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DTU Environment
Department of Environmental Engineering

PhD Thesis
November 2015

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Preface

The thesis is organized in two parts: the first concerns risk assessment of contaminated sites and provides the context for paper I, II and III (See list below). The second part presents a discussion of uncertainty in risk assessment, and provides the context of paper IV (See list below). The papers will be referred to in the text by their paper number written with the Roman numerals **I-IV**.

I. Thomsen, N.I., Milosevic N. and Bjerg, P.L., 2012, Application of a contaminant mass balance method at an old landfill to assess the impact on water resources, Waste Management, 32: 2406-2417, doi: 10.1016/j.wasman.2012.06.014.

II. Milosevic N., Thomsen, N.I., Juhler, R.K., Albrechtsen, H.-J. and Bjerg P.L., 2012, Identification of discharge zones and quantification of contaminant mass discharges into a local stream from a landfill in a heterogeneous geologic setting, Journal of Hydrology, 446-447: 13-23, doi: 10.1016/j.jhydrol.2012.04.012.

III. Rasmussen, J.J., McKnight, U.S., Loinaz, M.C., Thomsen, N.I., Olsson, M.E., Bjerg, P.L., Binning, P.J. and Kronvang, B., 2013, A catchment scale evaluation of multiple stressor effects in headwater streams, Science of the total environment, 442: 420-431, doi: 10.1016/j.scitotenv.2012.10.076.

IV. Thomsen, N.I., Troldborg, M., McKnight, U.S., Bjerg, P.L., Binning, P.J. (2015). A Bayesian Belief Network approach for assessing uncertainty in conceptual site models at contaminated sites, Submitted to Journal of Contaminant Hydrology.

In this online version of the thesis, paper **I-IV** are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from DTU Environment, Technical University of Denmark, Miljøvej, Building 113, 2800 Kgs. Lyngby, Denmark, info@env.dtu.dk.

The following reports and publications, were co-authored during the PhD, and will be referred to in the thesis.

Overheu, N. D., Tuxen, N., Thomsen, N.I., Binning, P.J., Bjerg, P.L. and Skou, H., 2011, Fastlæggelse af oprensningskriterier for grundvandstruende forureninger (English title: Determination of clean-up criteria for contaminated sites threatening groundwater), Miljøprojekt Nr. 137 2011, Miljøstyrelsen, Miljøministeriet.

Chambon, J., Thomsen, N.I., Kessler, T., Nilsson, B., Klint, K.E., Binning, P.J. and Bjerg, P.L., 2011, Risikovurdering af forurenede grunde på Vadsbyvej i forhold til Vandressourcen og Soderup Vandværk (English title: Risk assessment of contamianted sites at Vadsbyvej with regards to the water ressources and Soderup water works), DTU Environment and The Capital Region of Denmark.

Copenhagen, August 2015

Nanna Isbak Thomsen

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Sincerely

Nanna Isbak Thomsen

Copenhagen August 2015

Summary

A large number of contaminated sites threaten the water resources worldwide. The means available are insufficient to cover the expenses associated with investigation and remediation at all these sites. Site managers are therefore posed with the challenge of distributing the financial resources available between sites and choosing between the need for further investigation or remediation. This is a question of prioritizing the sites that pose the greatest risk, and it is a matter of making decisions under uncertainty. Both tasks require a structured assessment of the risk posed by the contaminated sites.

In a conventional risk assessment of a contaminated site, risk is evaluated by assessing whether a concentration guideline is exceeded at a specific point of compliance in the water resource of interest. If the guideline is exceeded, it is concluded that the site poses a risk. However, a contaminated site may pose a threat to multiple water resources, or multiple contaminated sites may threaten a single water resource. For more advanced risk assessments, it is therefore relevant to develop methods that can handle this challenge.

In this thesis, four contributions are made to the field of contaminated site risk assessment. They include: 1) the use of mass discharge estimates in the assessment of the impact of old unlined landfill sites in clay till geology on multiple water resources; 2) the characterization of the spatial variability and attenuation of the leachate from landfills located in clay till geology and the impact on streams; 3) the characterization of the dominating anthropogenic stressors in headwater streams at catchment scale and 4) the development of a method for assessing the uncertainty in conceptual site models.

Advances in risk assessment methods for contaminated sites have shown that mass discharge estimates are useful when considering the impact of a contaminated site on multiple water resources and between multiple sites. Mass discharge estimates were applied at Risby landfill, an old and unlined landfill located adjacent to Risby stream. Old unlined landfill sites can be especially challenging in a risk assessment context, because they often are located near streams and wetlands, and because the source can be very heterogeneous both with regards to strength and composition. In addition Risby landfill is located in an area with a complex geological setting dominated by clay till. A mass balance approach was developed in order to estimate the impact of old unlined landfills on multiple water resources. The contaminant mass discharge was estimated for three leachate indicators:

chloride, dissolved organic carbon and ammonium. From the landfill, the mass discharge of chloride was estimated to 9.4 ton/year. This resulted in an impact on the deep limestone aquifer of 1.4 ton/year. The impact on Risby Stream located down-gradient of Risby Landfill was approximately 31 kg/year, causing elevated concentrations of leachate indicators (chloride, dissolved organic carbon and ammonium) in the groundwater and the stream.

Based on the results of the mass balance method, significant spatial heterogeneity was expected in the contaminant mass discharge pattern to Risby Stream. To obtain a better understanding of this impact, a detailed investigation was conducted. The investigation involved an array of methods including studies of the site hydrogeology, groundwater and surface water discharge and landfill leachate composition and distribution. The methods included driven wells, seepage meters, grab samples, measurement of the temperature gradient in the stream bed and samples collected in traditional groundwater boreholes. The detailed investigation revealed considerable variation in source composition, source strength and redox parameters. The variation was caused by the complex clay till geology and the heterogeneous nature of the landfill source. The impact on Risby Stream, based on the detailed investigation, showed significant seasonal variation and was largest during the dry summer season. Only a small part of the contaminant mass discharge in the stream could be explained by discharging groundwater. It is therefore likely that other sources such as seepage from ponds and surface run-off contribute to the impact on the stream. The analysis of the chemical effect of Risby landfill on the groundwater and surface water improved the basis for conducting investigations and risk assessments at landfills located in clay till and adjacent to streams. But they did not take into account the potential effects of the stream ecology, required under the European Water Framework Directive (WFD) (2000/60/EØF).

The ecological effect must be studied at the catchment scale, and an approach was developed and applied for the Hove catchment, which contains Risby landfill. The ecological effects of identified anthropogenic stressors were studied in 11 headwater streams. Head water streams are sometimes disregarded for mitigation activities under the European WFD, despite their importance for supporting the ecological quality in higher order streams. The anthropogenic stressors in the catchment include agriculture, residential settlements (urban discharges) and multiple contaminated sites. In all streams, ecological impacts were documented, including the physical quality of the habitats (hydromorphology), water quality (chemical) and impairment of the benthic macroinvertebrate community. A robust rank-ordering of the anthropogenic stressors, however, could not be made. This suggests that targeted mitigation efforts on single stressors in the catchment are unlikely to substantially improve the conditions these streams. The results of the catchment scale investigation suggest that headwater streams are important to consider in mitigation plans, and need to be evaluated holistically.

Risk assessments of contaminated sites are generally associated with large uncertainties, it is important to include these in risk assessment, because this allows for more robust decision-making. Uncertainty in risk assessments originates from multiple sources, including e.g. input and parameter uncertainty, and uncertainties associated with the conceptual site model (CSM). The CSM describes the most important fate and transport processes at the contaminated site in a simplified manner and is used to communicate how the site operates. The complexity of the CSM usually reflects the detail of the investigations. A literature review suggested that the most important type of uncertainty may be the uncertainty concerning the CSM but it is not routinely accounted for. In order to evaluate the uncertainty concerning the CSM, a Bayesian Belief Network (BBN) approach was developed. The approach determines the belief for each of several CSMs that may represent a given contaminated site. This is done based on a variety of data types and/or expert opinion. The method was applied to the Vadsbyvej 16A study site, located within the Hove Catchment. The geology at the site is similar to that at Risby landfill, i.e. dominated by clay till, in which sand lenses and fractures may create a complex network of preferential flow paths. The contaminant source consists of chlorinated solvents (PCE and TCE). Four different CSMs were developed that could potentially represent the contaminated site. Weights for each of the four CSMs were assessed sequentially based on data from three increasingly detailed investigations (a screening investigation, a more detailed investigation, and an expert consultation). This demonstrates that the method is flexible and that the beliefs can be assessed based on different types and levels of detail in the data.

This work has addressed some important challenges in contaminated sites risk assessment and made great advances. These advances are now being applied by regulatory authorities, leading to improved management practices for contaminated sites.

Dansk resume

Et stort antal forurenede grunde truer vandressourcerne på verdens plan. De forventede udgifter overstiger langt budgetterne for kortlægning og oprensning. Myndighederne står derfor med en prioriterings opgave, som består i at fordele de økonomiske ressourcer mellem de mange kortlagte forurenede grunde. For at lykkedes med opgaven bør man prioriterer indsats på de grunde, som udgør den største risiko. Da der er et begrænset datagrundlag, er denne prioritering et spørgsmål om at tage beslutninger under usikkerhed.

En risikovurdering af en forurenet grund udføres traditionelt ved at undersøge, om et kvalitetskriterie er overskredet i en bestemt afstand fra forureningskilden. Hvis kvalitetskriteriet er overskredet, vurderes det at grunden udgør en risiko. Virkeligheden er ofte mere kompleks end som så. En enkelt forurenet grund kan udgøre en risiko for flere vandressourcer, og/eller flere forurenede grunde kan påvirke en enkelt vandressource. Det er derfor relevant at udvikle metoder, som kan håndtere dette.

Denne PhD afhandling bidrager til risikovurdering af forurenede grunde på fire områder: 1) anvendelse af massefluksestimater i forbindelse med estimeringen af påvirkningen fra lossepladser, beliggende i moræneler som på omkring liggende vandressourcer; 2) karakterisering af fordelingen og nedbrydningen af perkolat fra en losseplads i moræneler, og hvordan den påvirker et vandløb; 3) karakterisering af de vigtigste menneskeskabte stress faktorer i mindre vandløb (1. og 2. ordens) på oplandsskala og 4) udviklingen af en metode, som kan kvantificere den konceptuelle usikkerhed i forbindelse med forureningsundersøgelser.

Forskning har vist at massefluksestimater er en god metode til at vurdere påvirkningen fra en forurenet grund på flere vandressourcer. Massefluksestimater blev derfor anvendt til at estimere påvirkningen fra en losseplads på grundvand og et mindre vandløb. Undersøgelsen blev gennemført på Risby Losseplads, som er en gammel losseplads uden membran eller anden perkolat opsamling. Nedstrøms for lossepladsen ligger Risby Å. Ældre lossepladser uden membran og perkolat-opsamlingssystem kan være udfordrende i en risikovurderingssammenhæng, fordi de ofte er beliggende nær vandløb og/eller vådområder, og de således udgør en risiko både for overfladevand og grundvand. Derudover er lossepladser meget heterogene forureningskilder, det gælder både styrke og sammensætning af

perkolatet. Desuden er Risby losseplads beliggende i et område med en meget kompleks geologi som domineres af moræneler. En massebalance-metode blev udviklet med det formål at estimere forureningspåvirkningen fra ældre lossepladser uden membran på omkringliggende vandressourcer. Forureningspåvirkningen blev estimeret for tre almindelige komponenter i lossepladsperkolat: klorid, opløst organisk kulstof og ammonium. Massefluksen af klorid fra lossepladsen var 9.4 ton/år. Dette resulterede i en påvirkning af den primære akvifer på 1.4 ton/år og i en påvirkning på Risby Å på 31 kg/år. Der blev målt forhøjede koncentrationer af klorid i begge vandressourcer.

Resultaterne fra massebalancemetoden indikerede, at massefluksen til Risby Å ville variere meget. Der blev derfor igangsat en detaljeret undersøgelse, som havde det formål at opnå en bedre forståelse af påvirkningen af Risby Å. Undersøgelsen inkluderede en lang række metoder til karakteriseringen af bl.a. hydrogeologien, grundvands-overfladevandsinteraktionen, og fordelingen af lossepladsperkolatet. Undersøgelsen anvendte bl.a. flukskamre, grab samples og måling af temperaturgradienter mellem å-bunden og å-vandet. Resultaterne viste stor variation i kompositionen af forureningskilden mht. styrke og redox-parametre. Variationen skyldes den komplekse geologi og lossepladsens heterogene natur. Forureningens påvirkning på Risby Å varierede både i styrke, distribution og med også årstiden. Den var størst om sommeren når flowet i Risby Å er mindst. Det var kun en mindre del af massefluksen af losseplads perkolat relaterede stoffer i Risby Å som kunne tilskrives indstrømmende grundvand. Det er derfor sandsynligt, at andre kilder langs åen har bidraget til massefluksen. Der kunne for eksempel være tale om overfladeafløb, dræn og udsivning fra mindre pytter langs åen. Studiet af den kemiske påvirkning fra Risby Losseplads på Risby Å forbedrede generelt vidensgrundlaget for at udføre undersøgelser og risikovurderinger af lossepladser beliggende i moræneler, som påvirker vandløb. Det bidrog dog ikke med information om den biologiske status i vandløbene, hvilket er et krav i vandrammedirektivet (2000/60/EØF).

Den biologiske effekt af forurenede grunde på vandløb bør undersøges på oplandsskala. Risby Losseplads er beliggende i Hove-oplandet og her blev et studie af de menneskeskabte påvirkninger på den biologiske status i 11 mindre vandløb gennemført. Mindre vandløb er ikke altid inkluderet i indsatsen i forbindelse med vandrammedirektivet, selv om deres biologiske status ofte er vigtigt for at sikre et godt biologisk miljø i vandløb med en højere orden. De menneskeskabte stress-faktorer i Hove Å oplandet er landbrug, bebyggelse (udledning af spildevand) og forurenede grunde. Der blev dokumenteret påvirkning af biologien i alle vandløb, dette inkluderede den fysiske kvalitet af habitaterne, vand kvaliteten (kemisk) og påvirkning af de bentiske makroinvertebrater. Det var ikke muligt at opnå en rangering af de menneskeskabte stressfaktorer. Dette viser, at tiltag, som skal begrænse påvirkningen på den biologiske status i oplandet, bør 1) være holistiske og ikke adressere specifikke stressfaktorer alene og 2) inkludere mindre vandløb.

Risikovurdering af forurenede grunde er generelt forbundet med store usikkerheder, og det er vigtigt at inkludere disse, da det er med til at sikre et mere robust beslutningsgrundlag. Der er mange kilder til usikkerhed forbundet med risikovurdering, som for eksempel input og parameterusikkerhed, samt usikkerheder mht. den konceptuelle model osv. Et litteraturstudie har indikeret, at usikkerheden forbundet med den konceptuelle model ofte er den væsentligste kilde til usikkerhed og den er derfor vigtig. En konceptuel model beskriver de mest relevante stoftransportsprocesser for den forurenede lokalitet. Detaljeringsgraden af den konceptuelle model bør reflektere detaljeringsgraden i de undersøgelser, den bygger på. Som en del af denne PhD blev det undersøgt, hvorvidt en metode, der er baseret på Bayesian Belief Networks, kan anvendes til at kvantificere usikkerheden i forbindelse med den konceptuelle model. Metoden beregner en vægt for hver af flere mulige konceptuelle modeller. Fordelen ved at bruge Bayesian Belief Networks er, at de kan benytte mange forskellige typer af data (for eksempel koncentrationsmålinger og ekspertudsagn). Metoden blev testet på Vadsbyvej 16A, som er beliggende i Hove oplandet. Geologien på grunden ligner den på Risby Losseplads, og domineres af moræneler med sandlinser. Moræneleret er muligvis opsprækket. Forureningskilden består af klorerede opløsningsmidler (PCE og TCE). Der blev udviklet fire forskellige konceptuelle modeller som alle er mulige repræsentationer af forureningssituationen. Der blev beregnet tre sæt af vægte (de såkaldte beliefs) på baggrund af tre på hinanden følgende undersøgelser (en indledede undersøgelse, og to videregående undersøgelser). Dette demonstrer metodens fleksibilitet mht. datakvalitet.

Arbejdet i denne PhD har adresseret vigtige udfordringer og opnået væsentlige forbedringer i forbindelse med risikovurdering af forurenede grunde. De opnåede forbedringer bliver i dag anvendt i forbindelse med indsatsen omkring risikovurdering.

Table of contents

1 Introduction

1.1 Background and motivation

There are as many as 2,5 million potentially contaminated sites in Europe, of these about 340.000 are highly likely to be contaminated (EEA, 2014). These sites pose a significant threat to the soil and water resources. The task of investigating and performing remediation is costly and the economic resources are scarce given the large number of sites. In this context risk assessment is the most important tool needed for prioritizing efforts and decision making (Cushman et al. 2001; Ferguson et al., 1998). Traditionally risk assessment of a contaminated site has focused on estimating whether the contaminant concentration exceeds a given guideline value; often represented by the maximum contaminant level (MCL) (US EPA, 2009).

Recently it has been discovered that mass discharge estimates are useful in a risk assessment context because they: 1) estimate the total impact of a contaminated site on a specific water resource (Einarson and Mackay, 2001; Hadley and Newell, 2012; Newell et al., 2011; Nichols, 2004), 2) quantify the total effect of remediation (ITRC, 2010), 3) can be used to prioritize between different contaminated sites (Enzenhoefer et al., 2015; Jamin et al., 2012; Newell et al., 2011; Pizzol et al., 2011; Pizzol et al, 2015 and Troldborg et al., 2008) and 4) can be used to assess and compare the effect of a single contaminated site on multiple water resources (Thomsen et al., I).

The implementation of the EU Water Framework Directive (WFD) (2000/60/EC) has led to increasing focus on risk assessment considering multiple water resources, ultimately requiring member states to obtain “good status” for all water bodies (McKnight et al., 2010; McKnight et al., 2012). Contaminant mass discharge estimates are especially useful in this context and can be applied both at both local and catchment scale.

1.1.1 Single site risk assessment

A single contaminated site may impact multiple water resources (Ford et al., 2011; Lambou et al., 1990; Lisk, 1991; Lorah et al., 2009; Thomsen et al. I). The assessment of this impact is not trivial (Ford et al., 2011; Lorah et al., 2009; Newell et al., 2011) and methods that can handle it are urged by the implementation of the WFD (2000/60/EC).

The traditional risk assessment approach provides an estimate of the impact at a given point in the water ressource. However the application of contaminant mass discharge estimates can potentially provide an estimate of the total impact on the resource (Einarson and Mackay, 2001; Newell et al., 2011) and make it easier to compare the impacts on different resources (Newell et al., 2011; Thomsen et al., I).

Old unlined landfills are a type of contaminated site that usually constitutes a risk for contaminating the groundwater. In addition, landfills are often located near surface water resources (Lambou et al., 1990; Lisk, 1991). They therefore potentially have an impact on both groundwater and surface water. Landfills have very complex source architecture, both with respect to distribution and composition of the leachate (Christensen et al. 2001). Landfills located in sandy geology have been subject to intense studies landfills (Christensen at al., 2001) studies of landfills located in clay till geology and/or their impact on surface water are few (Bjerg et al., 2011).

As part of this thesis, a mass discharge based mass balance method was developed that is suitable to estimate the impact of landfills located in a clay till geology on multiple water resources. The method was applied to Risby Landfill, a study site located west of Copenhagen and adjacent to Risby Stream (Thomsen et al. I). During the investigation of Risby Landfill, it was particularly hard to accurately account for the impact on Risby Stream. In fact an array of methods was needed in order to delineate the zones of groundwater discharge to and couple it to the concentrations observed in the landfill (Milosevic et al., II).

The mass balance method and the detailed study of the impact on Risby stream provided results that are useful in relation to the implementation of the Water framework Directive. But they also provide general knowledge about the leachate behavior in clay till geology.

1.1.2 Risk assessment at the catchment scale

Prioritization of contaminated sites to address those sites that pose the greatest risk requires risk assessment approaches at larger scales. Large scale assessment makes it possible to compare the risks associated with multiple contaminated sites and other stressors on one or more water resources.

Various methods have been developed for risk assessment at larger scales. For an initial screening of the groundwater vulnerability, the DRASTIC tool is useful (Aller et al., 1987). The DRASTIC tool assigns scores to different indicators of aquifer vulnerability (e.g. depth to groundwater, recharge, top layer geology). This is commonly done in a GIS environment. The aim is to identify areas that are susceptible to contamination. Another vulnerability mapping tool was presented by Zabeo et al. (2011), who map the vulnerability of receptors (humans, surface water, groundwater and protected areas) by combining multi-criteria decision techniques with spatial analysis.

Contaminated site prioritization follows the initial vulnerability mapping and requires methods that calculate and compare the impact of a number of contaminated sites in a specific area. Examples from the literature are Enzenhoefer et al. (2015), Jamin et al. (2012), Overheu et al, 2014, Pizzol et al. (2011), Pizzol et al (2015), and Troldborg et al. (2008). The above mentioned are primarily frameworks that focus on human health risk from contaminated groundwater (the exception is Pizzol et al. (2011) who include surface waters).

Working at larger scales makes it possible to include the effect of stressors other than contaminated sites and thereby also study their significance. Methods that can assess the effect of multiple stressors on ecological health and work to disentangle their respective contribution have been urged by several authors (e.g. Beketov and Liess, 2012; Segner, 2011; Statzner and Beche, 2010).

As a part of this thesis, an approach was developed that 1) attempts to identify the main stressors impacting headwater streams at the catchment scale, 2) assesses the total impact to benthic macroinvertebrate communities, and 3) gives guidance on how to design mitigation activities at the catchment scale.

The study was conducted in the Hove Catchment, where 11 headwater streams were studied. The focus on headwater streams is controversial because these are not necessarily included in the Water Framework Directive (2000/60/EC). We focused on this knowledge gap because ecosystem health in higher order streams often is connected to the health of the catchment's headwater streams (Rasmussen et al. III).

1.1.3 Uncertainty in risk assessment

The assessment of contaminated site impact on water resources begins with the construction of a CSM. The CSM is used as a framework for site understanding and is the first step in the construction of mathematical models of a site for risk assessment and site management (US EPA, 1996).

A CSM "illustrates contaminant distributions, release mechanisms, exposure pathways, migration routes, and potential receptors" (US EPA, 1996). The CSM evolves in complexity as more data concerning the contaminated site is collected (ASTM Standard E2531, 2009; McMahon et al., 1999; Neuman and Wierenga, 2003; Suter, 1999; US EPA, 1996; US EPA, 2002). Regardless of how much data is collected, the CSM will always be uncertain due to the complexity of the subsurface and contaminant spills. It has been suggested that the uncertainty concerning the CSM is a major source if not the most important source of uncertainty (Bredehoeft, 2005; Refsgaard et al., 2006)

The heterogeneity of contaminated sites and the limited resources available to conduct investigations means that site descriptions and risk assessment modelling are uncertain. The uncertainty manifests itself in many ways, in the conceptual model, the parameters, the applied model algorithm, and in the input data. The uncertainty concerns not only the magnitude of the impact (the maximum concentration or mass discharge), but also the time of arrival of the impact at the receptor and duration of the impact (Beven, 2009; Frind et al., 2006 and Walker et al., 2003,).

Actual risk assessments conducted by practitioners often do not consider uncertainty at all, or they limit the consideration to listing the sources of uncertainty, or apply the precautionary principle and use the worst case parameters in calculations. Including quantified uncertainties in risk assessments is important because it determines the reliability of the investigations and can clarify if more investigations are needed in order to decide if remediation is necessary. Recent research advances in the field have developed methods that can quantify uncertainty, including both parameter and conceptual model uncertainty (Dentz, 2012; Fernandez-Garcia et al., 2012; James and Oldenburg, 1997; Nowak et al., 2012; Rojas et al., 2008; Sohn et al., 2000; Troldborg et al., 2010). These methods are all developed for well investigated sites, where multiple samples have been taken and models have been developed. But many sites are poorly characterized, and methods that can account for conceptual uncertainty at all data levels are therefore of interest.

Bayesian belief networks (BBNs) are graphical probabilistic networks. They have the advantages of 1) a strong graphical component that makes the model transparent and the included processes easy to follow, and 2) they can include multiple types of data (Nielsen, and Jensen, 2007). BBNs have not previously been used to account for the conceptual uncertainty at contaminated sites. An important contribution of this PhD was to develop a BBN approach that can account for the conceptual uncertainty at contaminated sites regardless of the knowledge level (Thomsen et al. IV).

The BBN approach was applied to the Vadsbyvej 16A study site, a contaminated site where PCE (Tetrachloroethylene) and TCE (trichloroethylene) were spilled at the surface in the 1970s. The site is located in an area with clay till geology. The conceptual uncertainty at the site concerns the existence of fractures in the clay till and the presence of a separate phase contaminant.

1.2 Objectives

The aim of this PhD thesis is to develop methods for assessing the risk of contaminated sites to water resources, focusing on several aspects of the risk assessment process. The specific aims are:

1. To develop a method that can quantify and compare the impact from old unlined landfills in clay tills and to assess the risks to groundwater and surface waters (streams) (Thomsen et al., I)

2. To assess the impact of contaminated sites on headwater streams at two scales, local and catchment. On the local scale, the impact of leachate from old unlined landfills in a clay till geology to a stream is quantified (Milosevic et al. II, Thomsen et al I). On the catchment scale, the impact of several anthropogenic stressors on headwater streams is examined (Rasmussen et al. III).

3. To develop an approach that can evaluate the uncertainty of conceptual site models. The approach should be applicable where only the first site investigation and risk assessment are conducted, and can be continually updated as new information becomes available (Thomsen et al. IV).

1.3 Organization of the thesis

The thesis is organized as follows. Chapter 2 describes the general terminology and definitions used in risk assessment to provide an overview for the context of the thesis. Chapter 3 and 4 presents the contributions made during the thesis to single and multiple site risk assessments (Catchment scale) of contaminated sites (Thomsen et al. I, Milosevic et al. II, and Rasmussen et al. III). Chapter 5 presents a new BBN based approach for the assessment of uncertainty in CSMs at contaminated sites (Thomsen et al. IV). Chapter 6 presents the conclusions and the perspectives for future work are presented in Chapter 7.

2 Concepts used in risk assessment of contaminated sites

A risk assessment is a useful tool for the management of contaminated sites. It communicates the risk posed by the site by assembling, structuring and organizing the site data. The term risk assessment is used in a wide range of contexts, i.e. different professions and academic topics, each with a specific set of definitions. This chapter therefore aims to present and clarify the risk assessment terminology and framework as applied in this PhD. In particular, the chapter; defines risk, explains the role of CSMs, introduces the concept of tiers and phases, defines the source-pathway-receptor concept, defines the points of compliance and discusses the use of concentration and contaminant mass discharge in assessing impact of a contaminated site on a water resource.

The Royal Society (1992) define risk as *"the probability that a particular adverse event occurs during a stated period of time, or results from a particular challenge"* (Royal Society, 1992). The adverse event is sometimes referred to as a hazard, which can be described as "*a property or situation that in particular circumstances could lead to harm*" (Royal Society, 1992). Environmental risk assessment can therefore be described as the examination of the possibility of hazardous events in the environment (Marcomini et al., 2009).

In a classical risk assessment, the aim is typically to predict the occurrence and risk of some unwanted future event. In the field of contaminated sites, risk assessments can be divided into two categories concerning either past or future events. In this thesis, only past events, where the contaminant source is already present, is considered, and methods that prevent the spill from occurring are therefore not relevant. Methods that cover past and future events have much in common, because risk assessments that cover past events aim at predicting the future effect of the contaminant spill (Ferguson et al., 1998).

A risk assessment for contaminated sites is usually based on a source-pathway-receptor concept (Figure 1). This means that, in order for a contaminant source to pose a risk, there has to be a complete linkage, in the form of a pathway, from the source to a given receptor (US EPA, 2014).

The characteristics of a contaminant point source generally include: the type of contaminant, the concentration levels, the source location and spatial distribution, and the hydrogeological and geographical settings of the site. The pathway that connects the source to the receptor may be through different media, depending on the site settings. The media could be groundwater, surface water, soil, air, food or non-food related products. Commonly two types of receptors are considered: humans and ecosystems. At the receptor, the exposure route can be through ingestion, dermal contact, inhalation or non-dietary behavior, such as ingestion of soil by children (US EPA, 2014). This thesis focuses in particular on two types of water resources: groundwater and streams. The focus of the risk assessment in this thesis is the human health, but with an outlook to ecological impacts.

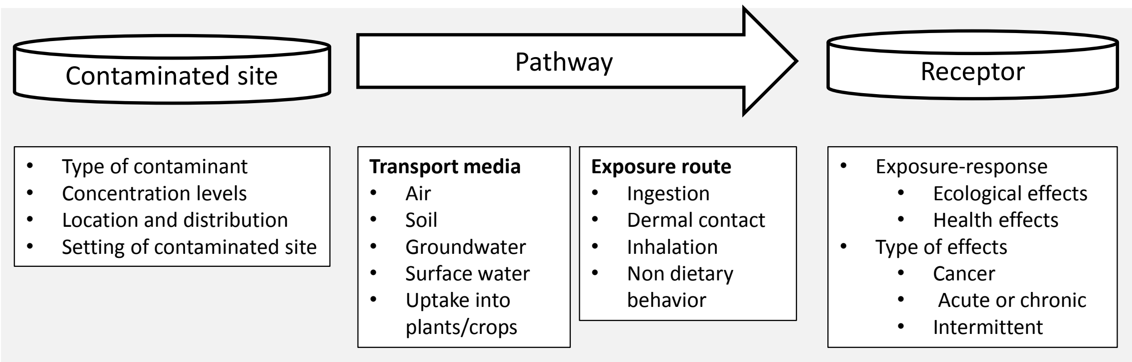


Figure 1 The source pathway receptor concept (Modified from Troldborg (2010)).

2.1 Tiered approach and risk assessment phases

Most countries apply a tiered approach to risk management (Bardos, 2002; Danish EPA, 2002; US EPA, 2001), where increasing tiers describe increasing investigation complexity, reduced uncertainty and less reliance on conservative assumptions (Bardos, 2002). The advantage of the tiered approach is that it provides a systematic way to describe the investigation and knowledge level at a specific site.

In the context of this thesis, four tiers (Figure 2) that have been adapted from the literature are considered: 1) the desktop study, 2) the screening site investigation, 3) further site-specific investigation and 4) a detailed site-specific investigation (Bardos, 2002, Danish EPA, 2002; US EPA, 2001).

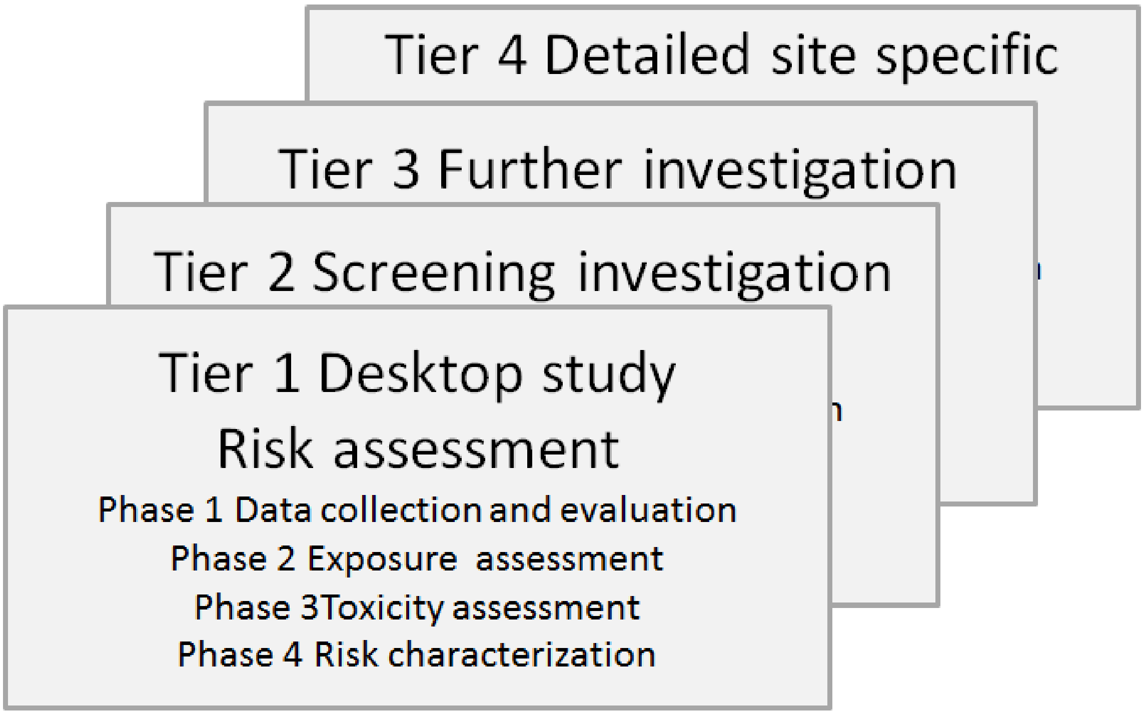


Figure 2 This figure illustrates the progression from one tier to another. As part of each tier, a risk assessment is conducted. The risk assessment may include up to four phases.

Tier 1 – The desktop study

The desktop study (Tier 1) is carried out for suspected contaminated sites and collects all information available prior to any actual field investigation. During this step, a semi-quantitative CSM is created and a semi-quantitative risk assessment is carried out. The aim is to establish whether the site may pose a risk and to identify possible receptors. In this Tier the aquifer vulnerability is often assessed and mapped using index methods. Good examples are DRASTIC (Aller et al., 1987), where different indicators/factors (e.g. depth to groundwater table, soil texture, recharge etc.) are scored and combined to provide an overall vulnerability index or Zabeo et al. (2011) who combines multi criteria decision analysis with spatial analysis methods in order to give scores to a defined set of receptors (humans, surface water, groundwater and protected areas).

Tier 2 – The screening investigation

The screening investigation (Tier 2) includes a field campaign, which is guided by the findings in Tier 1, where for example an old photo or map may indicate relevant areas to search for contaminant sources. The inventory of the field campaign does not vary much between sites (Table 1). It commonly includes a small number of shallow boreholes that do not always reach the groundwater. If water is present in the boreholes, they are sampled and analyzed. The investigation also typically includes soil samples and samples of pore air. Risk assessments carried out at this tier compare the measured concentrations to guideline values, e.g. MCLs, and it is concluded that a site poses a risk when these are exceeded. This is a conservative approach, because it commonly does not consider attenuation processes.

Tier 3 – Further investigation

In the third tier the investigation is more site-specific. The aim of this tier is a more detailed site characterization with focus on source delineation in addition to predicting and measuring contaminant concentrations at specific points of compliance (PoC) (Section 2.2.1) and/or for identified receptors. This tier involves a supplementary field investigation and some modelling. The investigation is tailored to the site, and may involve more complex investigation methods. The modelling at this stage commonly relies on analytical tools such as RISC5 (Spence, 2011), Premchlor (Liang et al., 2010), ConSim (Davidson and Hall, 2014), DTU V1D (Chambon et al., 2011a), $\text{CARO}_{\text{plus}}$ (McKnight and Finkel, 2013) or JAGG (Danish EPA, 2002).

Tier 4 – Detailed investigation

The fourth tier is very site-specific and often directed towards selection of remediation technologies. The tier may involve both site investigations and modelling. The models applied at this stage are typically numerical and can account for site heterogeneity, time dependent transport and complex attenuation processes. The risk assessment performed at this stage is often less conservative and describes the actual risk posed by the site.

Table 1 A typical data inventory for the first two tiers. The inventory of tier 3 and 4 are very site-specific and are therefore not included (From Thomsen et al., IV).

Investigations and data sources		
Tier	**Information collected**	**Sources**
1 Desktop study	The site and spill history, including land use and applied chemicals	Phone books, walk-overs, historical/aerial maps, local and national archives, old newspapers and interviews of former staff, neighbors and regulators
	Regional geology	Geological maps of soil and strata, geological models, and information from available boreholes
	Regional hydrology including groundwater flow	Maps of groundwater potential, regional groundwater models, topography maps/Digital Elevation Models, and information from available boreholes
2 Screening investigation	Geological profiles, redox boundary and water table.	Boreholes. It is common to install a small number of shallow boreholes to investigate the site. These boreholes typically do not reach the deeper groundwater.
	Soil concentration (mg/kg)	Soil samples
	Aqueous concentration (mg/l)	Water samples
	Pore air concentration (ppm)	Pore air samples

2.1.1 Risk assessment phases

For each tier, a risk assessment is commonly conducted (Figure 2). A risk assessment may have up to four phases: phase 1) data collection and evaluation; phase 2) exposure assessment; phase 3) toxicity assessment; and phase 4) risk characterization (Cushman et al., 2001; Ferguson et al., 1998 and Marcomini et al., 2009). This thesis is especially concerned with exposure assessment (Phase 2) in tier 2 and 3 level investigations. We present an overview of the additional phases, in order to provide the context in which the results of the exposure assessment should be seen.

Phase 1- Data collection and evaluation

The first phase of a risk assessment, the data collection and evaluation phase, is concerned with collecting data and the identification of possible hazards.

The available data for Phase 1, in Tier 1, is collected via a desktop study. In the desktop study the historical activities that may have caused contamination are firstly identified. Following this, existing maps and models are examined for relevant information concerning the hydrogeology and geography of the area. Based on this information, possible sources, pathways and receptors are identified. Then a semi-quantitative CSM is designed (US EPA, 2014). The last step of Phase 1 is the hazard identification. Here it is examined whether properties of the potential contaminants may cause harm. Commonly this information can be found in the scientific literature or government established databases. The quality of the information may vary because of the ethical considerations concerned with human testing of environmental hazards. It is therefore common to rely on results of animal studies (US EPA, 2014).

During the following tiers, additional data is collected through field investigations and modelling. Important information to collect concerns concentration levels, distribution and changes with time, but there could also be more focus on factors controlling fate, transport and exposure (US EPA, 2014).

Phase 2- Exposure assessment

The aim of the exposure assessment (Phase 2) is to estimate the magnitude; duration and frequency of the contaminant impact (concentration or mass discharge) on a PoC and/or affected receptor. The contaminant pathway from the source to the PoC/receptor is quantified using calculations, simulation models or less frequently via direct measurement. There are a number of relevant types of receptors (See Chapter 2.2.1). According to the US EPA (human health risk assessment guidelines), the person is the receptor. For example, under the US EPA human health risk assessment, they define exposure as "contact between an agent and the visible exterior of a person (e.g. skin and openings into the body)" (US EPA, 2014). Another example is the Danish guidelines for remediation of contaminated sites (Danish EPA, 2002), where the receptor is the groundwater.

Phase 3- Toxicity assessment

Phase 3 is the toxicity assessment, which estimates the relationship between the exposure (duration, level and frequency) and the likelihood of adverse effects. The relationship may be either linear or nonlinear and depends on the receptor. When the relationship between dose and response is nonlinear, we assume that a threshold exists where doses below the threshold have zero effect, with effects (or their precursors) beginning when the threshold is exceeded. The nonlinear relationship is characterized by a reference dose defined as "an estimate of a daily oral exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime" (US EPA, 2014).

When the effect is linear, as is common for carcinogenic compounds, there is no threshold value, rather the response increases linearly with increasing dose. The relationship is characterized by a slope factor, where the dose is multiplied with the slope factor to calculate e.g. the excess lifetime cancer risk (US EPA, 2014). The toxicity can also be evaluated by comparing the contaminant concentration to a MCL. If the MCL is exceeded, then the site is at risk for adverse effects towards the specific receptor (Cushman et al., 2001; US EPA, 2014).

In an ecological risk assessment there are a number of methods to quantify toxicity; in the context of this thesis, we apply toxic units as a measure for the toxicity of xenobiotic compounds and pesticides to the benthic macroinvertebrates (Rasmussen et al. III).

Phase 4- Risk characterization

The last phase is the risk characterization. The risk characterization phase summarizes the information collected during the previous phases. Important aspects of the risk characterization phase are transparency, clarity, consistency and reasonability.

- The transparency concerns the methods, assumptions and uncertainties and the results of each step in the assessment must be explained.
- The clarity concerns the products from the risk assessment; they should be readily understood.
- The risk assessment should be conducted in a manner that is consistent with the regulatory framework in the relevant region.
- Reasonability concerns the judgement in the assessment, which must be sound and based on state-of-the-art science.

2.2 The role of the conceptual site model

The formulation of a CSM is an essential part of any risk assessment and is crucial to consider when studying conceptual uncertainty (Chapter 5.2 and Chapter 5.3). This section presents the terms and concepts related to CSMs.

In a risk assessment the purpose of creating a CSM for a contaminated site is to organize and communicate the information gathered during investigations. A CSM can be defined as “a three-dimensional picture of site conditions that illustrates contaminant distributions, release mechanisms, exposure pathways, migration routes, and potential receptors. The CSM documents current site conditions, the documentation is supported by maps, cross sections, and site diagrams that illustrate human and environmental exposure through contaminant release and migration to potential receptors" (US EPA, 1996). In the risk assessment context the CSM is used to identify whether there is a link between the source and the receptor, and thereby establish if the site poses a risk.

Developing a CSM is an iterative process where the complexity evolves as more data is collected. If the CSM is seen as a hypothesis for how the site operates, then continuous data collection can be used to test this hypothesis and thereby increase confidence in the CSM (ASTM Standard E1689, 2009; McMahon et al., 1999).

The presentation of a CSM may vary depending on the complexity of the site, the amount of data available and the application. Figure 3 presents an example of a CSM. The CSM presentation may include pictorial elements such as drawings of the site, cross sections and maps, and text in the form of a written description including tables etc. when relevant. As more data is collected, quantifiable elements may be presented such as mass balance estimates. This allows a more rigorous testing of the CSM, because new data can be used to confirm the estimates (McMahon et al., 1999).

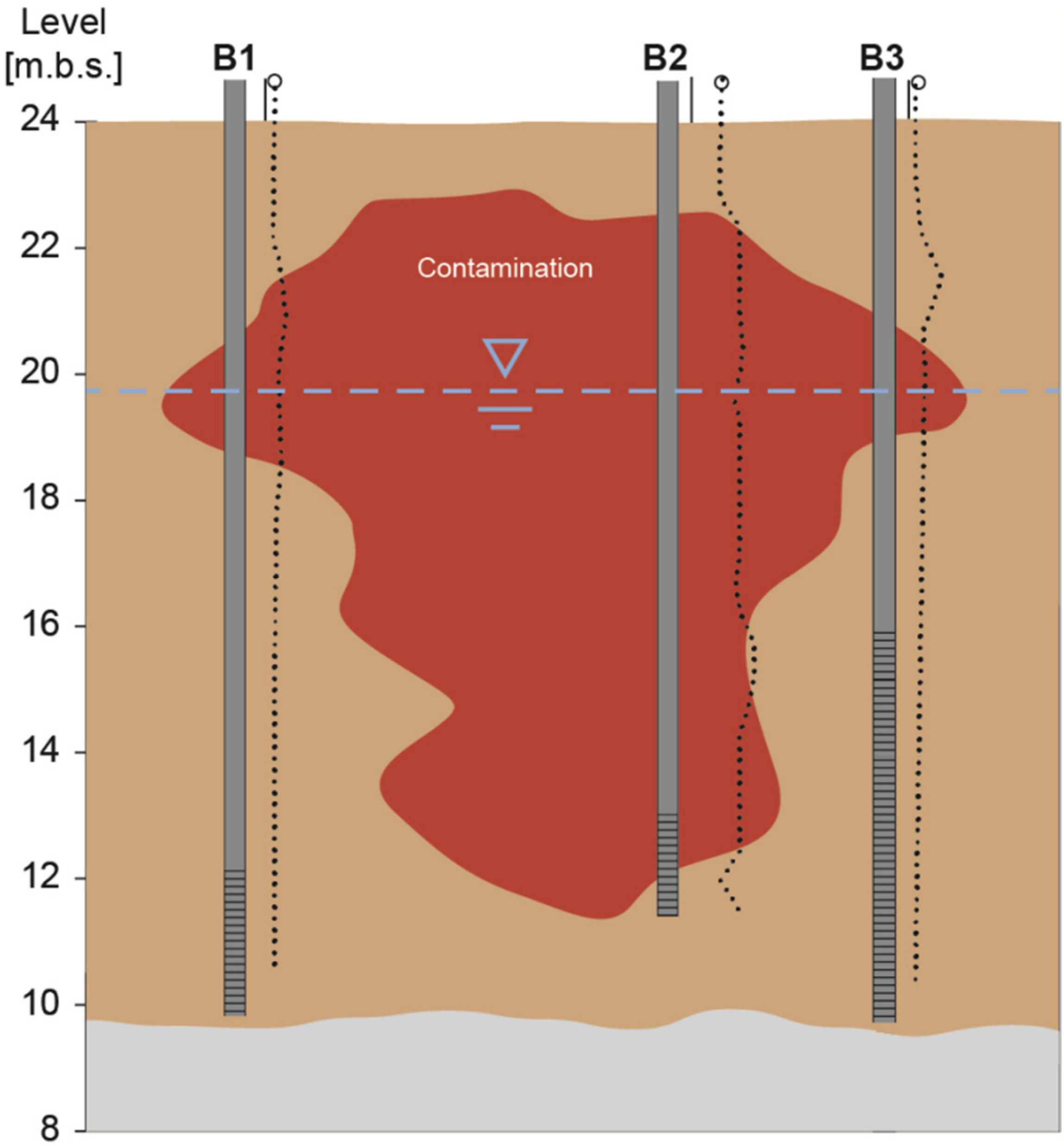


Figure 3 Conceptual model for risk assessment of a contaminated site (From Thomsen et al. IV).

2.2.1 Points of compliance and receptors

Identification of PoCs and receptors are an important part of formulating a CSM, because they represent the units that need protection from contamination (US EPA, 2014). The receptors considered in a risk assessment of a contaminated site depend on the context. Commonly we consider two types: human health risk assessment in which the receptor is the human being, and ecological risk assessment in which the receptor is the environment (plants, animals, ecosystems as a whole) US EPA (2014). The identification of the receptors is a key activity in a risk assessment because if there are no receptors which can be linked to the contaminated site, there is no real risk associated with the contamination.

This thesis is mainly concerned with the chemical status of groundwater and streams with an outlook to the ecological status of streams. We therefore consider mainly human health risk assessments, but also ecological risk assessment. This means that the receptors are the human being and the stream ecology, and that the main pathways are through the groundwater and streams. Exposure and the following adverse effects in the receptor occur when there is contact between the receptor and the contaminant (US EPA, 2014). Exposure can be quantified by measuring the exposure concentration and time of contact and at the point of contact (US EPA, 2014). In human health risk assessment the point of contact is at the outer boundary of the body, often the skin (US EPA, 2014). In order to prevent the contaminant from actually entering the body it is useful to measure the contaminant along the pathway, before it enters the receptor and causes harm. We therefore apply the concept of PoC.

The PoC is the location or locations at which media clean-up levels are achieved (US DOE, 2002) (Figure 4). The clean-up levels in drinking water are commonly specified as MCLs "The maximum concentration levels are the highest level of contamination that is allowed in drinking water" (US EPA, 2009). The location of the PoC can be calculated using a model or specified by the regulatory authorities. If the PoC is estimated based on model calculations and found to be located in a water resource, where there is contact to a receptor, there is a risk of adverse effects. This could for example be a PoC located in a groundwater based drinking water resource. If the PoC is defined by the authorities, it is used to regulate the risk posed by the site. This is done by specifying a point a certain distance downstream from a contamination (Danish EPA, 2002), where the contamination has to comply with the MCL. This ensures that after the PoC and in the direction of the water flow there is acceptable risk associated with the contaminated site.

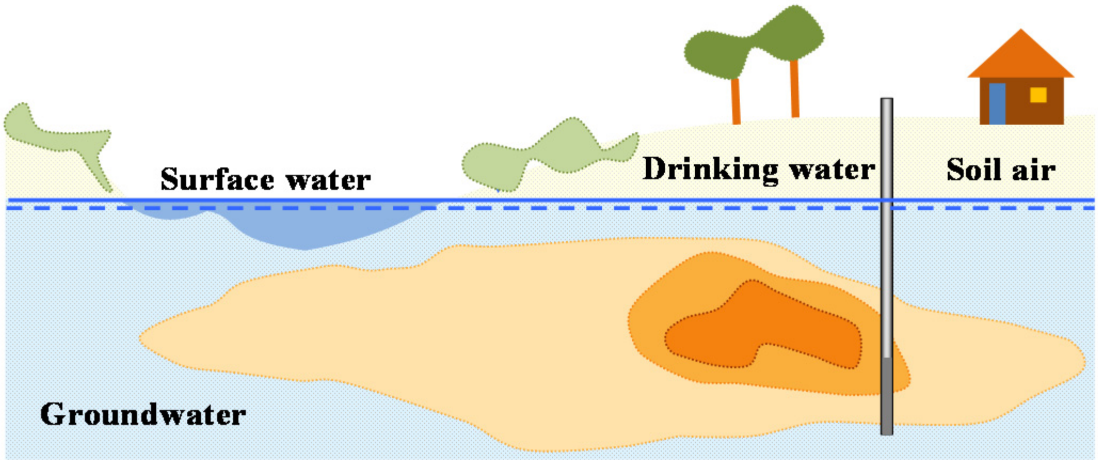


Figure 4 Possible locations of the point of compliance considered in risk assessment of contaminated sites.

An important pathway in this thesis is the interaction between groundwater and surface water. The concepts behind is described extensively in the literature; see for example Dingmann (2002). This thesis concerns contaminated sites and their effect on groundwater and surface water; I therefore focus on the case of a gaining stream; where there is discharge of groundwater to surface water (Figure 5).

The case of groundwater discharging to surface water is one of the pathways available for transport of contaminants from a contaminated site to a stream; it is relevant for the papers Thomsen at al. (I), Milosevic et al. (II) and Rasmussen et al. (III). An important concept is the hyporheic zone, which is the zone below the streambed where there is mixing of groundwater and surface water (Dingmann, 2002).

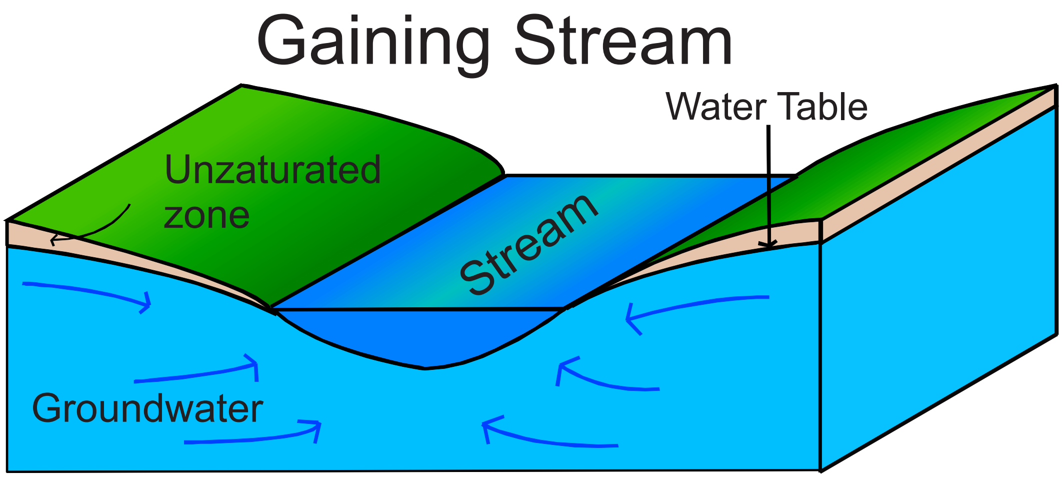


Figure 5 Sketch of groundwater discharging to a stream, the arrows indicate the flow direction of the water (From Thomsen 2010, originally inspired by Winter et al. 1998).

2.3 Methods for estimating contaminant impact

Different metrics are needed in order to assess the impact of a contaminated site at a PoC or on a water resource. The following three sections present two metrics: the concentration and the mass discharge, and relevant field methods for their estimation.

2.3.1 Concentration

Estimates of contaminant concentration are important in risk assessments. As stated previously, they can be compared to a guideline value, for example a MCL, to determine whether the site poses a risk. Concentration measurements can also be used to delineate contaminant sources and to identify hotspots. Measurements of concentrations of redox species are useful for delineating redox zones where conditions may or may not favor degradation of certain compounds. Contaminant concentrations are also a direct measurement of the effect of the contamination on a water resource in a specific point.

For the purpose of estimating the effect of contaminated sites on streams, concentrations may be sampled in: 1) groundwater, 2) surface water and 3) in the interface between groundwater and surface water, i.e. the hyporheic zone. A detailed source characterization may also be helpful. Extensive sampling campaigns (Figure 6) were conducted as part of this PhD in connection with the papers Thomsen et al. (I), Milosevic et al. (II) and Rasmussen et al. (III).

Figure 6 Left: Collecting samples from seepage meters on a cold Decembers day. Middle: Drilling boreholes on Risby Landfill. Right: Inspecting event-triggered water samples.

Boreholes for groundwater sampling were installed as part of Milosevic et al. (II) and Thomsen et al. (I). Three types of wells were used: Traditional boreholes, Geoprobe and driven boreholes. The purpose of the traditional boreholes was to investigate an aquifer located in the limestone. They were drilled and a screen was installed in the aquifer. The boreholes that were either hand drilled (driven into the soil) or installed with the Geoprobe system were used to sample the upper saturated zone. Driven wells are described in detail in Kjeldsen et al. (1998). The Geoprobe system is useful at sites where driven boreholes are not possible. This could for example be the case at landfill sites, where the solid waste layers can be hard.

Sampling of surface water is often done as manual grab sampling, where one collects a sample of water by gently placing a bottle under the water surface. Depending on the time where the sample is collected it may represent different things. Sampling a gaining stream during base flow conditions results in groundwater dominated samples. Sampling immediately after a heavy rain event results in samples that are dominated by run off. In Rasmussen et al. (III) event triggered samplers (storm samples) were used in addition to grab sampling. An event triggered sampler is a bottle with a tube fitted through the cap. Inside there is a small ball which closes the bottle when it is full. The sampler is placed with the tube app. 5 cm above the water surface. When a major rain event occurs, the water rises above the neck of the bottle, which is filled and a sample is collected. This sample represents water with a larger percentage of surface run off from e.g. fields and of course some rain water. Event triggered samplers are described extensively in Liess and von der Ohe (2005).

Samples from the hyporheic zone can be taken in three ways, by i) hand-pushed piezometers (Kjeldsen et al., 1998), ii) multilevel samplers (Rivett et al., 2008; Weatherill et al., 2014) and iii) seepage meters (Brodie et al., 2009).

Seepage meters were installed as part of Milosevic et al. (II) and Thomsen et al. (I). The seepage meters are bottomless cylinders that are pushed into the stream bed. Attached to the cylinder at the top is a hose which connects to a bag where the sample is collected (Kalbus et al., 2006; Landon et al., 2001). Seepage meters can also be used to estimate the groundwater discharge to the stream.

Alternatively samples can be taken by hand –pushed steel piezometers (see example: Geist et al., 2002; Kjeldsen et al., 1998; Milosevic et al., II). Samples are collected by pumping the water out of the pipe. The piezometers have the advantage that they allow for measuring hydraulic head, but are not suitable for measuring groundwater discharge to the stream. Multilevel samplers have proven useful for investigating flow exchange, geochemical trends, and contaminant transport. They can measure over depths from 0.25 to 2 m (Rivett et al., 2008).

2.3.2 Mass discharge

Concentrations have traditionally been used to assess the effect of a contamination on a water resource. However, mass discharge is an alternate measure that has received increasing attention in risk assessments of contaminated sites (Einarson and Mackay, 2001; Hadley and Newell, 2012; Newell et al., 2011; Nichols, 2004). This section describes the mass discharge metric.

Mass discharge is the mass of a chemical passing through a given area during a given time (Equation 1).

$$MD = C \cdot Q \qquad \text{Equation 1}$$

$$Q = -K \cdot i \cdot A \qquad \text{Equation 2}$$

Where *MD* is the mass discharge (M/T), *C* is the concentration (M/L^3) and *Q* is the water discharge (L^3/T). In the groundwater context the water discharge *(Q)* can be calculated by Darcy's law (Equation 2), where *K* is the hydraulic conductivity (L/T), i is the gradient of the water table (-) and A is the contaminated area perpendicular to the flow direction (L^2).

Mass discharge to groundwater bodies can be estimated based on data collected in the field in a variety of ways: (1) the transect method (Figure 7, Top) where concentration is measured in a monitoring network, commonly involving some form of multi-level sampling, and where flow data are estimated by e.g. aquifer or tracer tests (Borden et al., 1997; Einarson and Mackay, 2001; Guilbeault et al., 2005; Kao and Wang, 2001; Tuxen et al., 2003); (2) the integral pump test method (Figure 7, Bottom) which determines the mass discharge based on an inversion of a series of concentration measurements taken from pump tests (Bauer et al., 2004; Bockelmann et al., 2001; Holder et al., 1998; Jarsjö et al., 2005); and (3) use of passive *in situ* flux meters (Acar et al., 2013; Hatfield et al., 2002; Hatfield et al., 2004) that provide point measurements of time averaged contaminant mass discharge using a permeable sorptive unit.

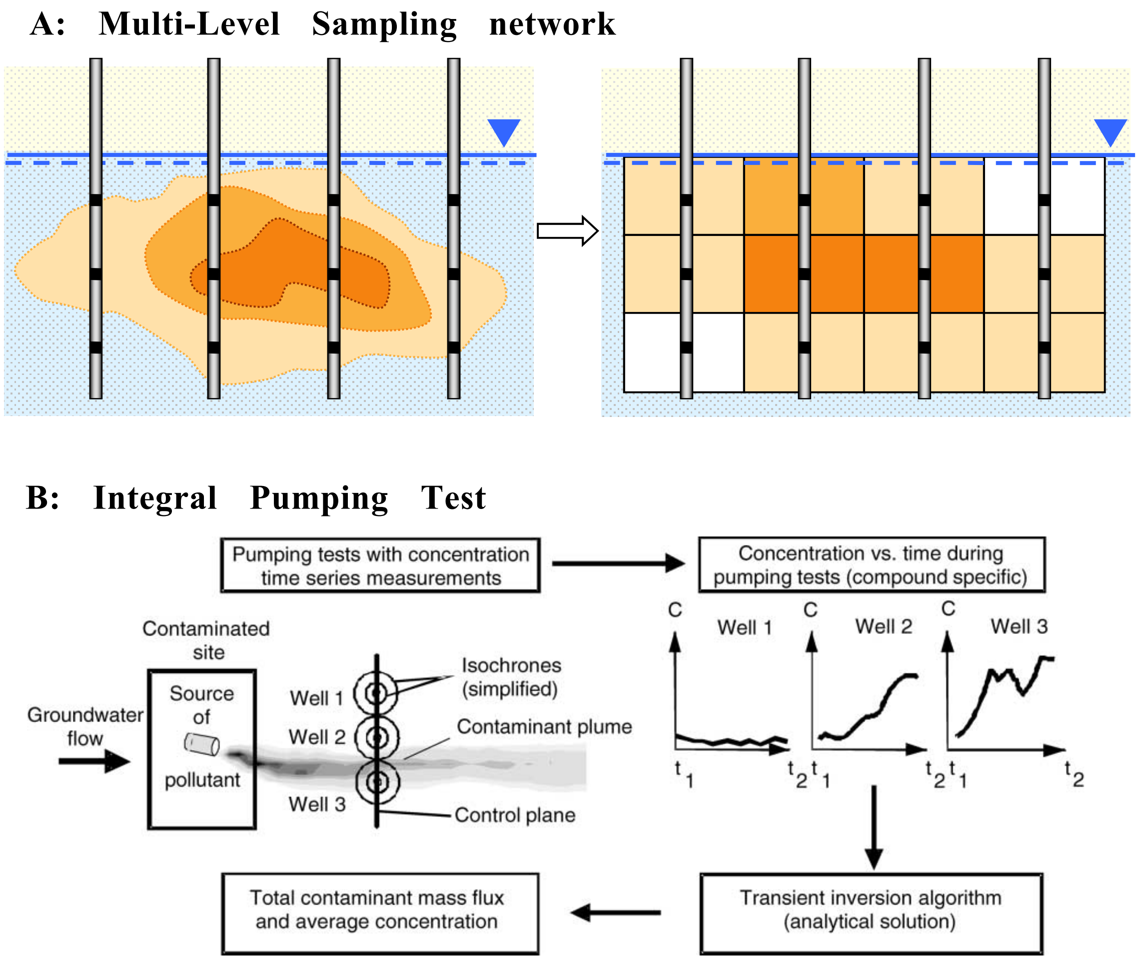


Figure 7 Methods for quantifying mass discharge in the field. A: multilevel sampling network (Figure is from Troldborg (2010), with permission). B: integral pumping test (Figure is from Bockelmann et al. (2001)).

Generally the three methods yield comparable results (Beland-Pelletier et al., 2011; Brooks et al., 2008; Kubert and Finkel, 2006). With respect to uncertainty, increasing heterogeneity seems to favor the integral pump test (Beland-Pelletier et al., 2011). If only results from a coarse sampling are available, Kubert and Finkel (2006) showed that averaging the hydraulic parameters over the wells, while disregarding vertical differences, yield less erroneous results.

2.3.3 Estimating the impact of a contaminated site on a receptor; mass discharge or concentration

The two metrics, mass discharge and concentration, can both be used in a risk assessment. This section discusses the advantages and disadvantages of each approach.

Recent studies have suggested that the mass discharge metric is useful in terms of predicting effect on water resources. The link between mass discharge and concentration at a given receptor was presented in Einarson and Mackay (2001), see Equation 3.

$$C_{Receptor} = \frac{MD}{Q_{Receptor}} \qquad \text{Equation 3}$$

Here *MD* is the contaminant mass discharge (M/T), Q is the water discharge (L^3/T) (e.g. pumping rate in an abstraction well) and $C_{Receptor}$ is the resulting concentration at the receptor. Employment of mass discharge as a measure of risk means that rather than focusing on meeting MCLs everywhere, efforts can be directed towards reducing concentrations at the water resources of interest (Hadley and Newell, 2012; ITRC, 2010; Newell et al., 2011).

An important feature of a mass discharge estimate is that it is a conservative property. This means that, if the contaminant is not undergoing transformation, 'mass discharge in' equals 'mass discharge out' (Nichols, 2004). Mass discharge estimates before and after remediation can therefore provide a clearer picture of its effect (ITRC, 2010). Where MCLs (at least in Denmark) may be hard to achieve without removing more than 99 pct. of the source (Overheu et al., 2011; Hadley and Newell, 2012), a clear effect of a lesser degree of remediation can be seen on the mass discharge (Hadley and Newell, 2012; Nichols, 2004). Also the effect of natural or enhanced attenuation is clearer if measured on a mass discharge metric (ITRC, 2010; Newell et al., 2011).

The mass discharge can also be used to prioritize effort between sites (Enzenhoefer et al., 2015; Jamin et al., 2012; Newell et al., 2011; Pizzol et al., 2011; Pizzol et al, 2015; Troldborg et al., 2008). This could be done by comparing the size of the mass discharge between contaminated sites or by diluting the mass discharge in a water volume or flow and comparing the resulting concentrations (as in equation 3).

Mass discharge estimates are often considered uncertain, especially in heterogeneous environments and when based on coarse discrete measurements such as the transect method or the passive flux meter method (Beland-Pelletier et al., 2011; Kubert and Finkel, 2006). The uncertainty is enhanced under these conditions, because mass discharge estimates aggregate flow and contaminant information. However these uncertainties are the same, as we have always considered in connection with contaminated sites in general (ITRC, 2010; Nichols, 2004).

Estimates of contaminant concentration are especially useful when communicating risk, because concentration can easily be compared to guideline values (e.g. MCL); so if a guideline value is exceeded, the contaminated site is believed to pose a risk. Concentration estimates are also used to delineate contaminant sources, hot spots and plumes. In assessment of toxicology, concentration is used to calculate dose response curves.

Concentration estimates of redox species are useful because they describe important site characteristics that may determine whether contaminants will degrade at the site.

2.4 Risk assessment at catchment scale

In catchment scale risk assessment, we consider a source, pathway, receptor concept similar to the concept described in (Figure 1). In the context of this thesis the source is a contaminated site, the pathway is through soil (in the aqueous phase), streams or groundwater and the receptor is either a human being or the ecology (Figure 8).

Conducting risk assessments of contaminated sites at the catchment scale is usually motivated by one of two factors: 1) the need for action at a contaminated site, this could be the need for remediation, or 2) that contaminated sites can be considered collectively and prioritized by comparing their effects (mass discharge or concentration) on a common receptor point.

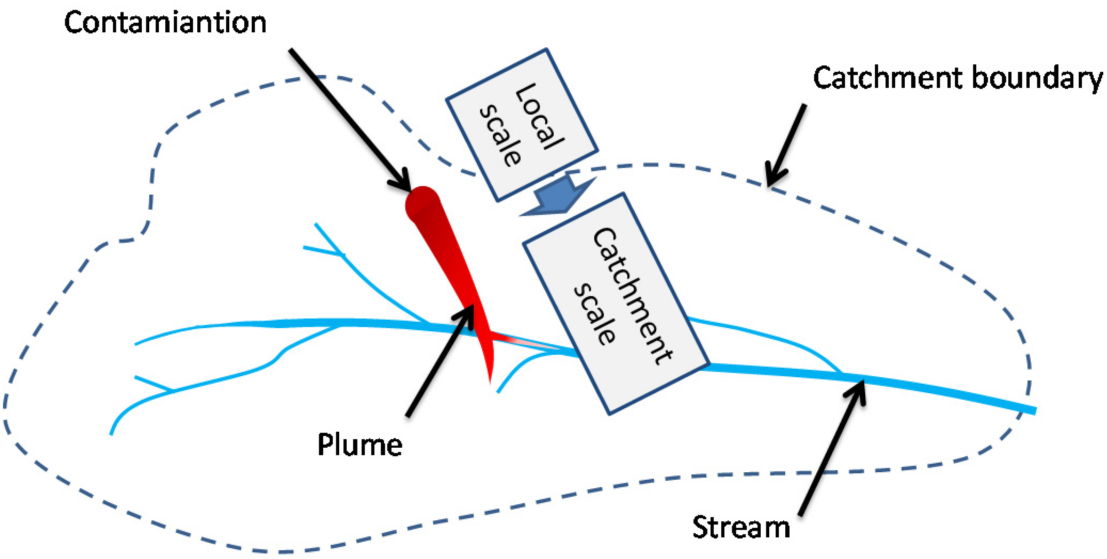


Figure 8 Conceptual model of catchment scale risk assessment of a point source within a river catchment. Modified from Troldborg et al. (2008) and Rasmussen et al (III).

There are numerous studies of catchment scale risk assessments; Table 2 gives an overview of selected relevant papers. Tait et al. (2004) presents a method for selecting an optimum borehole location, a method that has been applied in the UK (Chisala et al., 2007). Aray and Gschwend (2005) developed a screening model that predicts aqueous concentrations of gasoline constituents in water supply wells. Frind et al. (2006) developed a method for predicting water supply well vulnerability towards contamination. The method was cast into a probabilistic framework by Enzenhoefer et al. (2012). Becker and Jiang et al. (2007) developed a GIS based method for predicting contaminant mass discharge at a specified boundary. The method was applied to calculate the nitrogen load to surface water from a source consisting of animal feedlot waste. Troldborg et al. (2008) presented a modeling tool (CatchRisk) for catchment scale risk assessment of contaminated point sources. CatchRisk evaluates the risk of abstracting contaminated groundwater. Pizzol et al. (2011) and Zabeo et al. (2011) developed a methodology that integrates spatial analysis of vulnerability (Zabeo et al., 2011) and a risk approach (Pizzol et al., 2011) to prioritize sites at the regional scale. The approach by Jamin et al. (2012) gives an indicator score to the quality of groundwater bodies at the regional scale. Overheu et al. (2014) presents a flexible framework for prioritizing contaminated point sources at regional or catchment scale.

Table 2 Risk assessment of contaminated sites at the catchment scale.

	Tait et al. (2004)	Arey and Gschwend (2005)	Frind et al., (2006)	Becker and Jiang (2007)	Troldborg et al. (2008)	Pizzol et al. (2011)	Zabeo et al., (2011)	Enzenhoefer et al. (2012)	Jamin et al. (2012)	Overheu et al.(2014)
Source										
Source type - No source (S0) - Constant source (C) - Decaying source (D) - Pulse source (P)	P	D	P	P	C,D	S0	S0	C	C	C,D
Time dependent - Transient (T) - Stationary (S)	S	T	S	S	T			T	S	T
Uncertainty - Parameter (P) - Conceptual (C)	P	P			P, C			P		P, C
Pathway										
Transport mechanisms - Not included (C0) - Retardation (R) - Dispersion (Disp) - Advection (A) - Degradation (Deg)	R, A, Deg	R, Disp, A	Disp, A	R, Disp, A, Deg	R, A, Deg	C0	C0	Disp, A	R, Disp, A, Deg	R, A, Deg
Time dependency - Transient (T) - Stationary (S)	S	S	S	T	S			T	S	S
Uncertainty analysis - Parameter (P) - Conceptual (C)	P	P			P, C			P		P
Receptor										
- Supply well (W) - Borehole (B) - Surface water (S) - Human health (H) - Groundwater (G)	W, B	W	W, B	S	W	S, H, G	S, H, G	W, B	G	W

2.5 Findings for concepts used in risk assessment of contaminated sites

The above chapter have described the theory and concepts used in risk assessment of contaminated sites. I have focused on describing important concepts for conducing site investigations, methods for estimating the effect of contaminated sites on water resources and presented the concept of scale of the investigation. This background information sets the stage for the discussing the novelty of the contributions of the thesis to the scientific literature.

- The application of a tiered approach for risk assessment is a useful way of organizing the data collection. The tiered approach allows regulators to plan their investigations based on information gaps in the data from the previous tier.

- The CSM is a tool used in risk assessment of contaminated sites to organize and communicate information collected during investigations.

- Mass discharge estimates are useful for estimating the total impact on a receptor, for determining the effects of potential remediation options, for prioritizing sites and comparing the effect of one contaminated site on multiple receptors.

- Contaminant concentrations are useful for estimating whether the effect of the exposure to the contaminant exceeds a given MCL, but they can also be used to delineate the source and to identify hot spots.

- The method for measuring a contaminant concentration or mass discharge depends strongly on the type of water resource.

- Catchment scale risk assessment considers the impact of contaminated sites on a catchment scale. The benefit is that it allows the regulator to prioritize and focus his or her resources and remediate the sites that pose the greatest risk first.

- Risk assessment of contaminated sites at catchment scale have focused on the chemical status of groundwater, drinking water, surface water and human health.

3 Risk assessment of landfills located in clay till geology on groundwater and surface water

Risk assessments are usually carried out for a single site and the focus is on the contaminant impact in the vicinity of the site (i.e. a local scale assessment). In this chapter, an example of the effect of a single site assessment (Risby Landfill) on adjacent water resources is presented.

3.1 Estimating the effect of old unlined landfills in clay tills on groundwater and surface water

There are very few studies of landfills in clay till geology (Bjerg et al. 2011) and none where the impact on streams through groundwater surface water interaction is quantified (Table 3). Risby landfill is interesting in this context because it is located in clay till geology and adjacent to Risby Stream. The novelty in our work thus lies in the quantification of the contaminant mass discharge from a landfill located in clay till geology to the groundwater and surface water and in the identification of methods that are useful in doing so.

There are a number of studies of the proximity of landfills to surface water bodies, good examples are Lambou et al. (1989), who studied the proximity of 1153 sanitary landfills to surface water and Borden and Yanoschak (1990) who studied the groundwater and surface water impact of 71 landfills. The conclusion is that there is a clear trend in the location of landfills close to surface water bodies.

There are examples of studies that go into further detail concerning the impact of landfills on surface water. Douglass and Borden (1992), studied a landfill located in North Carolina, on a saprolite geology (classified as sandy loams or loamy sands possibly with clayey sands). They quantified the impact on the nearby Crabtree Creek by assuming that all groundwater eventually would discharge to the stream. They therefore estimated the mass discharge to the Crabtree Creek as the sum of the mass discharge from base flow and storm flow. Yusof et al. (2009), studied the impact of an active uncontrolled landfill (located in clay geology) on the adjacent river. The leachate was discharged from the landfill to the river by a drain. In the study they compared the contaminant mass discharges from the landfill with the contaminant mass discharge in the river system up and down gradient from the landfill and found that the landfill had a high impact on the stream. Ford et al. (2011) and Ford et al. (2006) studied a superfund site in Massachusetts (Shepley's Hill Landfill), they focus on arsenic discharge to the nearby Red Cove, the geology at the site is not the focus of the papers and therefore not described in detail. They find that the highest arsenic concentrations within the cove are caused by discharging groundwater. Lorah et al. (2009) studied the Norman Landfill, located in Oklahoma. The landfill is located in the Canadian rive alluvial aquifer (predominantly sand and silty sand) and adjacent to a shallow ponded wetland. They studied which factors in groundwater surface water interaction that can affect natural attenuation of landfill leachate. They did not observe enhanced natural attenuation in the wetland compared to the aquifer, which could be due to the anoxic conditions in the wetland and the recalcitrant nature of the dissolved organic carbon (DOC).

The attenuation processes and distribution of landfill leachate in sandy aquifers have been studied intensively (Christensen et al. 2001), but to date only few studies (See Table 3) have investigated landfills in clay till geology (Bjerg et al. 2011). Mckay et al. (1993a), Mckay et al. (1993b) and Mckay et al. (1998) studied the Laidlaw Disposal, Ontario, Canada. The Laidlaw facility is located in clay rich glacial deposits and the studies focused on lateral chloride migration (Mckay et al., 1998), assessment of hydraulic conductivity and fracture aperture (Mckay et al., 1993a) and on solute (tracer) transport in a fractured clay till geology (Mckay et al., 199b).

Landfills represent a group of contaminated sites, where mass discharge estimates have proven especially useful. Landfills are heterogeneous sites often with multiple concentration hotspots and a wide range of contaminant types (Christensen et al. 2001). Therefore, if a landfill source is characterized by concentration measurements, a very large number of samples are required in order to properly characterize the source. In this context the use of mass discharge estimates down gradient from the landfill, has two important advantages over the traditional concentration based approach: 1) they represent a bulk estimate of the impact of the landfill on the water resource and 2) they can be used to assess attenuation processes in the leachate.

Thomsen et al. (I) and Milosevic et al. (II) investigated Risby Landfill (Figure 9) and its impact on surrounding water resources. This was done using mass discharge estimates and concentrations in combination. The study by Thomsen et al. (I) was conducted based on tier 3 data and the study by Milosevic et al. (II) was based on tier 4.

Table 3 This table presents studies of landfills in clay and indicates whether they also studied the impact of landfill leachate on surface water.

	Geology (Near surface)			**Water resource(s)**		**Discharge to surface water**		
	Saprolite (possibly clayey)	Clay till	Clay (unspecified)	Groundwater	Stream	Groundwater	Surface runoff	Drain
Douglas and Borden 1992	X			X	X	X	X	
Mckay et al. 1998		X		X				
Yusof et al. 2009			X		X			X
Thomsen et al I		X		X	X	X		
Milosevic et al II		X		X	X	X	X	
Milosevic et al. 2013		X		X	X	X	X	

Risby Landfill was in operation from 1959-1985. The landfill is comprised mainly of household and gardening waste, and based on archive records; chemical waste may have been disposed. The landfill has no liner or leachate collection system. Risby stream flows from east to west and is located north of the landfill. The heterogeneous clay till geology at the site, in combination with the complex landfill source proved a challenge (Milosevic et al., II; Thomsen et al., I).

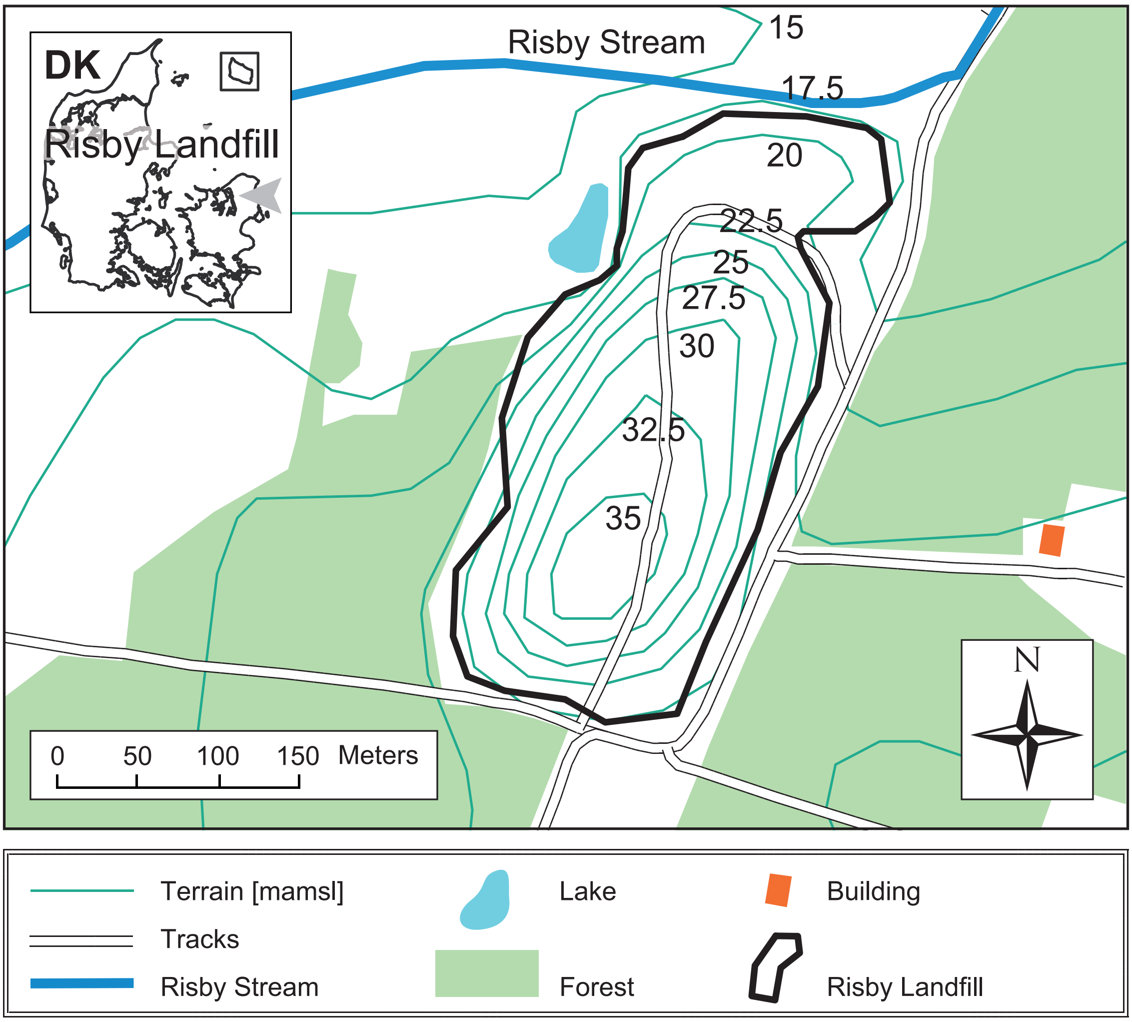


Figure 9 Risby Landfill location and outline. Risby Stream is located north of the landfill and runs from east to west (From Thomsen et al., I).

Mass balance method Thomsen et al. (I) used a mass balance method (Figure 11) to quantify the mass discharge of chloride, DOC and ammonium from Risby Landfill to the surrounding water resources. The mass balance was constructed by comparing the estimated mass discharge through the sides of a mass balance box placed under the landfill. The sides of the box were the borders of the landfill. The top of the box was formed by the hydraulic potential surface in the upper saturated zone. The interface between the limestone aquifer and the upper saturated zone formed the bottom.

The mass discharge estimates were obtained using the transect method (Section 2.3.2 and equation 1 and 2). The hydraulic conductivities were based on a groundwater model (Balicki and Christensen, 2010), and the gradients from measuring the hydraulic potential. The concentrations were sampled in wells (traditional, driven and geoprobe) located along the sides of the box. The mass discharge to the stream was calculated using data from the seepage meters (See location on Figure 10). The zones with groundwater discharge to the stream were identified by estimating temperature gradients between the stream water and the stream bed. In summer or winter time, a large gradient between surface and groundwater exists, and indicates a zone of groundwater discharge (See Figure 12 bottom). The large temperature gradients coincided with the focus area. It was therefore expected that leachate from the focus area would enter Risby stream within the stretch between D1 and D2.

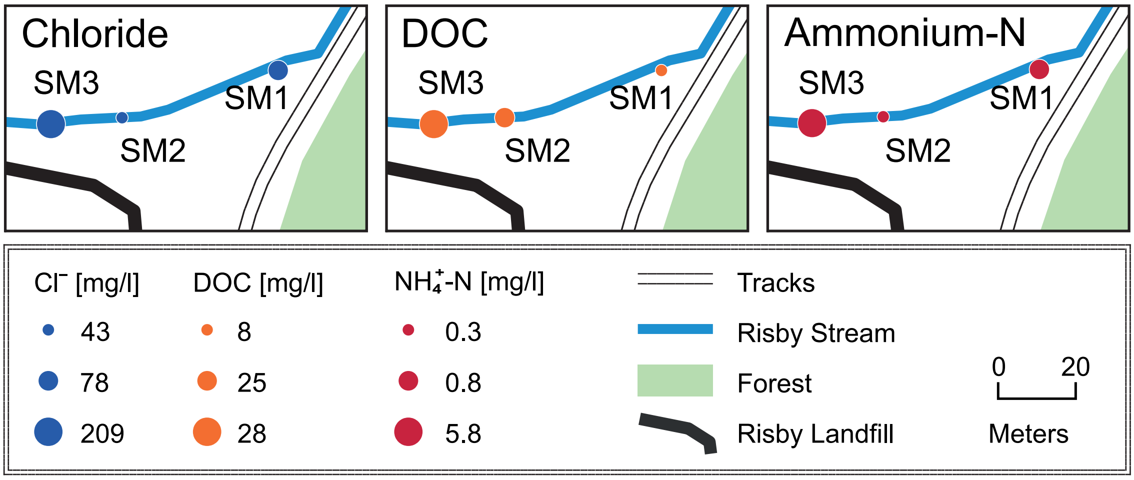


Figure 10 Measurement of chloride, DOC and ammonium–N concentration (mg/l) of in the seepage meters. The magnitude of the measured impact is reflected in the size of the dots (Thomsen et al., I).

As an example, the mass balance for chloride is presented. The total mass discharge from the landfill was 9.4 ton/year with the resulting impact on the limestone aquifer estimated to approximately 1.4 ton/year. The impact of the landfill leachate on the limestone aquifer caused elevated concentrations of leachate indicators and pesticides in the groundwater. The mass discharge of chloride to Risby Stream was estimated to 31 kg/year. The mass balance method thus provides useful estimates of the impact of the landfill on the water resources.

The mass balance method is useful in clay till settings because the mass discharge estimates can be compared and the cause of losses or gains can be assessed. For example; if there are large discrepancies in the mass balance it is possible that the transects are not accurate enough to characterize the contaminant distribution. This is especially useful in heterogeneous settings where the variability in the leachate flow field is expected to be high. The mass balance method also provides comparable estimates of the impact on the relevant water resources.

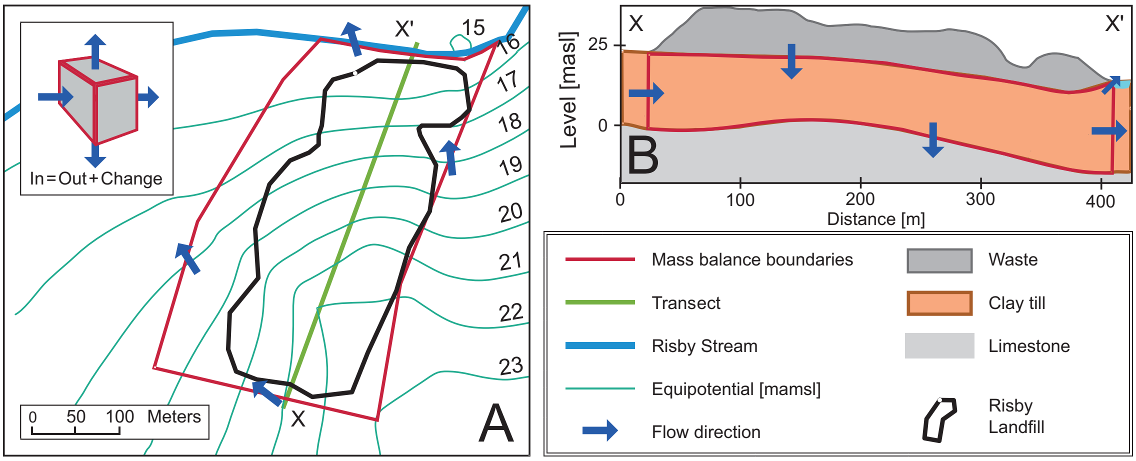


Figure 11 (A) Map showing the mass balance boundaries. Contour map of isopotential curves is for the hydraulic heads in upper saturated zone. (B) Cross section showing the mass balance boundaries. The blue arrows indicate the direction of the water flow (From Thomsen et al., I).

Source heterogeneity and the impact on Risby stream The impact on Risby stream was investigated in detail in Milosevic et al. (II). An array of field methods was employed to identify the zones where contaminants were discharging to Risby Stream. This is an iterative process, which began with the identification of hot spots in the source and then connected these to the stream chemistry.

First driven wells were installed along the transect running from B-B' between Risby Landfill and Risby stream (Figure 12). The wells were used to locate preferential flow paths and zones of high leachate concentrations in the landfill source. The preferential flow paths were found to be less than one meter wide and located at different depths and often in connection with sand lenses (Milosevic et al., II). In the zone between D1 and D2 they coincided with the area where the most contaminated groundwater was sampled (Figure 12, middle), which was selected as the focus area (Figure 12, top).

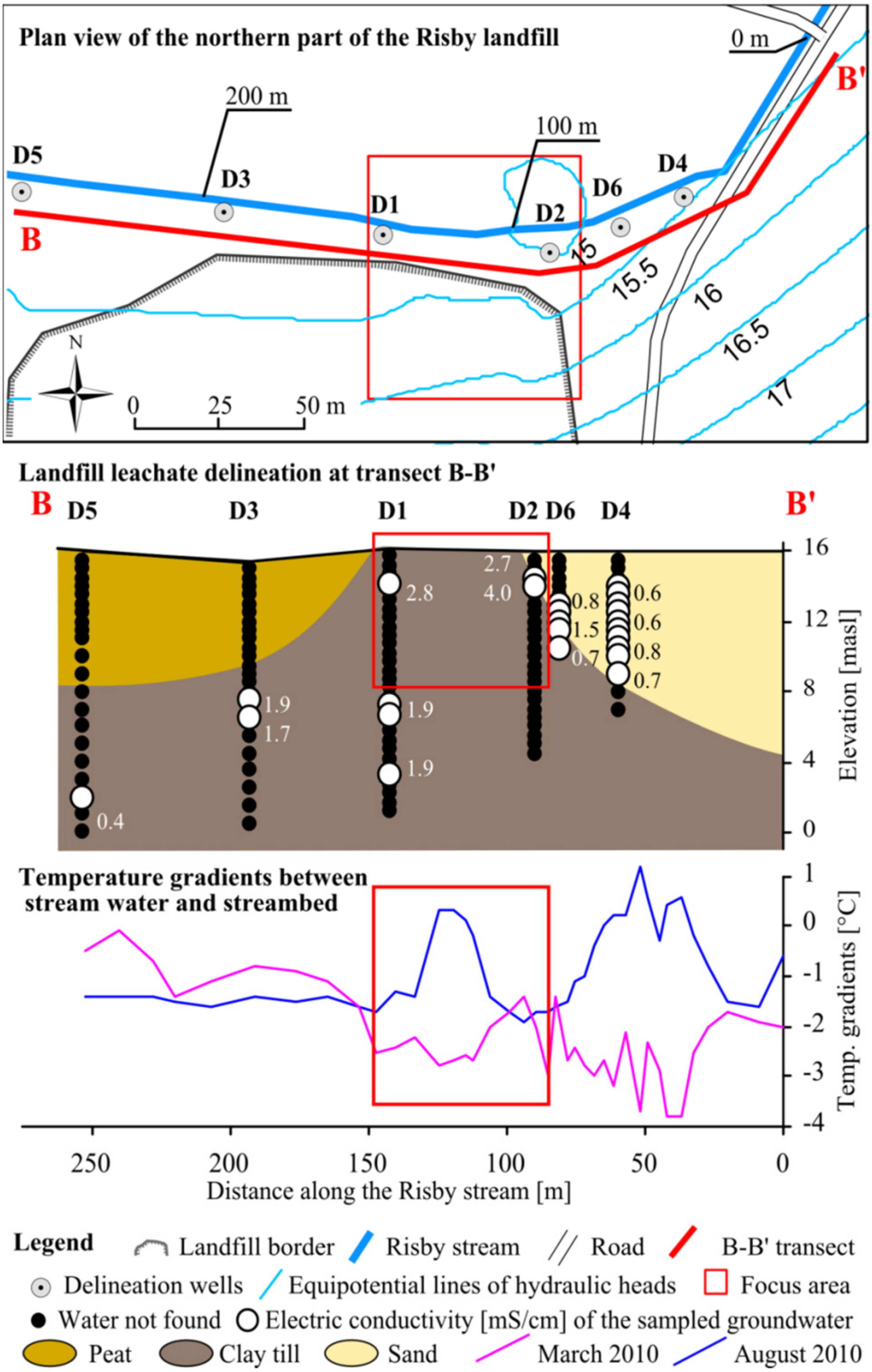


Figure 12 Top: plan view of the identified focus area. Leachate parameters were investigated along the transect B-B'. Middle: during the investigation the presence of groundwater was inspected and as an indicator of the leachate strength we used electrical conductivity. Bottom: temperature gradient, a large gradient indicates a groundwater discharge zone (From Milosevic et al., II).

The concentrations in the focus area were investigated in detail, and showed large variations (Figure 13). The inorganic compounds decreased as a function of distance along the groundwater flow from the landfill to the stream. The dilution of chloride from the hot spot to the stream was between 44 and 95 % and ammonium was between 84 and 98% (Calculated according to Lyngkilde and Christensen (1992)). The herbicides; MCPP (methylchlorophenoxypropionic acid), dichlorprop and 4-CPP (2-(4-chlorophenoxy)propanoic acid) decreased similar to ammonium (79-100, 99-100 and 67-100 % respectively). 4-CPP either result from impurities in the synthesis of MCPP and dichlorprop or it is the result of degradation (Reitzel et al., 2004). In this study, the elevated concentrations indicate that degradation is occurring. While spatial variability is expected in the source of old unlined landfills, it is likely that the spatial variability of contaminants from Risby Landfill was enhanced due to the spreading in clay till.

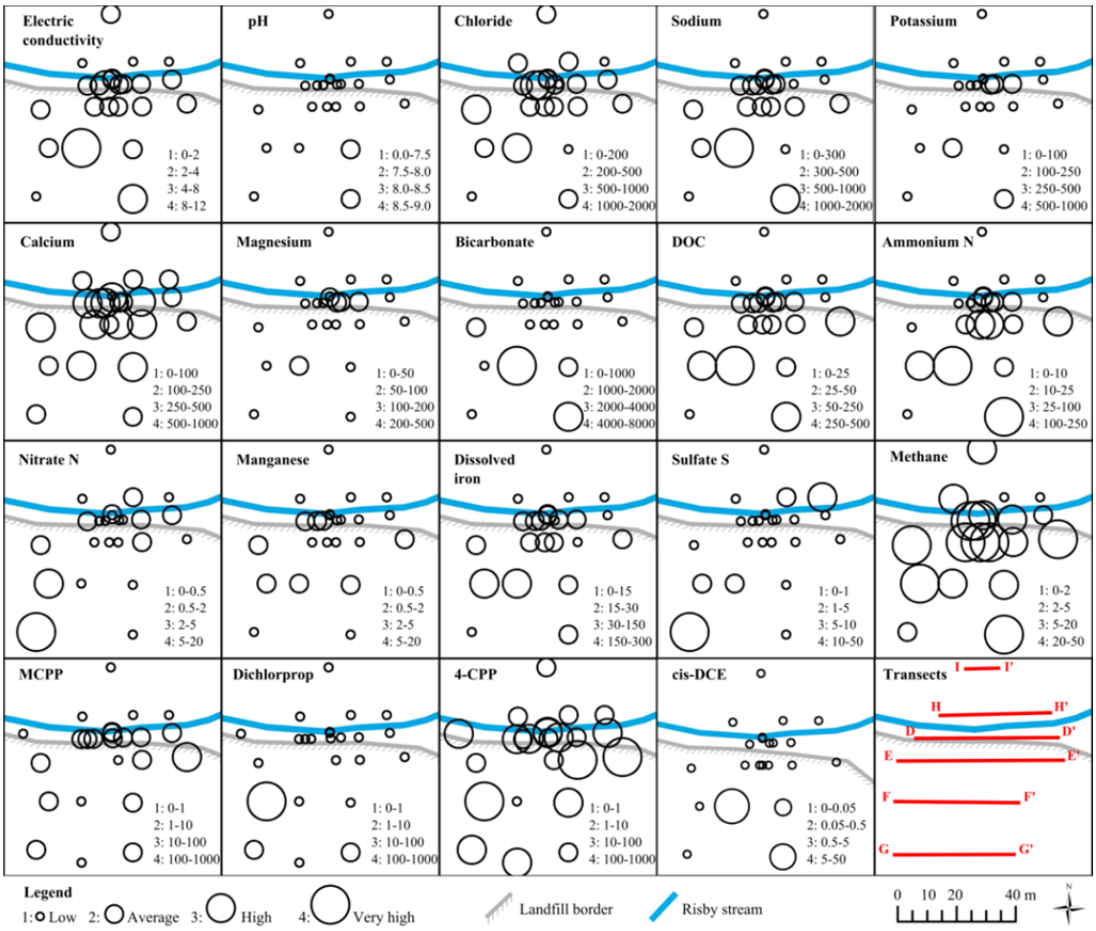


Figure 13 Maximum concentrations of leachate indicators, redox species and xenobiotic compounds are sampled beneath the landfill. The values are in mg/l except for electrical conductivity which is in µS/cm and xenobiotic organic compounds µg/l (From Milosevic et al., II).

A mass balance of Risby Stream was compiled by breaking the stream down into consecutive stream segments according to the underlying geology (Milosevic et al., II). A mass balance for each segment revealed that the impact on the stream originated from discharging groundwater, surface water runoff and seepage from ponds along the stream. Significant seasonal variation in the contaminant concentrations was observed. The impact of the landfill on the stream was most evident during dry (low flow) seasons where concentrations reached groundwater levels. During low flow the concentrations in the stream increase immediately before the focus area and level off shortly after the landfill. The decrease in stream concentrations downstream of the landfill was most likely cause by attenuation by dilution and degradation (Milosevic et al., II).

3.2 Findings for risk assessment of landfills located in clay till geology on groundwater and surface water

The studies by Thomsen et al. (I) and Milosevic et al. (II) have contributed significantly to the understanding of the impact from landfills located in clay till geology on adjacent water resources. They have successfully quantified the impact of important leachate indicators on the adjacent water bodies, and studied the attenuation processes in the clay till, zones of groundwater surface water interaction and in the stream. This was possible by the development of a mass balance method and the application of an array of field based methods. Finally, the two studies show that even though only a small percentage of the total contaminant mass discharge from the landfill enters the stream, it may pose a risk, indicating that this may be the case at other sites with similar conditions. Future studies should be directed towards assessing the chemical and ecological status of the stream.

The specific findings are:

- At Risby Landfill, using a mass balance method provides useful estimates of the impact of the landfill on the water resources. For chloride, total mass discharge from the landfill was 9.4 ton/year. This resulted in an impact on the limestone aquifer of approximately 1.4 ton/year. The mass balance method is especially interesting in terms of assessing the impact of landfill source on multiple water resources.

- The total mass discharge of chloride to the stream was 31 kg/year, which is equivalent to 0.3 % of the chloride mass discharge from the landfill.

- An array of methods was required to identify the zones where contaminants were discharging to the stream from the groundwater.

- The impact on Risby stream originated from discharging groundwater, surface water runoff and seepage from ponds along the stream.

- Significant spatial variability was observed in the landfill leachate. This is common in landfill sources but is most likely pronounced because of the underlying clay till.

- The contributions from run off and seepage from ponds were not included in the mass balance. Their contribution was concluded, because the mass balance (including contributions from the groundwater and the stream) could not fully account for the contaminant mass discharge estimated in the stream down-gradient of the focus area.

4 Risk assessment of a stream catchment

While risk assessment commonly is conducted for a single site with the focus on one adjacent water resource, there are important advantages to considering the impact of contaminated sites at catchment scale or larger scale. In this chapter, I present an example of risk assessment of a stream catchment.

4.1 The impact of contaminated sites on a stream catchment

The study catchment is the Hove catchment located west of Copenhagen in Denmark. The novelty in the assessment is an evaluation of the influence of anthropogenic stressors on the ecological (i.e. benthic macroinvertebrate) status of headwater streams at the catchment scale.

In the literature describing risk assessment of contaminated sites at the catchment scale (see Table 2), focus is on assessing the water quality in groundwater, drinking water or surface water or the risk towards human health. None of the listed studies have focus on the ecology. This is interesting because the implementation of the Water Framework Directive (WFD) requires member states to obtain "good ecological and chemical status" in surface waters (River Basin Management Plans, RBMPs). In addition, the need for the development of ecological approaches that disentangle the effects of anthropogenic stressors has been suggested by e.g. Beketov and Liess (2012), Segner (2011) and Statzner and Bêche (2010).

The focus on headwater streams is controversial because they only are considered by the WFD when: 1) they are included in a catchment with an area of at least 10 km^2, 2) they are included in a specific part of the legislation or 3) the headwater stream is significant with regards to connected surface water bodies that are regulated by the WFD (EC, 2003; EC, 2012). But Rasmussen et al. (III) argue that headwater steams are important because: 1) low order streams sometimes constitute the majority of stream networks, 2) there exists a close connection stream and land in headwater systems, 3) they add important biodiversity to the steam network, and 4) they are responsible for the dispersal of species between streams in the network. In this section, a new approach for catchment scale risk assessment is presented, with a focus on addressing the need for headwater stream analysis.

The Hove catchment is located west of Copenhagen, Denmark and represents a complex geological setting, a network of smaller streams and different types of contaminated sites (e.g. landfills, former facilities for storage of chemicals etc.). Risby landfill (discussed in Chapter 3) is located within the Hove Catchment (Figure 14).

The area of the Hove surface water catchment is 195 km2. The Quaternary deposits in the catchment consist of glacial sediments that vary between 15-30 m in thickness. The pre-Quaternary bedrock consists of chalk and limestone (Houmark-Nielsen, 1999; Kessler et al., 2012) and constitutes a deep regional aquifer used for drinking water abstraction. There is no continuous upper aquifer in the area, but several larger sand lenses in the glacial sediments are saturated and represent local aquifers (Kürstein, 2009).

The Hove catchment contains two dominant streams, the Hove stream and the Nybølle stream, and a network of smaller tributaries, connecting lakes and wetlands. The two dominating streams join in the center of the catchment. All the streams are shallow and narrow and many have been channelized. Approximately 80 pct. of the Hove Catchment is used for agriculture; the remaining area is comprised of 15 pct. natural area and 5 pct. urban area (Rasmussen et al., III).

From a total of 123 potential contaminated sites within the catchment, we selected 31 contaminated sites that were of interest. The sites were selected if contamination was documented and if the contamination was assessed to pose a threat to the groundwater. The risk assessment was not part of this project and was done by the Danish municipalities; the regions in most cases.

Two investigations were conducted at the catchment scale. The aim of the first was to calculate the impact posed by the 31 contaminated sites and to prioritize the sites in terms of mass discharge. The aim of the second study was to identify the main anthropogenic stressors, and investigate the ecological status (impairment of the benthic macroinvertebrate communities) of the headwater streams. This was done in order to help prioritize and target mitigation activities (Rasmussen et al., III).

In the first investigation I used the approach described in Overheu et al. (2014) and Troldborg et al. (2008) to calculate the mass discharge estimates to the groundwater for the contaminated sites in the catchment. This differed slightly from the approach by Overheu et al., (2014) and Troldborg et al., (2008), which focused on drinking water supply wells. The site with the largest mass discharge was Kohøjvej Landfill, with a mass discharge of approx. 179 kg/year of BTEX compounds (Benzene, Toluene, Ethylbenzene, xylene). This was due to very high sampled concentrations, but also due to a very large and very uncertain landfill area. The sites with the largest mass discharges of chlorinated solvents and pesticides were Vadsbyvej 16A (0.22 kg/year) and Kohøjvej 2-4 (0.33 kg/year) (Figure 14).

In the second investigation, we focused on the effects of identified anthropogenic stressors potentially impacting benthic macroinvertebrates in 11 headwater streams in the Hove catchment. The four anthropogenic stressors identified within the catchment are: 1) pesticide pollution from agriculture, 2) residential settlements (urban discharges), 3) multiple contaminated sites and 4) habitat degradation. The impact of the 31 contaminated sites was coupled to the headwater streams by simulation of particle tracking, from the sites to the streams. This was done using a catchment scale model set up in MIKE SHE. 11 stream reaches were identified where groundwater surface water interaction could potentially be relevant. (Rasmussen et al., III). Sampling campaigns were conducted in the 11 identified streams, during 2010 and 2011. The campaigns included a number of different techniques (Rasmussen et al., III).

Based on analysis of the results of the sampling campaigns, the impact of the multiple anthropogenic stressors on the headwater streams in the Hove Catchment was evident. This included the physical quality of the habitats (hydromorphology), water quality (chemical) and impairment of the benthic macroinvertebrate community. It was not possible to obtain a robust rank-ordering of the importance of the anthropogenic stressors which suggests that mitigation efforts targeted on a single stressor will most likely not improve the quality of the head water streams. An important contribution of the catchment scale investigation is the recognition that headwater streams are important to consider in management and mitigation efforts.

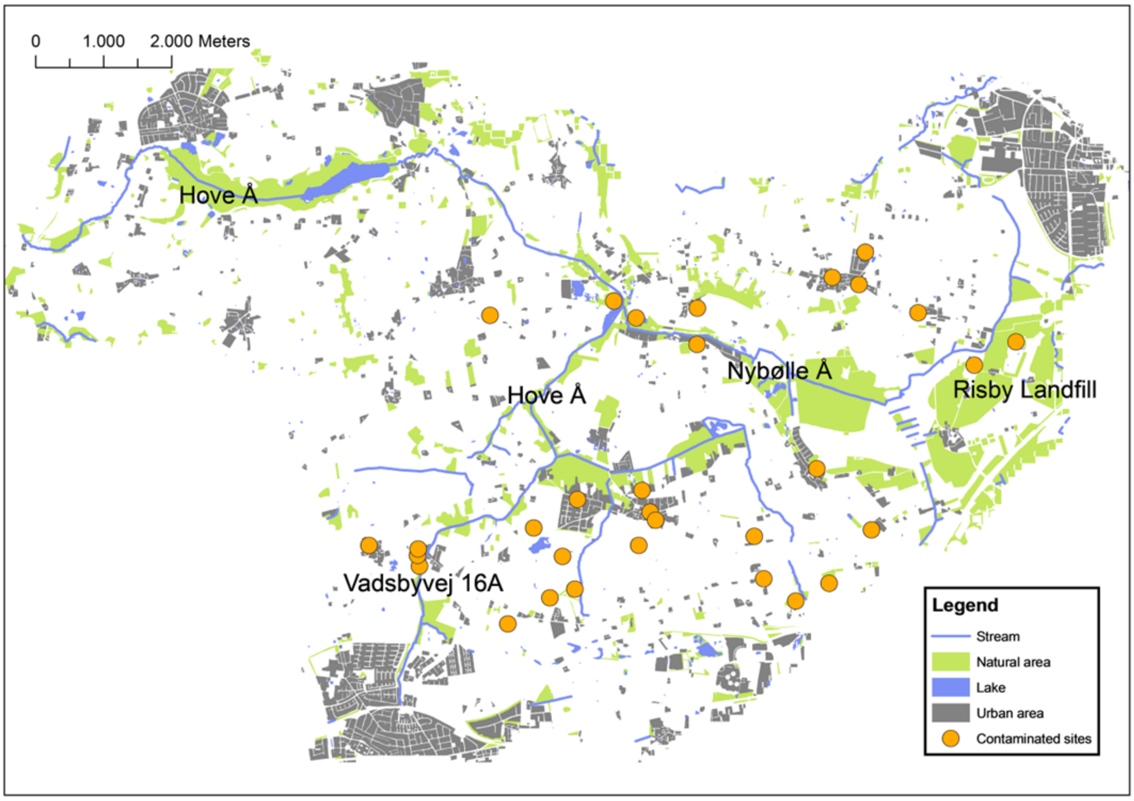


Figure 14 Hove Catchment map.

4.2 Findings for risk assessment of a stream catchment

The study by Rasmussen et al. (I) documents the importance of including headwater streams in the management and mitigation efforts of stream catchments.

The specific findings were:

- The 11 headwater streams all show impairment of water quality and physical habitat, due to anthropogenic stressors.

- The headwater streams in the Hove catchment are impacted by four anthropogenic stressors, including: Contaminated sites, urban discharges, pesticide pollution from agriculture and habitat degradation.

- A robust rank-ordering could not be provided for the anthropogenic stressors. This suggests that mitigation efforts targeted towards a specific stressor would have little effect and that a holistic catchment scale mitigation approach is needed.

5 Uncertainty in risk assessment of contaminated sites

Combining the information from field investigations and models in a risk assessment of a contaminated site is challenging. Most contaminated sites are very complex with respect to both source characteristics and transport processes and a robust risk assessment therefore needs to consider uncertainty (Tartakovsky et al., 2012, McMahon et al., 1999). The task of communicating the uncertainty is challenging (Pappenberger and Beven, 2006), partly because the topic is complex, but also because the meaning of uncertainty varies according to the context (Loewenstein et al., 2001). Most people understand uncertainty by the emotional synonyms such as anxiety, confusion or worry. However, in the field of risk assessment of contaminated sites, uncertainty is usually concerned with the characterization and understanding of the contaminant sources, the pathways, the receptors as well as with the formulation of models to support the risk assessment. But uncertainty concerning contaminated sites can also exist in the more traditional form where it concerns the probability of adverse health effects from the site.

The aim of this chapter is firstly: 1) to introduce the general uncertainty terminology in the context of conducting a risk assessment for a contaminated site; 2) to present how uncertainty can be quantified in actual risk assessments, focusing especially on uncertainty concerning the CSM and on risk assessments at "lower tiers", i.e. where there is no or very limited data available, and 3) to show the value of the BBNs in order to systematically construct CSMs and asses the conceptual uncertainty.

5.1 Uncertainty terminology in risk assessment of contaminated sites.

In this thesis we use the framework developed by Walker et al. (2003), and it is therefore presented in the following subsections with a few modifications, inspired by (Refsgaard et al. 2007). This particular framework is useful because it, in a very general and holistic way, describes an uncertainty taxonomy that can be used in model-based decision-support.

5.1.1 Location of uncertainty

The location of uncertainty refers to where uncertainty manifests itself within a model complex (Walker et al., 2003), the same properties are called sources of uncertainty by Refsgaard et al. (2007). Walker et al., (2003) identify five generic locations within the model that may be associated with uncertainty: (1) the context, (2) the model, (3) the inputs, (4) the parameters and (5) the outcome.

Model context uncertainty refers to the identification of the system boundaries with respect to the real world. It is important to consider in a risk assessment because it frames the problem(s) to be addressed and describes the context in which the risk assessment should be seen. The context is typically decided during the planning stage; it concerns the selection of system boundaries, clarifies the specific problems to be addressed and identifies the targets/outputs of interest for the risk assessment. In this thesis, context uncertainty concerns for example the identification of the relevant contaminated sites or stressors included in the analysis of the impact on the correct number of water resources, at the correct scale. Model context also considers the acceptable/required degree of accuracy and hence the necessary degree of detail in the site investigations. The consideration of context uncertainty is beyond the scope of this thesis.

Model uncertainty is uncertainty concerning the model and can refer to both the uncertainty concerning the model structure (i.e. CSM) and the implementation of the computer model. We will discuss uncertainty concerning the CSM extensively in Chapter 5.2. The uncertainty arising from the computer implementation of the model is referred to as model technical uncertainty. The consideration of model uncertainty is beyond the scope of this thesis.

Input uncertainty describes uncertainty concerning the data that drives the model. This could be soil maps, pumping rates, climatic data etc. and is often/always a measurable quantity with a physical meaning.

Parameter uncertainty is, together with input uncertainty, probably the most widely explored type of uncertainty in the context of water resources. The difference between parameter and input uncertainty can be somewhat confusing, because a quantity considered an input in one model, may sometimes be considered a parameter in another model. Parameters are typically portrayed as constants in the model, and can for example be the hydraulic conductivity or the degradation rate. Parameters are not always measurable and sometimes they even lack a physical meaning. Inputs are usually not changed during a model calibration but parameters are. The model parameters and inputs are closely linked to the, because the complexity of the CSM defines the type and number of the parameters needed in the model.

Outcome uncertainty results from the propagation and accumulation of the uncertainty from all of the above mentioned locations and affects our confidence in the results.

5.1.2 Level of uncertainty

The level of uncertainty essentially refers to how well the conditions at the study site are known. The characterization of a contaminated site ranges from a state where all is known (only in synthetic cases) to total ignorance, and within this spectra we find different levels of uncertainty (Figure 15).

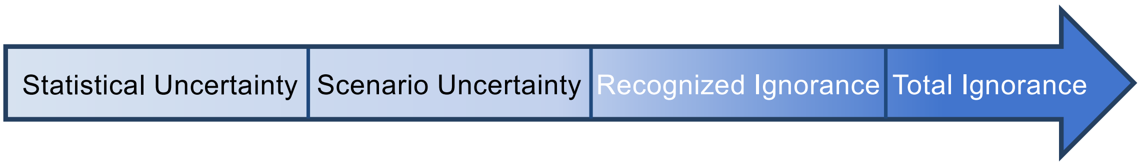


Figure 15 The progressive transition between determinism and total ignorance (Modified from Walker et al. (2003)).

Statistical uncertainty describes the situation where statistical terms are sufficient to describe the uncertainty and where it can be fully quantified. This is the type of uncertainty that is most often considered in natural sciences. When the focus of an analysis is on statistical uncertainty alone, it requires that the model can sufficiently account for the behavior of the phenomena that are being modelled.

Scenario uncertainty concerns uncertainty about mainly, but not exclusively, the future of the system. Scenarios are a useful way of describing how a system may develop. Scenarios do not forecast what will happen, they describe what might happen.

Recognized ignorance is uncertainty about the fundamental mechanisms of the system. This occurs when we do not understand the system, its drivers and how they are connected. Under these circumstances developing scenarios is impractical because an infinite number would need to be developed to cover the uncertainty space.

Total ignorance describes the situation where we do not know what we do not know. This is a deep level of uncertainty where we have no way of knowing the full extent of our ignorance.

Level of uncertainty in Tier 1 and 2 actual risk assessments While there are defined levels of uncertainty described in the literature, the terminology is not well connected to the risk assessment knowledge tiers as applied by practitioners. Because it is logical that there is a connection between increased knowledge level (Tier 1-4) and decrease in level of uncertainty (Figure 15), an attempt to relate the investigation tiers to the level of uncertainty is made in this chapter. This is important in this thesis because I apply a consultant's report of a contaminated site investigation (later in chapter 5.3) of a tier 2 investigation in a scientific context.

Explicit consideration of the uncertainty in actual risk assessments conducted by practitioners is rare, especially early in the investigations (tier 1 and 2). An example of the inventory of a screening level (tier 2) field campaign is specified in Table 1 and it has been common practice within many countries not to conduct a quantitative model based uncertainty analysis on this data basis (ASTM Standard E1739 - 95(2010)e1, 2010; Danish EPA, 2002; UK Environment Agency, 2004). In actual risk assessments based on data from tier 1 and 2, uncertainty may be considered by specifying a conservative MCL (UK Environment Agency, 2004), or by listing potential sources of uncertainty (Danish EPA, 2002; Marcomini et al., 2009; UK Environment Agency, 2004).

In the scientific literature there are a number of risk assessment tools that can quantify parameter uncertainty based on screening level data using Monte Carlo simulations. Examples include RISC5 (Spence, 2011), Premchlor (Liang et al., 2010), ConSim (Davidson and Hall, 2014) and $CARO_{plus}$ (McKnight and Finkel, 2013). There are no records of tools that address conceptual model uncertainty based on a screening level investigation.

The level of uncertainty in screening level investigations is somewhere between scenario uncertainty and statistical uncertainty, depending strongly on the circumstances. For example if we are considering a case of emerging contaminants the level of uncertainty would be recognized ignorance, because we are uncertain about some of the drivers of the system. But for most risk assessments it is a fair assumption that the uncertainty can be assessed by statistical methods. However there may be elements of conceptual uncertainty that we cannot imagine, these can be considered ignorance.

5.1.3 Nature of uncertainty

The nature of uncertainty can be divided into two categories: uncertainty due to imperfection in our knowledge (Epistemic uncertainty) and uncertainty due to the natural variability of the system (Variability uncertainty). Epistemic uncertainty can be reduced by collecting more data, but this will not necessarily reduce uncertainty due to variability (Walker et al., 2003).

Epistemic uncertainty originates from imperfect models, limited data availability, measurement errors and/or subjective judgements. Sources of variability uncertainty include the chaotic nature of natural processes, that human behavior is not always rational and may be hard to account for, that the dynamics of the society and culture are unpredictable, and that technological breakthroughs may cause surprises.

5.2 Conceptual uncertainty

A branch of model uncertainty concerns the model structure, or the CSM. This has been recognized to be the main source of uncertainty in model predictions under some circumstances (Bredehoeft, 2005; Refsgaard et al., 2006).

The difference between the terms conceptual and structural uncertainty is subtle and not discussed that widely in the literature, but one distinction seems to be that structural uncertainty is used more in the broader water resources context (Ajami et al., 2007; Butts, et al., 2004; Refsgaard et al., 2006; Refsgaard et al., 2007) and conceptual uncertainty dominates in contaminant hydrology (Brooks et al., 2015; Koch and Nowak 2015; Sohn et al. 2000; Troldborg et al. 2010; Troldborg et al., 2012). The reason for this could be that structural uncertainty includes considerations of the implementation of the mathematical model, e.g. in the relations between the variables, while conceptual uncertainty is concerned with our understanding of how the site operates, but does not necessarily need to be formulated in terms of equations. Because this thesis is concerned with contaminant hydrology, I apply the term conceptual uncertainty.

Conceptual uncertainty concerns uncertainty in the formulation of CSMs. It can manifest itself in the source, pathways and receptors, and in the related fate and transport processes. Determining which features of the CSM that are uncertain (and therefore should be addressed) is often somewhat subjective and depends strongly on the context of the model.

The conceptual model evolves in complexity at each tier (McMahon et al., 1999) and this is reflected in the complexity of the methods used to quantify the conceptual uncertainty. Uncertainty in the CSM prior to the mathematical model development is hard to quantify and has therefore been assessed qualitatively, e.g. by listing sources or similar (Danish EPA, 2002; Marcomini et al, 2009; UK Environment Agency, 2004). Mathematical models evolve in complexity from analytical models to numerical models. Conceptual uncertainty concerning a contaminated site has rarely been studied based on analytical solutions, but studies are emerging. For example Brooks et al. (2015) studied the conceptual uncertainty in mass discharge measurements using two different conceptual models of the mass discharge distribution. They represented the uncertainty by deriving analytical solutions for the mass discharge coefficient of variation. Analytical solutions are normally applied as part of an advanced tier 2 or a tier 3 investigation, as described in this thesis. At sites with more data (tier 4), conceptual uncertainty has been addressed by creating multiple conceptual models, where each CSM is a plausible representation of reality (see examples in Table 4). The different models may be combined using Bayesian model averaging (BMA) (Hoeting et al., 1999) as done in a number of studies (see e.g. Neuman, 2002; Rojas et al., 2008; Troldborg et al., 2010). BMA combines the predictions from the different models using weights that reflect each model's relative ability to reproduce the system behavior. BMA is usually adopted after the individual models have been conditioned to available data by use of some inverse method such as Bayesian or maximum likelihood approaches. The GLUE (generalized likelihood uncertainty estimation) approach is an alternative to the formal Bayesian approach for model calibration (Beven and Binley, 1992). In the GLUE approach, acceptance criteria may be specified for the goodness of fit of the model results to the data; if the model fails to meet the criteria it may be discarded. The remaining models can be seen as representing the conceptual uncertainty. An important limitation of the multiple model approach is that it can only account for the models we can imagine and important model configurations may be overlooked.

The importance of conceptual uncertainty within the total uncertainty budget has been discussed in the literature (Refsgaard et al., 2007). As stated above (Section 5.1.1) there are multiple locations or sources of uncertainty and it is interesting to quantify them all. However, a complete uncertainty budget for a contaminated site, including quantified estimates of the uncertainty at all five locations has not been presented in the literature. Parameter and input uncertainty have been investigated in detail, and for the past decade conceptual uncertainty has received increasing attention (Refsgaard et al., 2006). Table 4 presents studies in which both conceptual and parameter uncertainties have been accounted for. From these studies it appears that conceptual uncertainty in many cases is found to be a dominant source of uncertainty, demonstrating that even for sites investigated at tier 4 level, the conceptual uncertainty is, at least, as important to consider as the uncertainty concerning parameters. To the knowledge of this author, no studies have attempted to quantify and compare parameter and conceptual uncertainty for sites at lower tiers.

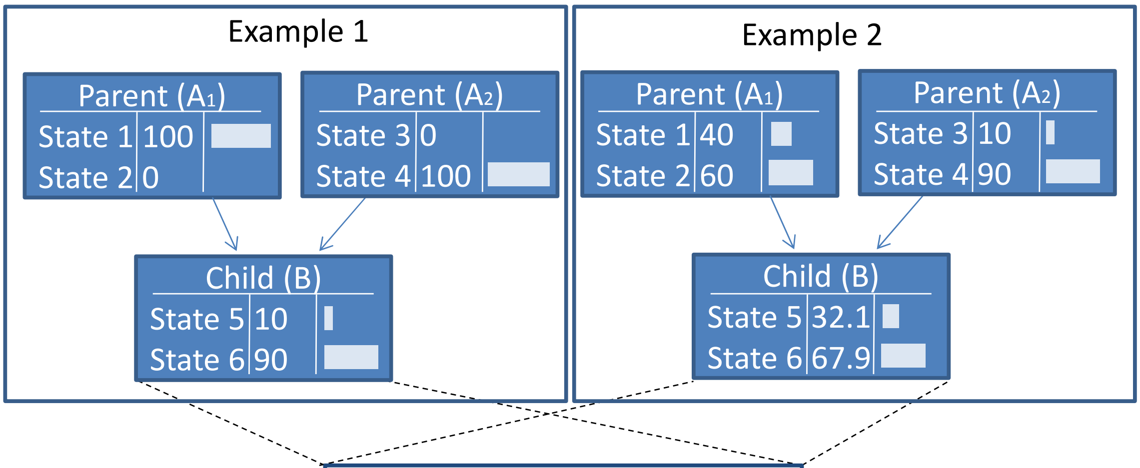
Table 4 Literature that compares conceptual and parameter uncertainty. The comparison of the size of the parameter and the conceptual uncertainty is always based explicitly on the evaluations in the paper, which may be either quantitative or qualitative.

	Troldborg et al. (2007)	Harrar et al. (2003)	Højberg and Refsgaard (2005)	James and Oldenburg (1997)	Troldborg et al. (2010)	Rojas et al. (2008)	Li and Tsai (2009)
Dominating location of uncertainty							
Parameter	X				X	X	X
Conceptual	X	X	X		X		
Undecided				X			
Tier (Knowledge level)							
Tier 1, 2, 3, 4 or Synthetic (S)	4	4	4	4	4	S	4 and S
Method of comparison							
Discussion		X		X			
Comparing residuals	X						
Analysis of predictions			X				
Within and between model variance					X	X	X
Nr. of conceptual site models (CSM)	4	6	3	4	4	7	3

5.3 Application of BBNs for analysis of conceptual uncertainty

An important contribution made during this PhD is to assess the conceptual uncertainty based on a tier 2 investigation (Screening level). As discussed above, most studies that assess conceptual uncertainty have been conducted at tier 4 sites (Chapter 2.1 and Table 4). A quantitative approach that is flexible with regards to available information and data was therefore developed using a BBN (Thomsen et al. IV). The use of BBNs in the context of formulating CSMs is promising, because it allows for integrating quantitative data with qualitative information and expert opinion. This is especially relevant at low tier investigations, where data is limited. Moreover, the modular formulation of the individual elements of conceptual uncertainty (fractures and DNAPL in Thomsen et al. (IV)) is useful, because these modules can be transferred between sites with similar challenges.

A BBN is a graphical probabilistic model. It has the important advantage that causal relations between variables are formulated as conditional probabilities, and that uncertainty therefore is explicitly accommodated. Variables are presented as so-called nodes and the relationship between variables are presented by links. If there is a link from node A to node B, then A is called the parent node and B is the child. The graphical component of a BBN makes it easy to identify the cause effect relationships (Figure 16) (Nielsen and Jensen, 2007).



Conditional probability table for child (node B)

Parent A_1	Parent A_2	State 5	State 6
State 1	State 3	60	40
State 2	State 3	30	70
State 1	State 4	10	90
State 2	State 4	45	55

Figure 16 Two example calculations using a Bayesian belief network. The probabilities are in % (From Thomsen et al (IV)).

Bayesian belief networks have previously been applied in contaminant hydrogeology (Table 5). Stiber et al. (1999; 2004) build a network that can quantify the belief in an ongoing anaerobic dechlorination process. Anaerobic dechlorination is the process by which chlorinated solvents are degraded. Other authors used BBNs to assess various aspects of groundwater quality. Examples include Henriksen et al. (2007a; 2007b) who assessed various management aspects related to groundwater contamination, Shihab (2008) who assessed and forecasted groundwater pollution based on indicators such as electrical conductivity and total dissolved solids, and Aguilera et al. (2013) who assessed groundwater quality through design and development of probabilistic clustering.

Table 5 BBNs in the literature of contaminant hydrology. The uncertainty rows (Conceptual, parameter and context) refers to the definitions of the uncertainty as described in chapters 5.1.1, 5.1.2 and 5.1.3. In the context of this table, this means that the aim of the network is to asses an element that is considered ex. conceptual uncertainty.

	Stiber et al. (1999)	Stiber et al. (2004)	Henriksen et al. (2007a)	Henriksen et al. (2007b)	Shihab (2008)	Aguilera et al. (2013)	Thomsen et al (IV)
Topic							
Reductive dechlorination	X	X					
Groundwater quality			X	X	X	X	
Conceptual site models							X
Uncertainty							
Conceptual	X	X			X	X	X
Parameter							
Context (Scenario)			X	X			
Outcome uncertainty					X	X	
Model learning							
Data	X	X	X	X	X	X	X
Experts	X	X	X	X			X

In Thomsen et al. (IV), a BBN has been developed that can assist the development of multiple CSMs at a contaminated site and quantify the related uncertainty. The BBN was applied at the Vadsbyvej 16A study site (within the Hove catchment), where the contaminant spill occurred in the 1970s. The spill consists partly of the chlorinated solvents PCE (perchloroethylene) and TCE (trichloroethylene), which occurred at the terrain surface due to leakage from (underground) chemical storage tanks. The local Soderup water works is located approximately 500 m west of the contaminated site (Chambon et al. 2011b; Thomsen et al., IV).

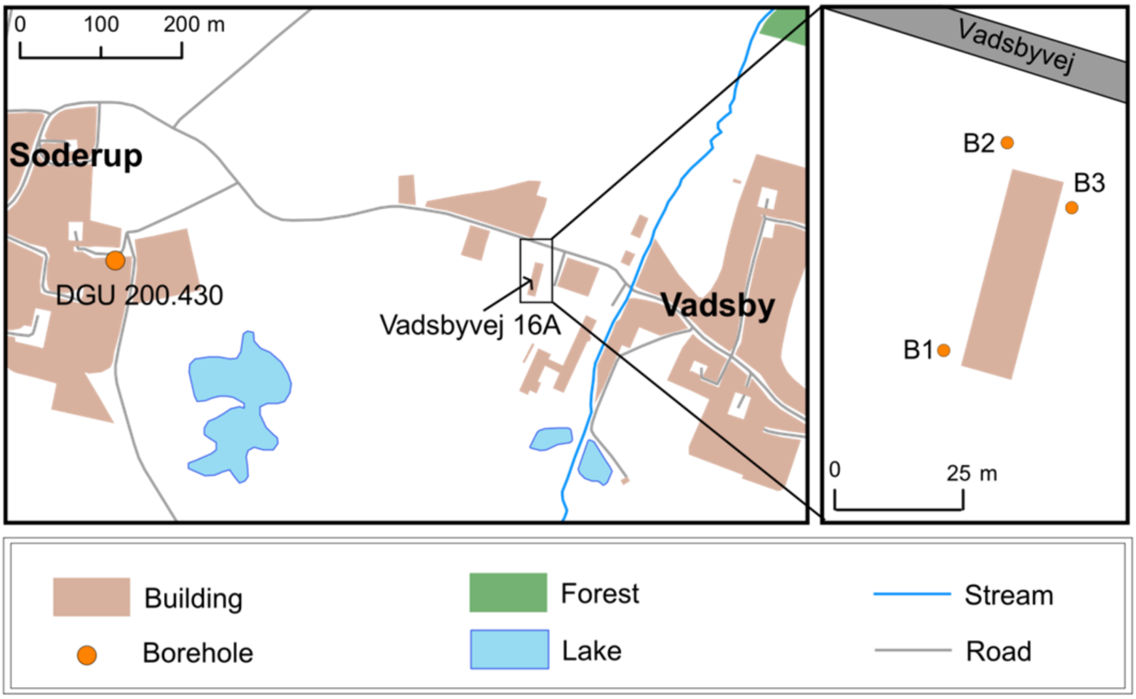


Figure 17 The Vadsbyvej 16 A contaminated site. The Borehole with the number DGU 200.430 indicates the location of the local water works in Soderup (Based on Chambon et al., 2011b).

To demonstrate the application of the BBN methodology at this site, Thomsen et al. (IV) deals with two crucial aspects of conceptual uncertainty: 1) the presence or absence of a separate phase contaminant (i.e. DNAPL) in the source and 2) the presence/absence of fractures in the clay till. Four conceptual models were then developed: FN (Fractured and DNAPL), FD (Fractured and Dissolved), UN (Unfractured and NAPL) and UD (Unfractured and Dissolved) (Figure 18).

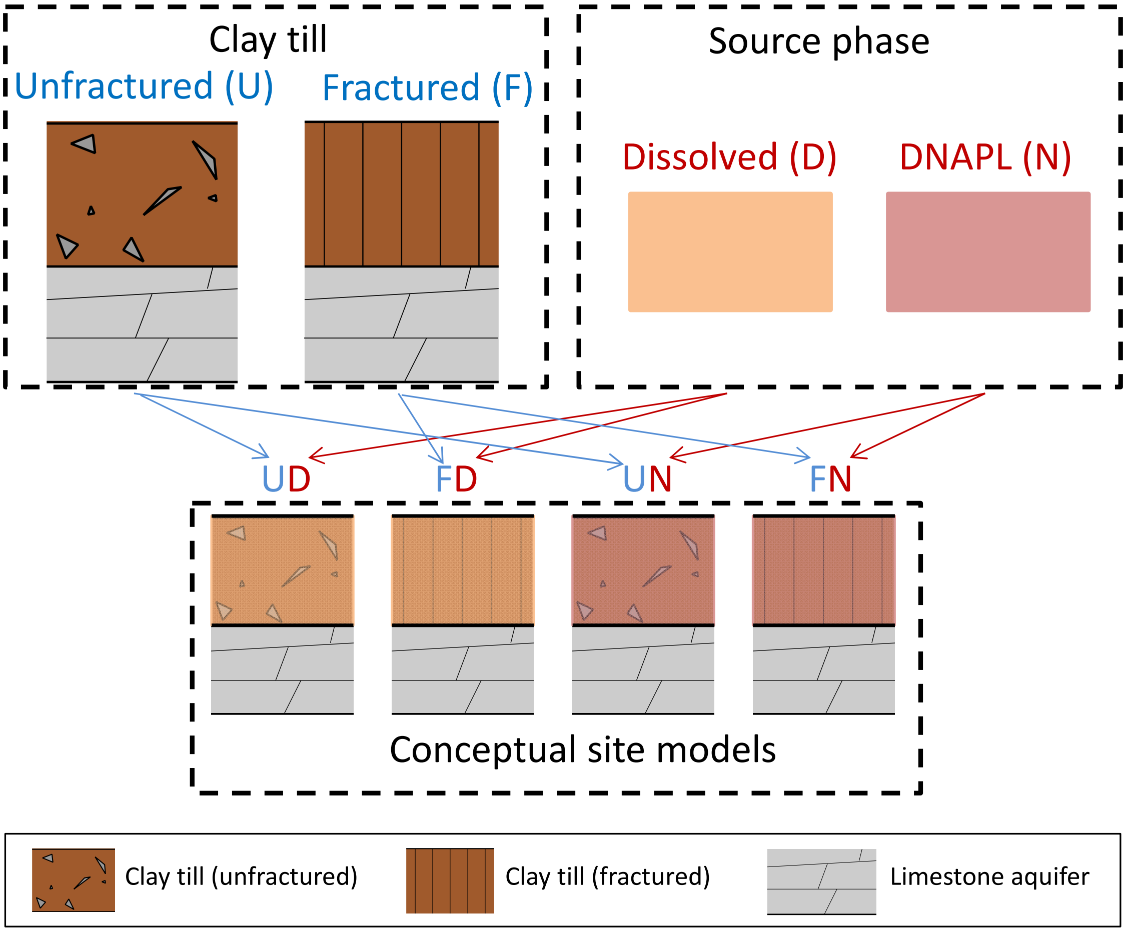


Figure 18 The four conceptual site models developed at the Vadsbyvej 16 A site, (from Thomsen et al. IV).

The network was applied to existing data collected in two separate field investigations and used additionally an expert consultation. The first investigation was a screening level investigation (tier 2). The second investigation included a field campaign with the aim to investigate the presence of DNAPL and to delineate the source (tier 3). Finally, an expert was consulted on the matter of (the expectation for) fractures in the clay till at the site. The BBN method was applied after each investigation and a weight for each CSM was calculated (Table 6). This demonstrates that the BBN method is flexible with respect to data.

Table 6 shows that after each investigation, the belief in the four CSMs changes, with one CSM becoming more favored over the others. This means that the data collected during the investigation increases our belief in one of the conceptual models.

The BBN method can be used in the planning of field campaigns, because an investigation can be directed towards collecting more information on a specific element of the identified conceptual uncertainty. Investigations can thereby become more focused.

An important limitation of the BBN method is that it can only consider the conceptual models we are able to perceive. This means that all conceptual uncertainty may not be fully accounted for. Also the application of the method to other sites with similar elements of conceptual uncertainty may be straight forward. But conceptual uncertainty may concern many elements of the CSM, for example the occurrence of anaerobic dechlorination, or degradation of other compounds, the presence of discharge zones and pathways to a surface water body etc. For the case of anaerobic dechlorination the BBN developed by Stiber et al. (1999) could be applied but for other elements new BBNs would have to be developed.

An interesting and potentially very useful expansion of the method would include a network that could assess the quality of the available information. The data quality network could be divided into the four separate networks one for each tier. The purpose of this addition would be a more detailed assessment of the quality of the information. Ex. the weights in the network concerning clay till could change according to the quality of the information from the investigations. By quality I, mean both trust in the collected data, but also a more quantitative assessment of for example the location of the boreholes with regards to the expected location of the spill or a geological feature.

The development of the BBN method and application to an actual screening level investigation conducted by practitioners (tier 2) bridges an important gap between science and actual management of contaminated sites. Because as stated in Chapter 5.1.2 there are many methods that can deal with uncertainty in the literature but these are not often included in actual site investigations especially at low tiers. In addition the methods that work based on screening level investigations consider only parameter uncertainty. Papers (Table 4) that consider conceptual uncertainty are conducted as part of investigations with a high level of data (tier 4) and methods that work at lower tiers are therefore relevant.

Table 6 The weights (%) for the four models after the screening investigation, the detailed investigation of the site with MIP and soil samples and after consulting an expert. The weight of the most likely model after each site investigation is shown in bold (Thomsen et al., IV).

CSM\Investigation level	Screening investigation	Detailed investigation	Expert opinion
FN (Fractured and (DNAPL)	20.1	29.8	42.9
UN (Unfractured and (DNAPL)	37.4	40.2	27.1
FD (Fractured and Dissolved)	14.9	12.8	18.4
UD (Unfractured and Dissolved)	20.1	17.3	11.6

5.4 Incorporating uncertainty in risk assessments and decision making

Although the field of uncertainty quantification in environmental modelling is well established in the scientific literature, the quantification and use of uncertainty in actual risk assessments by practitioners is still rare, especially at screening level (See Chapter 5.1.2). By the introduction of the BBN concept and the application to an actual tier 2 site investigation (Thomsen et al., IV) I have bridged a small part of the gap between science and practical management of a contaminated site. However, there is still a long way from considering uncertainty in tier 2 investigations to understanding the benefits of doing this with regards to decision making. Pappenberger and Beven (2006) listed some of the benefits of including uncertainty in decision-making good examples are: 1) better insight into the site behavior, 2) more transparent communication of the quantified risk, 3) structured use of expert knowledge and 4) more robust management decisions. But it still remains to describe these improvements in more detail. The aim of this section is to initialize a discussion of how uncertainty estimates may become useful in that context.

The fact that quantified estimates of uncertainty is not included in site assessments does not mean that decisions are made with no consideration of the quantity and quality of the information available at the site. The application of tiered approach to risk assessment (Chapter 2.1) and construction of CSMs (Chapter 2.2) ensures that the available information is communicated in a structured and transparent way. But including quantified estimates uncertainty and comparing these to the estimated impact of the site on the water resource provides important information concerning the risk at the site. This is illustrated on Figure 19, which depicts the impact (concentration or mass discharge) on the y-axis and the uncertainty on the x-axis. The space between the variables is then allocated to one of three management decisions: (1) action, (2) investigation and (3) no action. The allocation is done so that unacceptably high uncertainties lead to further investigations, and that a decision about action or no action is only taken when the level of uncertainty is acceptable.

The benefits of comparing quantified estimates of uncertainty to estimates of the impact are that it makes the decision making process transparent and intuitive. Once an impact and the associated uncertainties have been calculated, they can be mapped on the figure and the relevant decision is indicated. This result can easily be communicated to the authorities and the public, and it becomes very clear why the decision was taken.

While the concept as such is relatively intuitive, it requires the formulation of acceptable and non-acceptable levels of uncertainty and adjustment of the x-axis on Figure 19 accordingly. The y-axis could be adjusted according to the MCL, with the action field always being above and the no action field below the MCL (as is done on Figure 19). Input data consists of concentration or mass discharge estimates from the site, coupled with uncertainty of the given estimates.

There are other often more complex attempts to deal explicitly with uncertainty in risk assessment and decision making. For example, McKnight and Finkel (2013) built a decision support system (CARO-PLUS: Cost-efficiency Analysis of Remediation Options) using system dynamics. This system includes uncertainty analysis and changes in impact with time. Among other things, they demonstrate how splitting parameter uncertainty into three categories can potentially guide further investigations. Enzenhoefer et al. (2015) developed the STakeholder-Objective Risk Model (STORM). The STORM method provides a framework for assessing the total risk of contaminant spill events. It combines information from source, pathway, and receptor models, estimates of mass discharge from spill events, estimates of uncertainty and stakeholder objectives.

Compared to the complexity of these systems, the above mentioned concept is rather simple. But in this simplicity lies the potential of the idea. Because regardless of the complexity of the underlying modelling process, the outcome is a point on a graph that indicates which decision is appropriate.

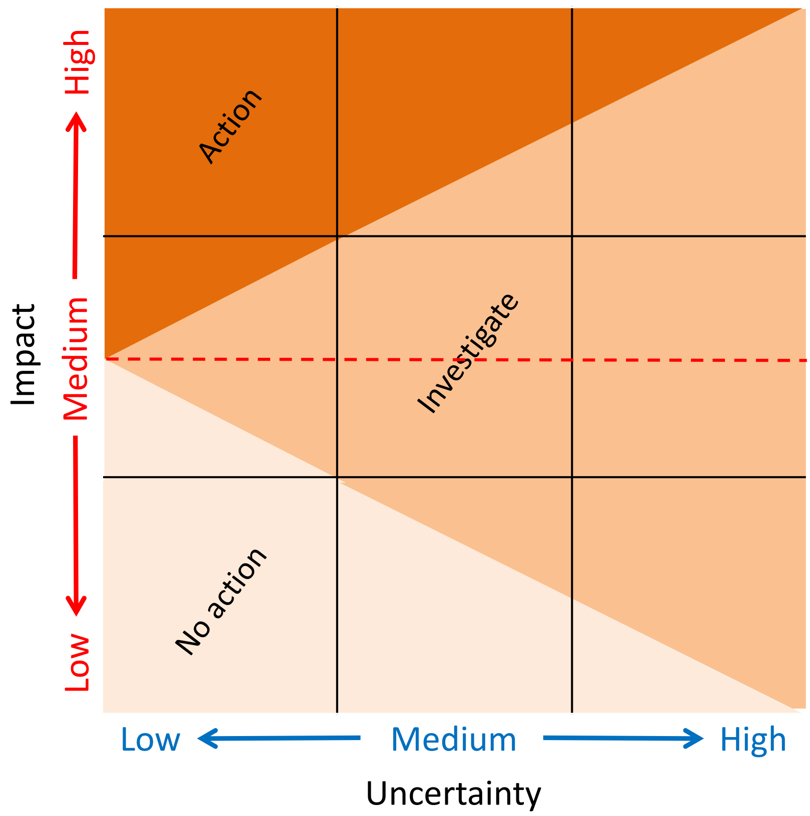


Figure 19 Left: Making decisions by comparing impact and uncertainty.

5.5 Findings for uncertainty in risk assessment of contaminated sites

The field of uncertainty is well described in the scientific literature. A number of frameworks exist that describe how uncertainty manifests itself in modeling and site investigations due to lack of different types of data. In all frameworks there is a term that describes uncertainty concerning the CSM (Conceptual uncertainty). Conceptual uncertainty is an important contributor to the total uncertainty budget. The BBN method developed by Thomsen et al. (IV) can assess the conceptual uncertainty at contaminated sites based in data from field investigations. The use of BBNs to assess the conceptual uncertainty is attractive because BBNs can handle multiple types of information, ranging from information collected during a field campaign to expert knowledge.

Thomsen et al. (IV) bridged an important gap between science and management by assessing the conceptual uncertainty in an actual risk assessment (tier 2) conducted by practitioners.

The specific findings were:

- In the field of uncertainty estimation there is a gap between science and the literature. Where there are multiple methods available in the scientific literature these are often not applied by practitioners, especially in early tier (1-2) investigations.

- Bayesian belief networks can be used to assess conceptual uncertainty at any knowledge tier for contaminated sites.

  It was shown that based on a tier 2 investigation there is little distinction between the multiple conceptual models that were relevant at the site, which implies that the conceptual uncertainty is large.

- An important limitation of the BBN method is that it only considers the CSMs we are able to perceive. All conceptual uncertainty may therefore not be accounted for.

- The application of the BBN method to other contaminated sites is promising. But requires development of BBNs that can assess their specific elements of conceptual uncertainty. The elements of conceptual uncertainty could for example the presence of a zone where contaminated groundwater enters a stream system.

- It is difficult to apply uncertainty estimates in decision making concerning contaminated sites. It is possible that comparing the impact to the uncertainty can provide a context where the uncertainty estimates may become useful.

6 Conclusions

The large number of contaminated sites threatens groundwater and surface water resources. The problem is that these contaminations pollute drinking water resources, but they may also damage ecosystems. The geology, hydrology, and spreading of the contamination at the sites are complex and typically require expensive investigations for proper site characterization. In this context, a risk assessment becomes an important tool, because it can present the risk posed by the sites in a systematic and transparent way. Based on a risk assessment including uncertainty, informed decisions about site management can be taken.

This PhD thesis investigated methods for the risk assessment and uncertainty estimation from contaminated sites impacting groundwater and surface water at the local scale, with an outlook to the catchment scale. The key findings were:

- Studies of landfills in clay tills are rare and so are studies that document their impact on streams. I deepened the knowledge on this topic by the study of Risby Landfill located in a clay till geological setting and adjacent to Risby Stream.

- A mass balance method was developed and found useful for estimating the impact of a landfill on the water resources. The advantages of using mass discharge estimates in a risk assessment context are that they provide an estimate of the total impact on a given resource. The method was applied to Risby landfill.

- Studies of the Risby landfill source zone show enhance variability of leachate concentrations in the groundwater located immediately below the landfill source. This was most likely caused by the heterogeneous clay till setting.

- The groundwater contaminant discharge from Risby Landfill to the adjacent Risby Stream varies spatially. The local scale impact on Risby Stream originated from discharging groundwater, surface water run-off and seepage from ponds along the stream and significantly altered stream chemistry in dry summer seasons.

- Holistic management and mitigation efforts of stream catchments dominated by headwater streams are important. Because efforts targeted a specific anthropogenic stressor in the catchment most likely will fail.

- I studied 11 headwater streams in the Hove Catchment all streams showed impairment of the water quality and physical habitat. This was caused by four anthropogenic stressors: 1) pesticide pollution from agriculture, 2) residential settlements (urban discharges), 3) multiple contaminated sites and 4) habitat degradation.

- Bayesian Belief Networks can be used to assess conceptual uncertainty for contaminated sites. This is important in risk assessments and site characterizations because conceptual uncertainty is often the dominant type of uncertainty.

- The advantages of using BBNs to assess the conceptual uncertainty are that they are ideal for handling the multiple types of data (e.g. site investigations and expert elicitation) related to the construction of a conceptual model.

- The BBN method was demonstrated at the Vadsbyvej 16 field site, accounting for two conceptual elements determined to be uncertain: the presence of a separate phase contaminant and fractures in the clay till geology.

7 Future research directions

During this PhD project, a number of areas that could be subject to further research were identified.

- **Screening methods for investigating contaminant hotspots in landfills.** As part of this thesis, an array of field methods was applied to locate contaminant hotspots in Risby landfill, which is situated in a clay till setting. Information concerning the location and strength of contaminant hotspots is critical in order to estimate the effect on identified receptors. Methods that can optimize this process, with regards to time and (economic) resources are therefore urgently needed.

- **Screening methods for locating contaminant discharge to streams.** The areas where landfill leachate is discharging to Risby stream are small. If this is a general problem with landfills in clay till, it is relevant to develop screening methods that can optimize the location of these areas.

- **Development of BBNs for other elements of conceptual uncertainty.** BBNs that can estimate the belief in the presence of fractures or DNAPL were developed as part of this PhD. However, the method could be extended, and BBNs for other elements of conceptual uncertainty could be explored. As an example, a BBN may be useful in order to predict if a landfill may have an impact on a stream.

- **Development of uncertainty methods** that include both parameter and conceptual uncertainty and can handle dynamic estimates of contaminant concentration or mass discharge**.** The method should work regardless of the data level (tier 1- tier 4). Contaminated sites may proceed from low to high tier investigations during a risk assessment. It is therefore interesting to develop methods that work at all tiers.

- **Comparing the contribution from conceptual and parameter uncertainty at low tiers.** It is interesting to investigate the contribution of different sources of uncertainty to the total uncertainty based on low tier investigations. The importance of conceptual uncertainty has been investigated at sites where tier 4 investigations have been conducted, and the conclusions are in general that it is important. But at lower tiers, there are only speculations available concerning the contribution from conceptual uncertainty compared to for example parameter uncertainty.

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9 Papers

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In this online version of the thesis, paper **I-IV** are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from.

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The Department of Environmental Engineering (DTU Environment) conducts science-based engineering research within four sections:
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The department dates back to 1865, when Ludvig August Colding, the founder of the department, gave the first lecture on sanitary engineering as response to the cholera epidemics in Copenhagen in the late 1800s.

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