for any given site, the following criteria are involved in decision making

- Applicability and site specific characteristics (contaminant levels, geology, redox conditions, access and site use)
- Remediation objectives and cleanup targets (including timeframe)
- Life cycle impacts (Environmental impact of the remediation technology)
- Capital and maintenance costs

Based on the above criteria, pros and cons for choosing ERD for the remediation of a clay site are presented in Table 1. It is important to keep in mind that this is not a comprehensive list but merely examples of situations that may support or oppose selecting ERD.

Table 1 – Pros and cons for ERD selection

	Pros	Cons
Applicability and site characteristics	Applicable at sites with limited access (under buildings, etc), where ex situ technologies are impractical.	
	Applicable for contamination located at relatively large depths where ex situ technologies are impractical.	
	Long lifespan of added reactants allows for diffusion into the clay matrix, which is often a limitation for chemical oxidants	Distribution of amendments in clay is difficult, and mainly driven by fractures and natural heterogeneities
	ERD is one of the technologies that are effective for treatment of high contaminant concentrations	Performance for treatment of high strength complex mixtures not demonstrated.
	Several successful applications worldwide and extensive knowhow of the processes in permeable media.	Few well documented applications in clay till. Technology performance in clay till has not rigorously demonstrated at field scale.
	May be used in combination with or sequenced with other technologies (treatment train)	
Remediation objectives	A great tool for mass flux reduction in cases where immediate contaminant removal is not required	Long clean up time in clay till (several decades)
		Inherent uncertainty of effect, due to the long time frame, challenges with the distribution of amendments in clay, and uncertainty in distribution of dechlorinating bacteria
		Risk for residual contamination, due to challenges with the distribution or consumption of amendments in clay
Life cycle impacts	Low consumption of energy, steels and activated carbon, compared to e.g. thermal technologies. This results in lower life cycle impacts	Risk for methane or H_2S built-up, due to the dechlorination process
	"Green" / "organic" remediation technology with relatively high public acceptance, unlike thermal technologies that are seen as CO_2 -intensive	Risk for build up of more toxic byproducts, mainly VC from incomplete dechlorination/ shortage of donor or bacteria. Correct dimensioning and establishment of a buffer treatment zone can usually help avoid this problem.
Costs	Can be cost effective for contamination located at large depths where ex situ technologies are impractical. Low energy consumption leads to low costs.	Need for long term monitoring may result in high maintenance costs
		Need for multiple injection rounds (with few years interval) may result in high costs

1.2 Purpose of this tool

Recent studies have shown that ERD in clay tills is challenging and its success depends on both site specific and design parameters. Therefore this tool was developed in order to assess mass removal and contaminant mass flux to the aquifer during ERD in clay tills, depending on these controlling parameters. This Excel-based tool can be used by consultants and authorities for several purposes:

- Decision-making support to select remediation technology
- Optimization of remediation design optimization
- Planning of risk management during remediation
- Input for other decision-support tools (LCA, environmental economics)

2 FLOW AND TRANSPORT IN FRACTURED CLAY TILL

Fractured clay tills are characterized by the presence of high permeability features (fractures and sand lenses) embedded in a low-permeability clay matrix. Therefore flow and transport in such settings are controlled by **advection processes** along the fast preferential pathways formed by the fractures and **diffusion processes** in adjacent matrix, cf. Figure 3.

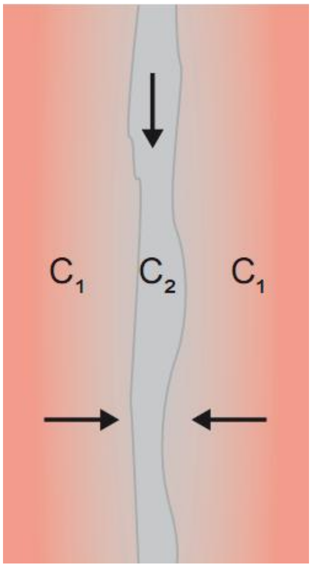

Figure 3 – Illustration of fast advection in fracture and slow diffusion in adjacent matrix

The water flow through a fractured clay till depends on the **net recharge *I*** and the **bulk hydraulic conductivity K_b**, which represents the equivalent hydraulic conductivity of both the vertical fractures network and the matrix. The flow ratio between the fractures and the matrix depends on the **matrix hydraulic conductivity K_m** and the average **fracture spacing *2B*** and **aperture *2b***. For typical hydraulic parameter values in Danish clay till, more than 80% of the recharge to the underlying aquifer flows along the vertical fractures (Harrison et al., 1992).

Transport along the vertical fractures is then controlled by advection (water velocity in the fracture) and by interaction at the fracture matrix interface. In the adjacent matrix, transport is mainly controlled by diffusion (because of the low K_m, the advection in the matrix is limited). Diffusion processes depend on the **matrix porosity Φ**, the **tortuosity τ** and the **free diffusion coefficient** of the contaminant D^*_i. Solute transport in the clay matrix is also influenced by sorption, which can enhance mass transfer limitations. The sorption of chlorinated ethenes on clay tills can be described by a linear isotherm based on a compound specific **distribution coefficient $K_{d,I}$** (Lu et al., 2011). As for the water flow, most of the contaminant leaching from a clay till to an underlying aquifer is transported by advection along the vertical fractures.

3 ENHANCED REDUCTIVE DECHLORINATION

3.1 Reductive dechlorination

Under anaerobic conditions and in the presence of an electron donor (hydrogen H2) and specific degraders (Dehalococcoides), chlorinated ethenes (PCE and TCE) can be sequentially degraded to the non-toxic compound ethene, cf. Figure 4. In a remediation perspective, this natural process can be enhanced by injecting specific dechlorinating bacteria and/or organic electron donors into the subsurface. The injected organic donor (vegetable oil, lactate, molasses, etc.) is fermented to produce hydrogen that can be used by the bacteria for dechlorination, cf. Figure 5. The produced hydrogen is also used by other geochemical processes, such as sulfate and iron reduction or methanogenesis. The injection of dechlorinating bacteria ensures the complete dechlorination of chlorinated ethenes to ethene, in order to avoid accumulation of intermediate products (DCE and VC). The kinetics of reductive dechlorination depend on biomass concentration X and degradation rates. In the practical tool, the influence of the kinetic of reductive dechlorination on ERD performance can be assessed by varying the biomass concentration.

Furthermore, the donor lifetime in the subsurface (which controls the need for re-injection) will mainly depend on long term methanogenesis at the site.

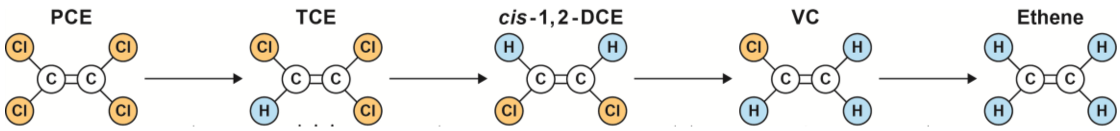

Figure 4 – Sequential reductive dechlorination of PCE to ethene

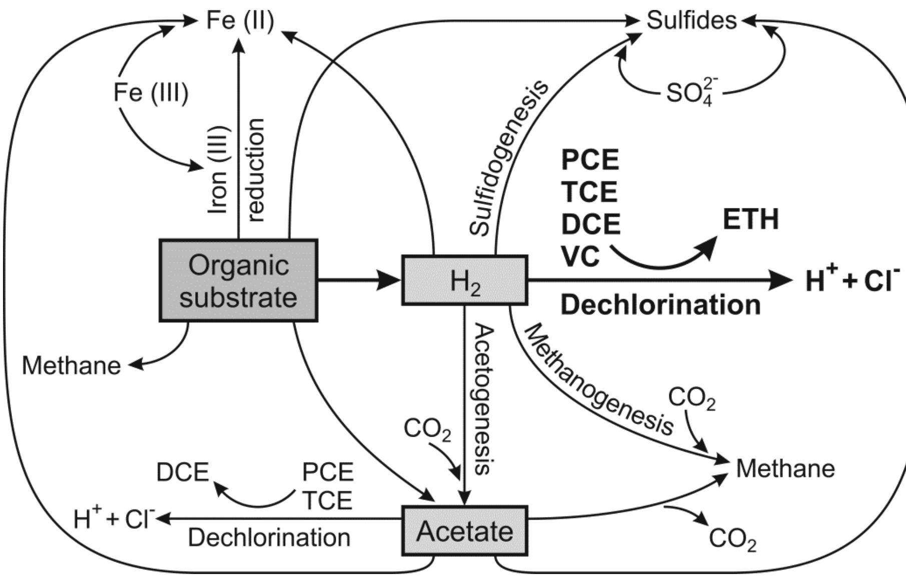

Figure 5 **– Illustration of the processes that are stimulated by organic donor amendment in the subsurface (modified from Fennell and Gossett, 2003, with kind permission from Springer Science + Business Media)**

3.2 Distribution of amendments

In low-permeability media, such as fractured clay till, the main challenge consists in ensuring contact between the contaminant trapped in the low-permeability matrix and the injected donor and bacteria (Christiansen, 2010). It is usually assumed that the amendments spread in horizontal high permeability features (induced or naturally occurring fractures and sand stringers). The **injection interval** determines the spacing between amended fractures/stringers (assuming successful injection at each depth interval). A recent field study (Christiansen, 2010) has shown successful tracer amendment down to 9.5 mbs with 25 cm interval using direct push delivery and 1 meter interval using pneumatic fracturing (Figure 1). Furthermore successful amendment with bacteria and electron donor was documented with 25 cm interval using direct push delivery in a full scale ERD application (Damgaard, 2012). Typical injection intervals can be assumed to vary between 25 and 100 cm, and a more optimistic value of 10 cm is also used in the practical tool.

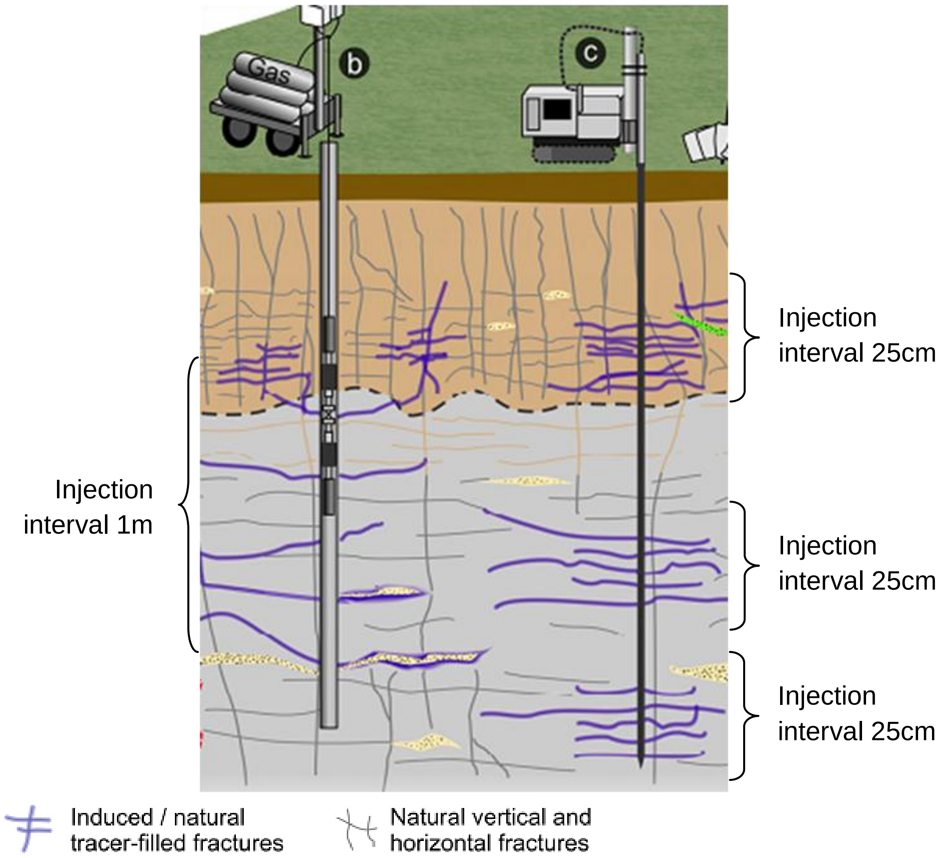

Figure 6 – Distribution of amendments in fractured clay till via e.g. pneumatic fracturing (b) or direct push (c) (modified from Christiansen, 2010)

3.3 Development of bioactive zones

From the injection depth the donor and bacteria can spread into the adjacent matrix to form bioactive zones, where dechlorination can take place (see Figure 7). The extent of dechlorination in the clay till matrix will influence the remediation time. The processes controlling the development of such bioactive zones are still uncertain, but the migration into the clay matrix of *Dehalococcoides* has been documented at three sites undergoing ERD, with microbes found at a distance up to 10-20 cm from high permeability features (Damgaard, 2010).

A bioactive zone of 5cm on one side of a hydraulic fracture was reported 150 days after injection at the ERD pilot scale site, Rugårdsvej (Figure 7), while degradation products were measured more than 25 cm from the fracture 540 days after injection (Scheutz et al., 2010). At a full scale ERD site (Sortebrovej), modeling has shown that bioactive zones in the source zone were limited to 2.5 cm on each side of the naturally occurring sand stringers both 2 and 4 years after injection (Manoli et al., 2012). However thicker bioactive zones were reported in another profile at the same site 4 years after injection, indicating that the development of dechlorination in clay till is very heterogeneous, both between sites and between locations at the same site (Damgaard, 2012). These results are confirmed by core sampling at Gl. Kongevej (full scale ERD site) 4 years after injection where bioactive zones vary between few centimeters around high permeability features to larger zones (up to 1.8 m) (Damgaard, 2012). Finally, a recent laboratory study (Mao et al., 2012) has shown promising results using eletrokinetic to spread bacteria and donor in clay and may help the development of such bioactive zones between injection depths.

The practical tool can be used to assess the influence of the **thickness of bioactive zones** on remediation timeframes, which is assumed to vary between 5 and 25 cm on **one side** of the injection depth, based on the results reported above. In this way also bioactivity in the entire system can be simulated (e.g., 50 cm injection interval with 25 cm bioactive zone).

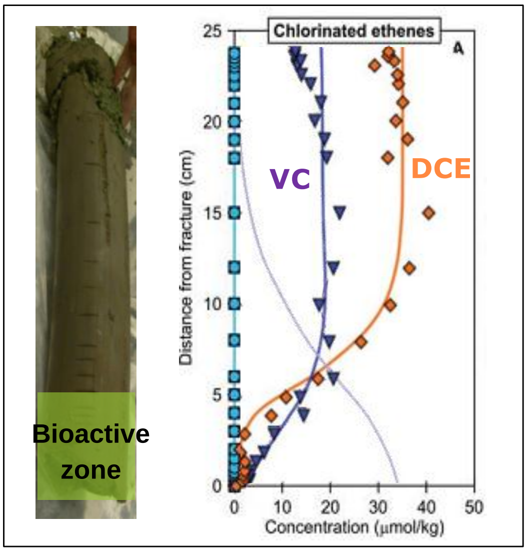

Figure 7 – Illustration of the development of a bioactive zone in the matrix (modified with permission from Scheutz et al., 2010. Copyright 2012 American Chemical Society)

4 MODEL DESCRIPTION

In the Excel-based tool, the mass in the source zone, as well as the mass flux to the aquifer are given for different sets of parameters (cf. Chapter 4.1). The results are based on a numerical model solved in Comsol Multiphysics. The model is based on models developed in Chambon et al. (2010) and Lemming et al. (2010) and takes into account flow and reactive transport in vertical fractures and adjacent matrix. The model represents a 2D cross section across the source zone in the clay till, and a uniform TCE concentration is assumed in the entire source. The natural fracture network is simplified so that only fully penetrating vertical fractures are included, and a constant spacing is assumed. The system is assumed to be fully saturated, and steady-state flow is applied. Horizontal bioactive zones, where dechlorination can occur, are assumed to form in the matrix, adjacent to each injection depth. Sequential reductive dechlorination is modeled in these bioactive zones using Monod kinetics, assuming constant biomass (cf. Chapter 4.1) and non-limiting substrate conditions (Chambon et al., 2010), and the kinetic parameters (maximum growth rates, specific yield and half-velocity constants) are based on laboratory dechlorination experiments (Chambon et al., 2010). The model outputs (remaining mass in the source zone and mass flux to the aquifer) are given per m^2 of source area, and can be converted to reflect the whole source by multiplying this area, under the assumption that the area is similar to a square. The conceptual model and model domain are illustrated in Figure 8.

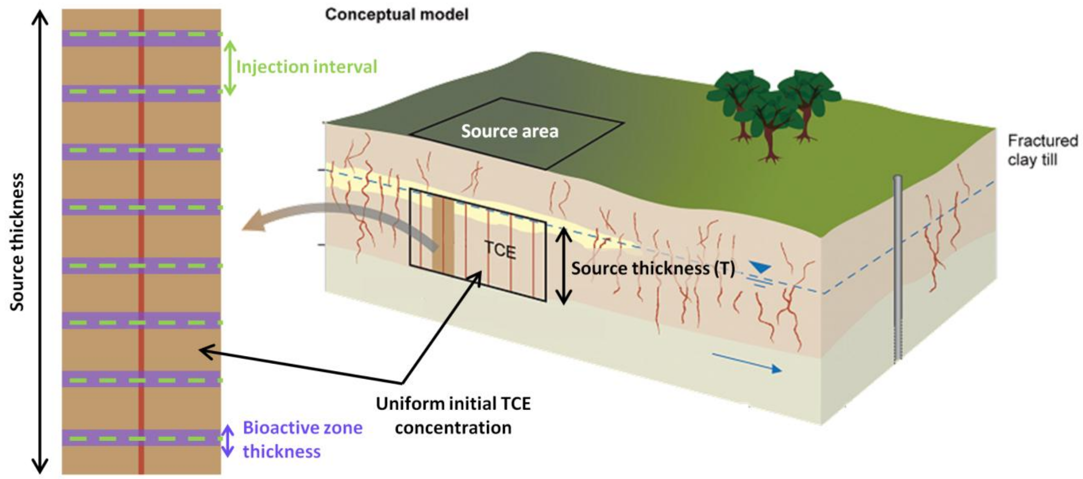

Figure 8 – Conceptual model of the system considered for modeling (modified from Lemming, 2010).

4.1 Model parameters

The model is controlled by many parameters, of which 11 are site and/or remediation design dependent, the other ones being specific to the contaminants and dechlorination (diffusion coefficients and kinetic parameters). The parameters can be divided in three categories:

- *Hydrogeological parameters*: hydraulic conductivity (bulk and matrix), matrix porosity and sorption, net recharge through the clay till and vertical fracture spacing
- *Source parameters*: source zone thickness and initial TCE concentration
- *Design parameters*: Injection spacing, thickness of bioactive zone and biomass concentration in bioactive zones

Of the above parameters, only the source and design related parameters are generally known for a specific site, while default values are often used for hydrogeological parameters, in the absence of site specific data. Therefore the hydrogeological parameters are fixed to default values in the tool and only the source and design parameters can be varied (cf. Chapter 4.4). However in order to illustrate the influence of the hydrogeological parameters on remediation progress and timeframe, sensitivity analysis is performed (cf. Chapter 4.2).

4.2 Sensitivity analysis

The parameters cited above are varied between the maximum and minimum range from the literature and knowledge from ERD in clay tills (for more details please consult Appendix A), and the influence on the remediation time (mass removal and flux reduction) and risk to the aquifer (accumulated contaminant flux to the aquifer over remediation period) is calculated using normalized sensitivity coefficients (Zheng and Bennett, 2002). The resulting sensitivity is shown in Figure 9, where a positive coefficient means that increasing the parameter corresponds to an increase in the output of interest (here remediation time or accumulated flux). It can be seen that sorption and matrix porosity are the most sensitive hydrogeological parameters, while hydraulic conductivity (matrix and bulk) does not influence the remediation time or the flux to the aquifer. The net recharge and the fracture spacing are both moderately sensitive. These hydrogeological parameters are fixed to baseline values in the practical tool (cf. Chapter 4.3), but the reader can refer to the sensitivity graph to assess the influence of the parameter values on the results, in case site-specific data is available.

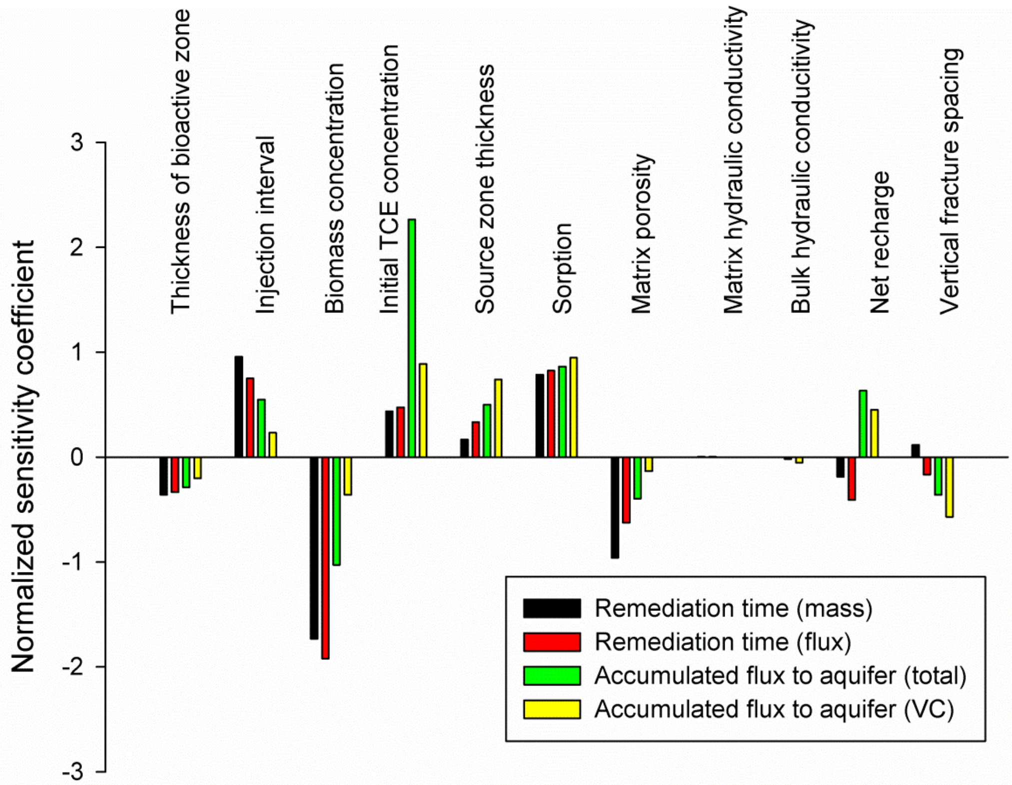

Figure 9 – Sensitivity of the remediation time and accumulated flux to the aquifer for the different parameters

4.3 Fixed baseline parameters

The hydrogeological parameters are fixed to baseline values in the practical tool (Table 2). The values for reductive dechlorination (maximum growth rates, specific yield and half velocity constant) are also fixed. These parameters vary over large range in the literature, and the values can significantly influenced dechlorination efficiency, therefore it has to be noticed that the values used in the practical tool (which are based on literature and experimental data) do not represent the variety of the kinetic parameters values found in the literature. However the biomass concentration can be varied in the practical tool (see Section 4.4), and the influence dechlorination kinetics on ERD in clay till can be assessed.
More details can be found in Appendix A on the fixed baseline parameters.

Table 2 – List of fixed baseline parameters and their values

Parameters	Value
Sorption – distribution coefficient (L/kg)	0.62 (TCE), 0.34 (DCE), 0.18 (VC)
Matrix porosity (-)	0.25
Matrix hydraulic conductivity (m/s)	10^{-10}
Matrix hydraulic conductivity (m/s)	10^{-8}
Net recharge (mm/y)	100
Vertical fracture spacing (m)	1

4.4 Flexible parameters

The practical tool allows the user to vary several site and design parameters and simulate the effect changes in these parameters or different parameter combinations may have on the remediation progress and timeframe.Table 3 shows a list of the available parameters and the range of values that can be used.

Table 3 – List of flexible parameters and parameter values. Suggested default values (if data are unavailable) are marked in green

Choice:	Parameter ranges (default):			
Thickness of bioactive zone (cm):	5	15	25	
Vertical injection interval (cm):	10	25	50	100
Biomass conc. in reaction zone (cells/L):	10^8	10^9	10^{10}	
Thickness of contaminated clay (m):	2	5	10	
Initial conc. of TCE (% of solubility):	1%	2%	10%	80%

4.5 Using the practical tool

A baseline scenario is calculated based on the default values or other baseline parameters chosen by the user. To evaluate the effect of varying different parameters, a model scenario is calculated based on another set of parameters chosen from Table 3.

As stated above, the flexible parameters can be grouped into source parameters (initial concentration of TCE, thickness of contaminated clay) and ERD design related parameters (vertical injection interval, biomass concentration in the reaction zone and thickness of the bioactive zone). Of these parameters, only the vertical injection interval can be chosen and controlled in real full scale applications (assuming successful injections at each depth

interval). The range of values is chosen based on measured or applied values at sites where ERD was applied or considered. For more details please consult Appendix A.
After the baseline and/or scenario values are chosen, pushing the button “Create charts” finds the relevant model runs and displays the results in eight different graphs.
The results shown are time series of mass in the source zone, the leached concentration to the underlying aquifer and the mass flux to the aquifer for the chosen baseline and scenario values.

To support the time series graphs, five graphs show the sensitivity on the model output from varying the variable parameters across the possible ranges given in Table 3. All the graphs can be copied and pasted into the relevant documents for a specific design case. Figure 10 and Figure 11 show examples of time series and sensitivity plots.

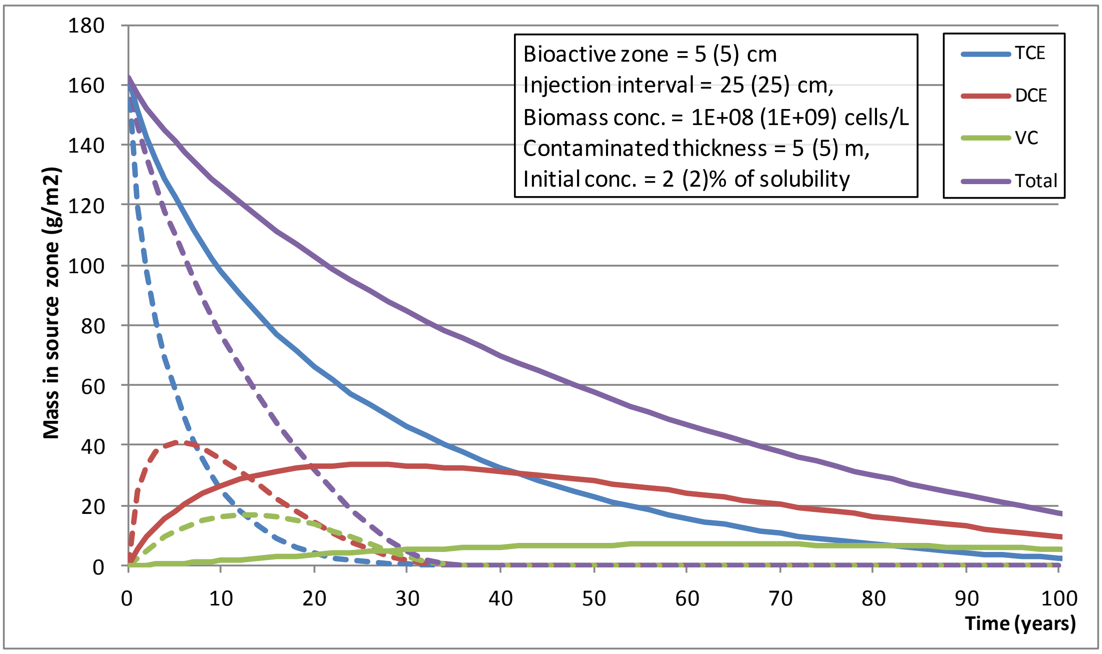

Figure 10 – Example of calculated mass in the source zone over time for chosen baseline values (numbers in parentheses and shown in dotted lines) as well as scenario values (first values and shown in solid lines).

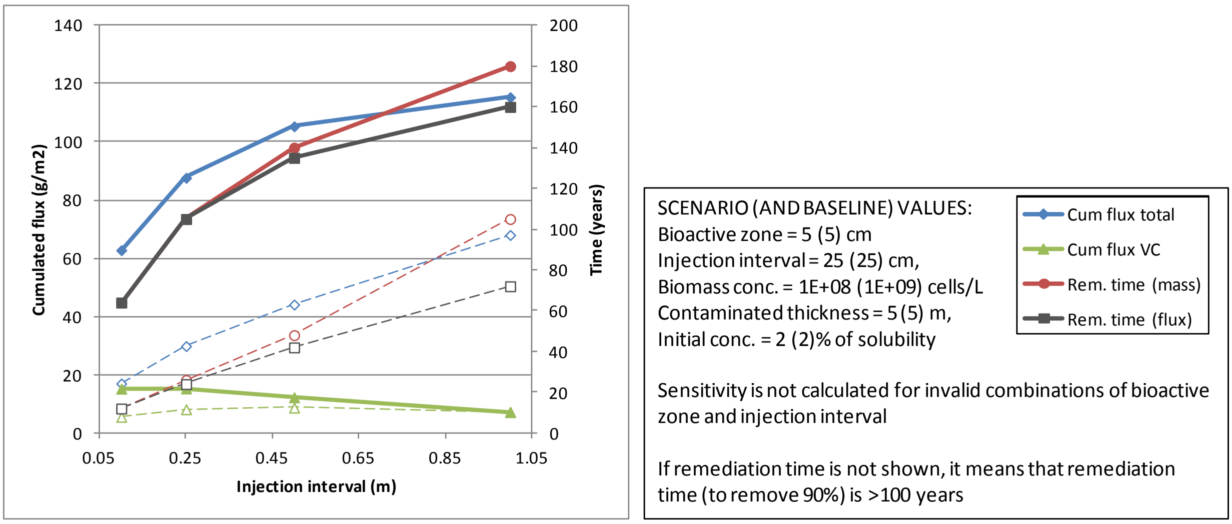

Figure 11 – Example of model output sensitivity on variation of injection interval for baseline (dotted lines) and scenario values (solid lines).

4.6 Model comparison with field performance

Limited data are available for model comparisons, because of the limited numbers of field scale ERD applications in clay tills. However the conceptual model used in the practical tool has been validated with core samples data from Sortebrovej taken 2 and 4 years after donor and bacteria injection, and a good match was found between the modeled and observed data (Manoli et al., 2012). Furthermore comparison of depth-averaged mass removal (based on core samples) at Sortebrovej (2 and 4 years after injection) and Gl. Kongevej (4 years after injection) has shown good agreement with modeled output from the modeling tool (Damgaard, 2012). However there is a lack of validation of the model for long term remediation timeframes, because of the lack of long term dataset and experience for ERD in clay till.

4.7 Model limitations (donor lifetime)

The present practical tool does not include organic substrate consumption (cf. Figure **5**), and therefore cannot be used for assessing donor lifetime after injection in the subsurface. Some tools and methods are available to estimate donor consumption, depending on redox parameters but they cannot be used to assess lifetime in the subsurface and need for reinjection (US Air Force, 2004; Robinson et al., 2009; Robinson and Barry, 2009). A recent modeling study (Manoli et al., 2012) has included donor consumption in a numerical model of ERD in clay till and predicted that the vegetable oil would be depleted 5 years after injection. Experience from other sites undergoing ERD in fractured clay tills (Sortebrovej and Gl. Kongevej) have shown that similar timeframes are expected for donor lifetime, corresponding to a 5 year injection frequency (Region Hovedstaden, 2011; Damgaard, 2012). Using the model developed in Manoli et al. (2012), the influence of sulfate, iron, TCE and methanogens initial concentration on donor lifetime is illustrated in Figure 12. For this case sulfate and methanogens are the most sensitive parameter for donor lifetime, in contrast to Fe(III) and TCE, but this depends on the site, the thickness of the bioactive zone, the bacterial populations, etc. Long term electron donor consumption is mainly influenced by methanogenesis, as sulfate depletion usually occurs fast after donor injection.

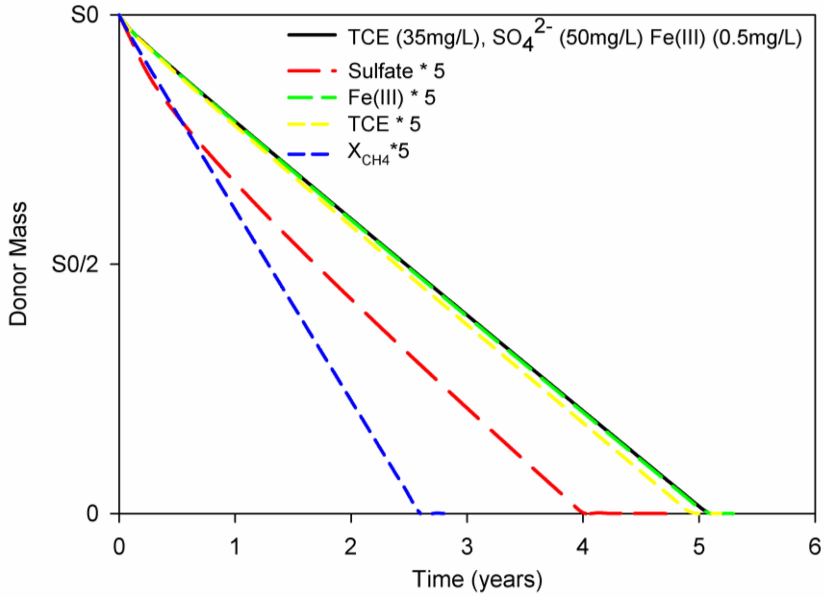

Figure 12 – Influence of TCE, Iron and sulfate initial concentration on donor lifetime, based on Manoli et al. (2012)

5 RISK REDUCTION AND REMEDIATION OBJECTIVES

The objective of remediation of contaminated sites that pose a risk to the groundwater is to protect the resource for drinking water usage. Often, the long-term objective of a cleanup is to achieve a specific concentration (often below MCL guidelines for groundwater) at a specific point of compliance (see Figure 13). A methodology for determining cleanup criteria has been developed as part of a previous project by the Danish EPA (Danish EPA, 2011).
In order to make this long-term objective operational, it is necessary to understand the relationship between the source concentration and the concentration at the downgradient point of compliance, so that the long-term criteria can be transformed into a short term local criteria at the source. The short term criteria at the site can then be used as the basis for an assessment of remediation progress and to determine the stop criteria for cleanup.

5.1 Remediation objectives for ERD sites

Defining a separate remediation objective for the source zone in the clay till is necessary for ERD sites. This source zone remediation objective is useful for determining when the stimulation with donor and bacteria can be terminated. It is possible to determine this by calculating backwards from the long term remediation objective to an acceptable concentration level in the source zone.
Remediation objectives for the source zone should be defined based on total concentrations and not only water concentration, because water concentration can be misrepresentative of the system as they originate from the more reactive zones in the clay till. Mass depletion in the source zone is also an expression of reduced total concentrations in the source zone. Moreover mass depletion provides an estimation of the remediation timeframe.

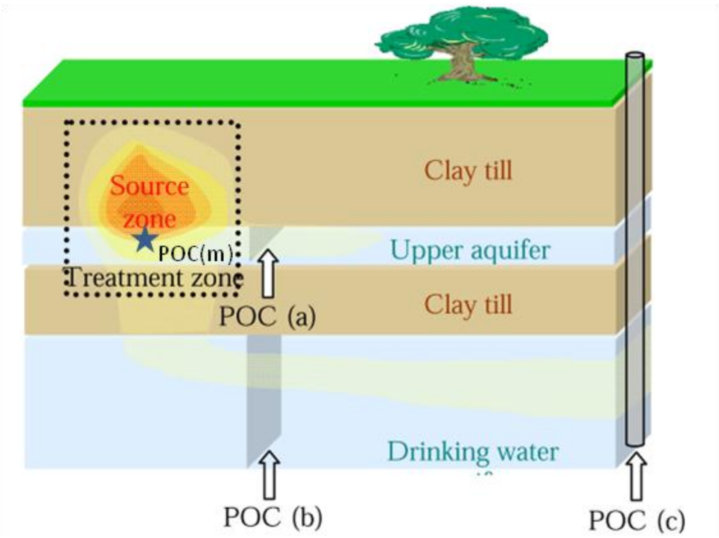

Figure 13 - Points of compliance. POC(m) is located directly below the source zone. POC (a, b,c) are examples of long term points of compliance (modified from Danish EPA, 2009)

For fractured clay till source zones it should be kept in mind that defining a remediation criterion as a reduction in contaminant flux with a certain factor does not imply that the average source concentration is reduced with the same factor. This is due to the fact that the contaminant flux depends on the concentration in the fracture outlet and not in the average source concentration. This practical tool provides a prediction of mass depletion in the source zone, as well as predicted values of concentration and flux at a point of compliance directly below the treated source zone (see Figure 13). All of these outputs can be used as clean-up criteria.

5.2 Mass depletion vs. mass discharge

When remedial projects are initiated, it is often based on an assumption that a reduction in contaminant mass in the source area will cause a corresponding reduction in the mass discharge affecting groundwater. International research has shown that there is rarely a linear relationship between these factors, which means it can be difficult to predict the effect on groundwater resources a given remedial action gets.

A simple way to describe the relationship between the reduction in mass and the flux is the "gamma" model, where the relative flux and the relative mass described by the term Γ, (Falta et al., 2005):

$$\frac{J(t)}{J(0)} = \left(\frac{M(t)}{M(0)}\right)^{\Gamma}$$

Gamma (Γ) is an empirical factor that incorporates source architecture, flow patterns and mass exchange processes. A gamma-value of 1 indicates a linear relationship between mass and flux reductions.
The function is illustrated on Figure 14, which shows that when the relative mass is reduced from 1 to 0.5, the flux is reduced to 0.25, 0.5 and 0.7 for Γ factors of 0.5, 1 and 2 respectively In the international literature review of a number of cases show that Γ usually lies between 0.5 and 2, and usually below 1 (where the relative flux reductions are less than the mass reduction).

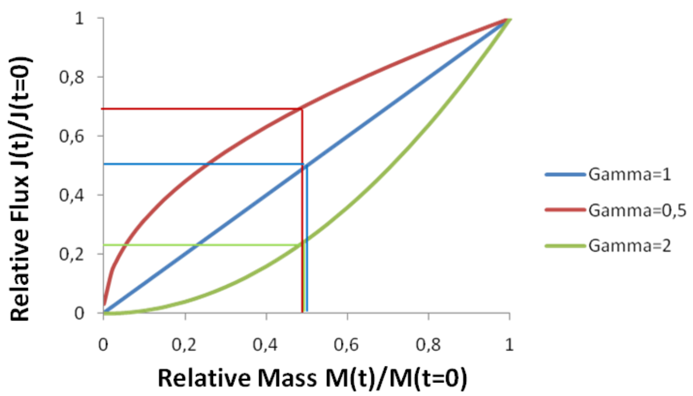

Figure 14 – Illustration of the mass removal/flux reduction relationship with the "gamma" model

Based on the model results, enhanced reductive dechlorination in clay till will rarely result in mass depletion higher than 90% within several decades. However, if high dechlorination rates are sustained in the zones that control flux to the aquifer, the mass discharge can be reduced to a higher degree. It is therefore advisable to use mass discharge as a remediation objective for ERD projects.

6 SUGGESTIONS

Several improvements could be made on the modeling tool, in order to obtain a better representation of the reality, both on the modeling of the geological media and the processes:

- **Adapting the model to a more realistic and flexible geological setting**

The present model takes into account only the vertical fully penetrating fractures, but it is known that the fracture networks have much more diversity and other features could be included in the model, like horizontal fractures, sand lenses, sandstringers, and partially penetrating vertical fractures (Danish EPA, 2009).

- **Extending the model to include flow through the matrix.** The present model assumes that the water is only flowing through the fracture network (and not in the matrix), but for cases where the clay has a higher hydraulic conductivity (due for example to a high sand content), it can be expected that water will also flow in the matrix. The hydraulic modeling could be improved to take this phenomenon into account and to produce an accurate water balance in the system (Danish EPA, 2009).

- **Include donor consumption processes in the model** The present model assumes that substrate and electron donor are available without limitation. In order to simulate the lifetime of the injected substrate and to produce some estimations of the required injection frequency for a given site, the reactive model could include the consumption of the injected substrate during dechlorination (Danish EPA, 2009).

- **Expand the model to calculate methane production** Methane production could also be considered, as it represents a risk when applying reductive dechlorination at a site.

- **Expand the model to take abiotic degradation processes into account.** Recent characterization of the degradation processes at 3 sites has shown that abiotic degradation processes may play a key role into converting cDCE to acetylene, ethene and ethane without generation of VC (Damgaard, 2012).

- **Develop tools to help predict the development of the reaction zones in the matrix.** The thickness of these zones is one of the most important parameters for predicting the extent and time frame of reductive dechlorination. The controlling parameters for the development of such zones vary and include: the thickness of the high permeability features (cm for hydraulically created fractures vs. mm for naturally occurring sandstringers), donor availability, redox conditions, and contaminant concentrations (Damgaard, 2012). At the moment predicting the extent of reactive zones is very difficult, but such predictions may be easier for well characterized sites, or when designing a second injection event at a specific site.

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Appendix A – Parameter values

The parameter values (baseline and range) have been set up based on the literature and knowledge from sites where ERD was applied or considered. A list of the parameters, with the values and range considered, is provided in the three tables below.

Table 1 – Values of the fixed parameters (not site specific) used in the practical tool.

Parameters		Fixed value	References
Free diffusion coefficient (m^2/s)	TCE	$6.2*10^{-10}$	(US EPA, 2012)
	DCE	$7.0*10^{-10}$	
	VC	$8.2*10^{-10}$	
Tortuosity (-)		Equal to porosity	(Parker et al., 1994)
Bulk density (kg/L)		(1 – porosity)*2.65	
Longitudinal dispersivity in matrix (m)		0.1	(Sudicky and McLaren, 1992)
Transverse dispersivity in matrix (m)		0.005	
Longitudinal dispersivity in fracture (m)		0.1	(Jørgensen et al., 1998)
Maximum growth rate (d^{-1})	TCE	2	(Chambon et al., 2010a)
	DCE	0.38	
	VC	0.14	
Half velocity constants (µmol/L)	TCE	10	(Chambon et al., 2010a; Cupples et al., 2004)
	DCE	9.9	
	VC	2.6	
Specific yield (cell/µmol)		$5.1*10^8$	(Cupples et al., 2004)
Inhibition constant (µmol/L)	TCE	10	
	DCE	3.6	
	VC	7.8	

Table 2 – Values and range for hydrogeological parameters (fixed to baseline values in the practical tool).

Parameters		Fixed value	Range (for sensitivity)	References
Sorption – Distribution coefficient (L/kg)	TCE	0.62	0.15 – 1.5	(Lu et al., 2011)
	DCE	0.34	0.08 – 0.83	
	VC	0.18	0.04 – 0.43	
Matrix porosity		0.25	0.2 – 0.35	Compilation from 21 Danish sites (Christiansen and Wood, 2006)
Matrix hydraulic conductivity (m/s)		10^{-10}	$10^{-12} – 10^{-9}$	(Fredericia, 1990; Region Hovedstaden, 2009; Region Syddanmark, 2009)
Bulk hydraulic conductivity (m/s)		10^{-8}	$5*10^{-9} – 5*10^{-7}$	(Region Hovedstaden, 2011; Fredericia, 1990; Harrar et al., 2007; Region Syddanmark, 2007)
Net recharge (mm/y)		100	10 – 150	(Harrar et al., 2007)
Vertical fracture spacing (m)		1	0.5 – 2	(DTU Miljø, Region Hovedstaden & Danish EPA, 2009)

Table 3 – Baseline values and range for flexible parameters in the practical tool.

Parameters	Baseline value	Range	References
Thickness of bioactive zone (cm)	5	5 – 25	(Region Hovedstatden, 2011; Damgaard, 2012; Manoli et al., 2012; Scheutz et al., 2010)
Vertical injection interval (cm)	25	10 – 100	(Chambon et al., 2010b; Christiansen et al., 2010; Region Hovedstatden, 2011)
Biomass conc. in reaction zone (cells/L)	10^9	$10^8 – 10^{10}$	(Region Hovedstatden, 2011; Damgaard, 2012; Scheutz et al., 2010; Region Syddanmark, 2011)
Thickness of contaminated clay (m)	5	2 – 10	
Initial conc. of TCE (% of solubility)	2	1 – 80	

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