#### Technical University of Denmark



#### Modelling tools for integrating geological, geophysical and contamination data for characterization of groundwater plumes

Balbarini, Nicola; Bjerg, Poul Løgstrup; Binning, Philip John; Christiansen, Anders V.

Publication date: 2017

Document Version Publisher's PDF, also known as Version of record

#### Link back to DTU Orbit

Citation (APA):

Balbarini, N., Bjerg, P. L., Binning, P. J., & Christiansen, A. V. (2017). Modelling tools for integrating geological, geophysical and contamination data for characterization of groundwater plumes. Kgs. Lyngby: Department of Environmental Engineering, Technical University of Denmark (DTU).

#### DTU Library Technical Information Center of Denmark

#### **General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.

- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.



#### Modelling tools for integrating geological, geophysical and contamination data for characterization of groundwater plumes



Nicola Balbarini

PhD Thesis November 2017

Modelling tools for integrating geological, geophysical and contamination data for characterization of groundwater plumes

Nicola Balbarini

PhD Thesis November 2017

DTU Environment Department of Environmental Engineering Technical University of Denmark

#### Modelling tools for integrating geological, geophysical and contamination data for characterization of groundwater plumes

#### Nicola Balbarini

PhD Thesis, November 2017

The synopsis part of this thesis is available as a pdf-file for download from the DTU research database ORBIT: http://www.orbit.dtu.dk.

| Address:         | DTU Environment<br>Department of Environmental Engineering |  |  |  |
|------------------|--|--|--|--|
|                  |  |  |  |  |
|                  | Technical University of Denmark                            |  |  |  |
|                  | Bygningstorvet 115   |  |  |  |
|                  | 2800 Kgs. Lyngby   |  |  |  |
|                  | Denmark  |  |  |  |
| Phone reception: | +45 4525 1600  |  |  |  |
| Fax:             | +45 4593 2850  |  |  |  |
| Homenage:        | http://www.env.dtu.dk                                      |  |  |  |
| E-mail:          | reception@env.dtu.dk                                       |  |  |  |
| C                |  |  |  |  |
| Cover:           | GraphicCo, Modified figure from Balbarini et al. (1)       |  |  |  |

#### Preface

This PhD thesis is based on research carried out from September 2014 to August 2017 at the Department of Environmental Engineering, Technical University of Denmark (DTU). The research was performed under the supervision of the main supervisor Professor Poul L. Bjerg (DTU Environment), of the co-supervisor Professor Philip J. Binning (DTU), and of the co-supervisor Associate Professor Anders V. Christiansen (AU Geoscience).

The project was supported by the research project GEOCON (Advancing GEOlogical, geophysical and CONtaminant monitoring technologies for contaminated site investigation) (contract 1305-00004B). The funding for GEOCON is provided by Innovation Fund Denmark.

The thesis is organized in two parts: the first part contextualizes the findings of the PhD in an introductory review; the second part consists of the papers listed below. These will be referred to in the text by their paper number written with the Roman numerals **I-VII**.

- I Balbarini, N., W. M. Boon, E. S. Nicolajsen, J. M. Nordbotten, P. L. Bjerg, and P. J. Binning, 2017, A 3-D model of the influence of meanders on groundwater discharge to a gaining stream in an unconfined sandy aquifer, Journal of Hydrology, Vol. 552, Pages 168-181.
- II Balbarini, N., V. K. Rønde, P. Maurya, G. Fiandaca, I. Møller, K. E. Klint, A. V. Christiansen, P. J. Binning, and P. L. Bjerg, Geophysics based contaminant mass discharge quantification downgradient of a landfill and a former pharmaceutical factory. Submitted.
- III Balbarini N., Rønde V., Balling I. M., Sonne, A. T., McKnight U. S. Binning P. J., Bjerg P. L., Integrated interpretation of the distribution of pharmaceutical compounds in a contaminant plume discharging to a stream in a layered aquifer. Manuscript.

- IV Maurya, P. K., V. K. Rønde, G. Fiandaca, N. Balbarini, E. Auken, P.L. Bjerg, and A. V. Christiansen (2017), Detailed landfill leachate plume mapping using 2D and 3D Electrical Resistivity Tomography with correlation to ionic strength measured in screens. Journal of Applied Geophysics, Vol. 138, Pages 1-8.
- V Fiandaca, G., P.K. Maurya, N. **Balbarini**, A. Hördt, A.V. Christiansen, N. Foged, P.L. Bjerg, and E. Auken, Hydraulic permeability estimation directly from logging-while-drilling Induced Polarization data. Submitted.
- VI Maurya, P. K., N. Balbarini, V. Rønde, I. M. Balling A.V. Christiansen, P.L. Bjerg, E. Auken, and G. Fiandaca, Imaging, lithology, water conductivity and hydraulic permeability at a contaminated site with induced polarization. Submitted.
- VII Rønde, V., U. S. McKnight, A. Th. Sonne, N. Balbarini, J. F. Devlin, and P. L. Bjerg, Contaminant mass discharge to streams: comparing direct groundwater velocity measurements and multi-level groundwater sampling with an in-stream approach, Journal of Contaminant Hydrology. Accepted.

In this online version of the thesis, paper **I-VII** 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, Bygningstorvet 115, 2800 Kgs. Lyngby, Denmark, info@env.dtu.dk

In addition, the following publications, not included in this thesis, were also completed during this PhD study:

Boon, W. M., N. **Balbarini**, P. J. Binning, and J. M. Nordbotten (2016), Efficient Water Table Evolution Discretization Using Domain Transformation, Computational Geoscience, Vol. 1, Issue 1, Pages 3-11.

i

### Acknowledgements

The work of the past three years which lead to this thesis could have not been completed without the help from so many people. The ones I am most grateful to, I would like to thank here.

Poul L. Bjerg and Philip J. Binning: my supervisors at DTU. Through your support and guidance, in the past three years I think, I developed a lot professionally, while enjoying the way. You are the main reason I decided to continue my studies at DTU and then do a PhD.

All the partners in the GEOCON project for inspiring meetings. I enjoyed the many visits and the work at Aarhus University, especially with Anders V. Christiansen and Gianluca Fiandaca, which introduced me to geophysics. Knud Erik Klint, Jørgen F. Christensen, and Ingelise Møller for the guidance through the challenging world of geology. Jørn K. Pedersen and Tom Birch Hansen for the help with the field sites. All other internal and external co-authors who provided their expertise. My companion PhD students Vinni Rønde and Pradip Maurya, for taking part in valuable discussions and fun times.

All my colleagues and friends at DTU Environment for great fun and good company. I would like to thank especially Mette Broholm and Ursula McKnight for discussions and good advices. Anne Harsting and Mette Topp Hansen for being always so kind and helpful. Sinh Hy Nguyen, Bent Skov, Jens Schaarup Sørensen, Flemming Møller, and Erik Rønn Lange for the support in the field and laboratory work, which may not be my strong point. Raphael and Klaus for helping in my hopeless attempts of climbing. Elena, Michele, Andrea, and Chiara for many relaxing lunches. Vinni, Gregory, and Bentje for making our office such a cozy place, where chocolate never lacks. Louise, Anne, Alex, Grith, and Pernille for making sure not one day passed without a good reason to smile.

Finally, I would like to express my exceptional gratitude to Jonas and my family for unconditional support and infinite patience.

### Summary

Contaminated sites are a major issue threatening the environment and the human health. The large number of contaminated sites require cost effective investigations to perform risk assessment and prioritize the sites that need remediation. Contaminated soil and groundwater investigations rely on borehole investigations to collect the geological, hydrological, and contaminant data. These data are integrated in conceptual and mathematical models describing the lithology, the groundwater flow, and the distribution of contaminant concentrations. Models are needed to analyze the potential risks to all receptors, including streams. Key risk assessment parameters, such as contaminant mass discharge estimates, and tools are then used to evaluate the risk.

The cost of drilling often makes investigations of large and/or deep contaminant plumes unfeasible. For this reason, it is important to develop cost effective tools that reduce the number of drillings required for proper characterization of contaminant plumes. Among these tools, non-invasive surface direct current resistivity and induced polarization (DCIP) geophysical methods for contaminant plume investigations are promising.

DCIP surveys provide data on the electrical properties of soil and groundwater. Thus, interpretation of DCIP surveys can supply indirect information on the geological and hydrological properties of soils. In addition, DCIP methods can be used to describe the distribution of concentration of ions in groundwater. However, the effects on the electrical signal of soil properties and of ionic compounds in groundwater can be similar. This means that the interpretation of DCIP surveys is challenging when contaminant plumes are present. Furthermore, these new types of data need to be integrated with the geological, hydrological, and contaminant data in modelling tools used for investigations of contaminated sites.

This thesis presents the development of modelling tools to integrate DCIP methods with geological, hydrological and contaminant concentration data. The developed tools describe groundwater flow to meandering streams, map the distribution of contaminant concentrations in contaminant plumes, and estimate the contaminant mass discharge. The tools are tested at the Grindsted landfill site and at the Grindsted stream site where a contaminant plume from a former factory site is discharging to the stream.

Groundwater flow to streams is affected by many factors, including stream channel geometry. In this study, numerical models simulating groundwater flow to synthetic sinuous streams and to a real meandering stream were developed. Comparison of the models showed that groundwater discharge to streams is greatly affected by the geometry of meanders. Groundwater flow paths near streams are also affected by the combination of meander bends and aquifer properties, such as the groundwater flow direction in the aquifer. The three-dimensional (3D) characteristics of the flow paths require 3D modelling tools to properly describe these sites.

This is confirmed by the migration of the contaminant plume originating from the old factory site and discharging to Grindsted stream. Groundwater flow simulations, developed using on a 3D hydrogeological model of the site, were combined with chemical fingerprinting. This indicated that a low permeability layer separates the contaminant plume in a shallow and a deep plume. These plumes have different chemical characteristics and different migration paths to the stream. This has implications for the risk assessment of the stream and groundwater in the area.

The difficulty of determining groundwater flow paths means that it is also difficult to predict the distribution of contaminants in the subsurface. Anomalies in DCIP surveys near contaminated sites have been used to indicate the presence of plumes with high concentrations of ionic compounds, such as landfill leachate plumes. In some field studies, DCIP anomalies have also been used to detect the presence of microbial degradation of dissolved organic contaminants. This study presents a conceptual model describing the possible links between inorganic and organic contaminants often found at contaminated sites and plumes. The model was used to establish correlations between DCIP derived bulk electrical conductivity and the distribution of concentration of selected inorganic compounds (e.g. chloride and dissolved iron) in the contaminant plumes originated from the landfill site and the factory site. DCIP derived data could also describe the distribution of selected xenobiotic organic compounds, including pharmaceutical compounds and chlorinated ethenes. The correlation between DCIP and organic compounds is indirect and depends on the chemical composition of the contaminant plume and the transport processes. Thus, the correlations are site specific and may change between different parts of a contaminated site.

DCIP data are also useful in risk assessments based on contaminant mass discharge, which is a measure of the contaminant load on an aquifer.

Contaminant mass discharge estimations often rely on multilevel wells to collect information on contaminant concentrations and groundwater flux. Thus, the error of the contaminant mass discharge depends on the density of the samples, on the site heterogeneity, and on the accuracy of the interpolation between data points. A novel contaminant mass discharge method was developed which integrates contaminant concentration data and DCIP data. The method enabled the determination of mass discharge with a lower error compared to only using contaminant concentrations. However, the method can only be applied when a correlation between DCIP and contaminant concentrations can be established. The geophysics based method performed better at low sample densities; thus, the geophysics based contaminant mass discharge method is in particular valuable at large sites and deep plumes, where the drilling costs often do not allow the installation of a sufficient number of sampling points.

In conclusion, this PhD project has developed new ways to improve contaminated site investigations by employing integrated surface DCIP geophysical data with modelling tools for contaminant plume characterization. These combined technologies may improve our ability to map groundwater flow and contaminant plumes more efficiently in the future.

#### Dansk sammenfatning

Forurenede grunde er en alvorlig trussel for både miljø og menneskers sundhed. Der er et meget stort antal af forurenede grunde, som kræver effektive undersøgelser for at kunne risikovurdere og prioritere hvilke lokaliteter, der kræver oprensning. Undersøgelserne af forurenet jord og grundvand kræver boringer, hvor data for geologiske, hydrologiske og forureningskemi indsamles. Disse data integreres i konceptuelle og matematiske modeller, som beskriver litologien, grundvandets strømning, og spredningen af forurenende stoffer. Der er behov for modeller til at analysere denne risiko for vandressourcer, inklusiv vandløb. Nøgleparametre i disse analyser, for eksempel estimater af forureningsfluxen, og risikovurderingsværktøjer bruges derefter til at vurdere risikoen.

Omkostningerne af boringerne gør det ofte vanskeligt at få gennemført undersøgelserne af store forureningsfaner. Derfor er det vigtigt at udvikle effektive metoder, som reducerer antallet af boringer. Blandt disse metoder er den geofysiske *non-invasive surface direct current resistivity and induced polarization* (DCIP)-metode lovende for undersøgelser af forurenede grunde.

DCIP-undersøgelser giver data for de elektriske egenskaber af de geologiske lag og grundvandet. Derved kan fortolkningen give indirekte information om de geologiske og hydrogeologiske egenskaber af undergrunden. Endvidere kan de give oplysninger om fordelingen af ionkoncentrationerne i grundvandet. Forskellige jordtyper og de ioniske stoffer i grundvandet kan give det samme eller lignende elektriske signaler. Dette medfører, at fortolkningen kan være en udfordring, når der er en forureningsfane tilstede. For at kunne bruge DCIP data i undersøgelserne af forurenende grunde, skal de integreres i traditionelle modeller for geologi, grundvandsstrømming og stoftransport.

Denne afhandling beskriver udviklingen af modelværktøjer til at integrere DCIP undersøgelser med geologiske, hydrologiske, hydrogeologiske og forureningsdata. De udviklede værktøjer beskriver grundvandsstrømninger til et naturligt, slyngende vandløb, kortlægger spredningen af og beregner forureningsfluxen. Studierne er foretaget i området ved Grindsted og omfatter grundvandsforureningen fra det tidligere Grindstedværket og Grindsted gamle Losseplads.

Grundvandsstrømningen til vandløb er påvirket af mange faktorer, inklusiv geometrien omkring vandløbet. I dette studie udvikles numeriske modeller, som simulerer grundvandsstrømningen til et syntetisk sinusformet vandløb og et naturligt, slyngende vandløb (Grindsted Å). En sammenligning af disse modeller viste, at grundvandsfluxen til vandløbet er stærkt påvirket af geometrien af slyngningerne. Grundvandsstrømningerne nær vandløbene er dog også påvirket af magasinets egenskaber såsom grundvandsstrømningens retning, tilstedeværelse af vandstandsende lag og artesiske magasinforhold. Da grundvandsstrømningen er tredimensionel, er det nødvendigt at benytte tredimensionelle modeller til at beskrive sådanne forhold fyldestgørende.

Dette er illustreret ved strømningen af forureningsfanen fra Grindstedværket mod Grindsted Å. Der er opbygget en geologisk og hydrogeologiske model for området, som er anvendt til modellering af vandstrømningen og kombineret med kemisk "fingerprinting". Herved er det påvist, at et lerlag skiller forureningsfanen i en dybdere og en overfladenær del, som har meget forskellig kemisk sammensætning og udstrømningsmønster til åen. Dette har implikationer for risikovurderingen af åen og grundvandet i området.

Udfordringen ved at beskrive grundvandsstrømning gør det ligeledes svært at kortlægge fordelingen af koncentrationerne af forureningsstofferne. Anomalier i DCIP undersøgelser nær de forurenede grunde har været brugt til at indikere fanerne med høje ionkoncentrationer, såsom lossepladsfaner. I nogle undersøgelser, har DCIP anomalier endvidere blevet brugt til at detektere tilstedeværelsen af mikrobiel nedbrydning af opløste organiske stoffer. Dette studie har udviklet en konceptuel model, som kan beskrive den mulige forbindelse mellem uorganiske og organiske stoffer, som ofte er fundet ved forurenede lokaliteter og grundvandsfaner. Modellen blev benyttet til at forbinde relationerne mellem DCIP afledte bulk electrical conductivity og koncentrationsfordelingen af udvalgte uorganiske stoffer (f.eks. klorid og opløst jern) i foureningsfanerne ved Grindsted gamle losseplads og Grindstedværket. DCIP afledte data viste sig også at kunne kortlægge koncentrationer af nogle miljøfremmede organiske stoffer bl.a. pharmaceutiske stoffer og klorerede ethener. DCIP er indirekte påvirket af de organiske stoffer og deres korrelation er afhængig af den kemiske sammensætning i og forureningsfanen transportprocesserne. Korrelationen derfor er lokalitetsspecifik ogsåledes også variere indenfor den samme lokalitet.

DCIP data kan derfor være nyttige til at estimere forureningsflux, som er et mål for forureningsmassen pr. tid, som strømmer i et grundvandsmagasin. Forureningsflux estimeringer er ofte baseret på boringsdata, som giver information om forureningskoncentrationer og grundvandsfluxe.Usikkerheden af disse estimeringer afhængiger af densiteten af prøverne, lokalitetens heterogenitet og nøjagtigheden af interpolationen mellem datapunkterne. En metode for at estimere en forureningsflux, hvor ny forureningskoncentrationerne og DCIP data blev benyttet, er præsenteret. Metoden kan estimere forureningsfluxer med en mindre afvigelse sammenlignet med metoden, hvor kun forureningskoncentrationer bliver benyttet. Dog kan metoden kun bruges, når der er en korrelation mellem DCIP og forureningskoncentrationer. Denne metode er især brugbar ved større lokaliteter, hvor boringsomkostningerne ofte ikke tillader installering af et tilstrækkelig antal af prøvetagningspunkter.

I dette PhD projekt er der blevet udviklet nye måder til at forbedre undersøgelser af forurenede grunde ved at benytte DCIP geofysiske data i forståelsen af geologi, hydrogeologi og forureningsudbredelse. Der er blevet udviklet modelleringsværktøjer, som kan beskrive vandstrømning omkring vandløb, kvantificering af forureningsflux med inddragelse af DCIP og forureningskemiske data. De nye metoder og øget anvendelse af de kombinerede teknikker kan forbedre og effektivisere vores evne til at kortlægge grundvandsstrømning og forureningsfaner i fremtiden.

## Table of contents

| Pr | efacev   |
|----|--|
| Ac | cknowledgementsii  |
| Su | ımmaryiv   |
| Da | ansk sammenfatningviii   |
| Tε | ble of contentsxii   |
| 1  | Introduction11.1 Background and Motivation11.2 Research objectives31.3 Outline of the PhD Thesis3  |
| 2  | The field sites52.1 Grindsted stream52.2 Grindsted landfill6   |
| 3  | Insight on groundwater flow to meandering streams93.1 Spatial variability of the groundwater discharge to meandering streams113.2 Groundwater flow paths to meandering streams123.3 Implications of groundwater flow paths to meandering streams on the14                                      |
| 4  | Mapping the distribution of contaminant concentrations by DCIP174.1 Contaminant plumes detected by DCIP174.2 Linking contaminant concentrations with the imaged bulk EC by DCIP20  |
| 5  | A tool for contaminant mass discharge quantification that combines   |
| D  | CIP and contaminant concentrations       25         5.1 The geophysics based method       26         5.2 The geophysics based method versus the contaminant concentration based       26         method       27         5.3 DCIP as a tool to model the hydraulic conductivity field       30 |
| 6  | Conclusions  |
| 7  | Perspectives   |
| 8  | References   |
| 9  | Papers Error! Bookmark not defined.  |

#### 1 Introduction

#### 1.1 Background and Motivation

Contaminated sites are a major risk to human health and the environment. There are more than two million potential contaminated sites in the European Union (WHO, 2013), and 35.461 in Denmark (Jordforureningslovens Areal Register database, 2017). The large number of contaminated sites and the remediation costs mean that a complete remediation of all sites is not possible. Thus, it is necessary to prioritize the sites that poses a higher threat for the environment and for the human population. Prioritization and management of contaminated sites is difficult because of the lack of data on many of the sites (European Commission, 2012).

Contaminant soil and groundwater characterization requires expensive site investigations to evaluate the risks and to define a cost-effective remediation strategy. These investigations obtain information on the lithology, groundwater flow, and the distribution of contaminant concentrations (e.g. Swartjes, 2011). The information is then used to perform a risk assessment of the contaminated site. For risk assessment, it is often important to estimate contaminated groundwater discharge, and one of the most difficult environments to work in is where groundwater discharges to surface water bodies such as streams (European Water Framework Directive, 2000). Near streams, groundwater flow paths are affected by several factors, including hydrogeological heterogeneity in the aquifer and in the streambed, steep hydraulic gradients, and stream channel geometry (Larkin and Sharp, 1992; Cey et al., 1998; Krause et al., 2007; Anibas et al., 2012; Binley et al., 2013; Fernando, 2013; Flipo et al., 2014). Flow processes between groundwater and streams are scale dependent and the reach scale (10-200 m) is often the appropriate scale when dealing with contaminant plumes. Stream meanders can greatly affect groundwater flow paths to streams and thus the transport of contaminants (Modica et al., 1998; Diem et al., 2014; Krause et al., 2014; Boano et al., 2014). Meandering streams are particularly challenging to investigate because groundwater flow paths change greatly with depth, requiring 3D field and modelling tools (Harvey and Bencala, 1993; Modica et al., 1998; Flipo et al., 2014). However, few studies have performed 3D investigations of groundwater flow paths and migration of contaminant plumes to meandering streams, especially at the reach scale.

In order to collect the geological, hydrological, and contaminant data necessary to estimate the contaminant mass discharge and to perform risk assessment drilling of wells are required (Einarson and Mackay, 2001; Cai et al., 2001; Kübert and Finkel, 2006; Basu et al., 2006; Brooks et al., 2008; Troldborg et al., 2012; Balbarini et al., II; Rønde et al., VII). The number of sampling points varies depending on the size of site and the required accuracy (Danish EPA 2000 and 1998). However, the error of the contaminant mass discharge estimation depends on the density of the sampling points as well as on the heterogeneity of both the flow and the contaminant concentration fields (Kübert and Finkel, 2006; Troldborg et al., 2012). Due to the cost of drilling, the density of boreholes is usually too low for a proper characterization of large contaminant plumes (Troldborg et al., 2010; Döberl et al., 2012; Nielsen, 2015).

It is important to develop cost-effective tools for contaminant plume characterization. Among these methods, the non-invasive surface direct current resistivity induced polarization (DCIP) geophysics method is promising. The DCIP method provides information on the electrical properties of the geological formation and on the groundwater filling the pore space. The interpretation of DCIP surveys can provide insight on lithological stratifications and hydrogeological properties (Rubin and Hubbard, 2005; Slater et al., 2007; Weller et al., 2010; Gazoty et al., 2012b; Weller et al., 2015; Binley et al., 2015; Fiandaca et al., V; Maurya et al., VI). DCIP investigations have been employed at landfills to detect leachate plumes (e.g. Abu-Zeid et al., 2004; Chambers et al., 2006; Rucker et al., 2009; Maurya et al., IV; Balbarini et al., II). In addition, microbial biodegradation of organic contaminants has been linked to DCIP anomalies in contaminant plumes from old industrial sites (e.g. Atekwana and Atekwana et al., 2010; Vaudelet et al., 2011).

Even though DCIP techniques have been employed to develop geological and hydrogeological models, their applications to modelling tools for contaminant plume characterization is still limited. The lithological and hydrological information needed to simulate groundwater flow by mathematical models could be provided by combining borehole data and DCIP surveys. Similarly, contaminant concentration data and DCIP survey could be integrated to describe the distribution of contaminant concentrations and to map the extension of contaminant plumes. Risk assessment key parameters, such as contaminant mass discharge estimations, could benefit from DCIP surveys to tackle the limited number of groundwater samples and provide more accurate values.

However, the currently limited knowledge and useful methods restricts the applicability of DCIP surveys for hydrogeological characterization as well as for describing the distribution of contaminant concentration.

#### 1.2 Research objectives

The purpose of this PhD thesis is to develop innovative methods to integrate geological, hydrological, contaminant, and geophysical data with modelling tools for contaminant plume characterization. The main objectives of the project are to:

- Provide insight on groundwater flow and contaminant plume migration to meandering streams by combining geological and hydrological data with surface geophysical data (Papers I, III, V, and VI);
- Determine the extent to which DCIP geophysical data can provide information on the distribution of contaminant concentrations in plumes (Papers II, IV, and VI);
- Develop modelling tools that combine concentration data with geophysical data to estimate the contaminant mass discharge (Papers II and VII);

#### 1.3 Outline of the PhD Thesis

The thesis describes the development of modelling tools for contaminant plume investigations that combines geological, hydrological, contaminant, and geophysical data. These tools were applied at two sites, described in Chapter 2: a landfill leachate plume and a meandering stream impacted by an old factory site plume. The modelling tools describe the groundwater flow field (Chapter 3), the distribution of contaminant concentrations (Chapter 4), and the contaminant mass discharge (Chapter 5). Conclusions and future research needs are presented in Chapters 6 and 7, respectively.

## 2 The field sites

The study focused on two field sites (Figure 1) located near Grindsted, Denmark: the Grindsted landfill and the Grindsted stream. The contaminant plumes present at the two sites originated from two different sources: an old landfill and an old factory site, respectively. Thus, the contaminant plumes have different size, extent, and chemical characteristics, allowing the developed modelling tools to be tested for different conditions and types of contaminants in a similar geological setting.



Figure 1: The map of Grindsted town (grey shading and inset map of Denmark) shows the two field sites (clear boxes): the landfill site and the stream site. The factory site (light brown) is located north of the stream site and the landfill (dark red) is located south of the stream. The equipotential lines [m above sea level] are indicated by the blue lines. The geological stratification is shown along two profiles, indicated also by red dashed lines on the map. The hotspot area of the stream where high concentrations of chlorinated ethenes were found is marked by the red box. Modified figure from Balbarini et al. (II)

#### 2.1 Grindsted stream

At the Grindsted stream site, a contaminant plume originating from the Grindsted factory located 1.5 km north of the stream, is discharging to the stream (Rønde et al., VII; Rasmussen et al., 2016). The factory site plume is characterized by high concentrations of xenobiotic organic compounds (XOCs), including benzene, chlorinated ethenes, and pharmaceutical compounds, mainly sulfonamides and barbiturates (NIRAS, 2009; Sonne et al., 2017).

A Quaternary meltwater sand formation is present in the top 10 m below groundwater surface (bgs) (Figure 1, profile A-A'). Underneath, a 70 m thick Miocene sand formation is underlain by a regionally extensive and thick clay layer. Three Miocene clay and lignite layers up to 1 m thick are embedded in the Miocene sand. An additional Miocene clay and lignite layer located at ca. 25 m asl has a thickness up to ca. 5 m near the stream (Balbarini et al., II, Maurya et al., VI). This low permeability clay layer has a large impact on the groundwater flow and partially hydrologically disconnects the unconfined aquifer in the Quaternary formation from the confined aquifer in the Miocene formation. The hydraulic head difference between the two aquifers is larger near the stream, where the clay layer is ca. 5 m thick. The difference in hydraulic head disappears 1 km north of the stream, at well 114.1447. No substantial difference in hydraulic head is observed between the other Miocene clay layers (Balbarini et al., III).

A 3D geological model for Grindsted stream site was developed using geological boreholes and DCIP surveys. DCIP surveys were useful in mapping the ca. 5 m thick clay and lignite layer located ca. 25 m asl near the stream. The imaged bulk electrical conductivity (EC) by DCIP could discriminate between the effects of the clay layer and of the high concentration of ions in the contaminant plume (Maurya et al., VI).

Groundwater flows toward the stream in the unconfined aquifer, as shown by the equipotential map (Figure 1). The mean hydraulic conductivity ranges between 1.4 10<sup>-6</sup> m/s in the Miocene clay to 1.8 10<sup>-4</sup> m/s in the meltwater sand (Maurya et al., VI; Rønde et al., VII; Balbarini et al., II).

A hotspot area was found in the stream (Figure 1) where high concentrations of chlorinated ethenes, mainly vinyl chloride and *cis*-1,2-Dichloroethene (*cis*-DCE) were detected (Rønde et al., VII). However, contaminated groundwater enters the stream along a 2 km stream stretch discharging mainly pharmaceutical compounds (Sonne et al., 2017).

#### 2.2 Grindsted landfill

At Grindsted landfill, 300,000 tons of waste were deposited between 1930 and 1977 over an area of 10 ha. The waste includes municipal solid waste, sewage sludge, and demolition waste. In the north-western part of the landfill, 85,000

tons of waste from a pharmaceutical factory were deposited. The waste was deposited directly on the surface and without any leachate collection at the site (Kjeldsen et al., 1998a).

The landfill is located on top of a ca. 10 m thick Quaternary meltwater sand layer (Figure 1, profile L-L'). A ca. 70 m thick Miocene sandy formation belonging to the Odderup formation is present underneath the Quaternary sand layer. Four Miocene clay and lignite layers up to 1 m thick are embedded in the sandy formation (Balbarini et al., II). At -40 m asl (ca. 80 m bgs), a thick and regionally extended clay layer underlines the unconfined aquifer (Heron et al., 1998).

The equipotential map shown in Figure 1 indicates that groundwater flows in the north-western direction. Seasonal changes in the groundwater flow direction near the landfill are responsible for the lateral spreading of the leachate plume (Kjeldsen et al., 1998b). The geometric mean of the hydraulic conductivities measured in the unconfined aquifer by 22 slug tests was  $1.7 \ 10^{-4} \text{ m/s}$  (Balbarini et al., II).

The landfill leachate plume contains high concentrations of ionic compounds, such as chloride and dissolved iron (Bjerg et al., 1995) and a mixture of XOCs, including chlorinated ethenes and petroleum hydrocarbons (Rügge et al., 1999). Pharmaceutical compounds, mainly sulfonamides and barbiturates, have been found in the northern part of the landfill (Kjeldsen et al., 1998a) and in downgradient groundwater (Holm et al., 1995).

# 3 Insight on groundwater flow to meandering streams

Groundwater contaminant plumes are a toxic concern for stream water quality (Roy and Bickerton, 2011). The management of streams and of restoration activities require understanding groundwater flow paths to streams and mapping groundwater fluxes. Water exchanges between streams and aquifers is governed by several factors, including the stream channel geometry, the hydraulic gradient, and the hydraulic conductivity distribution (Larkin and Sharp, 1992; Cey et al., 1998; Krause et al., 2007; Anibas et al., 2012; Binley et al., 2013; Fernando, 2013; Flipo et al., 2014; Balbarini et al., I and III).

Most studies looking at the effects of meander bends on the groundwater interaction with streams has focused on the hyporheic flow (e.g. Wroblicky et al., 1998; Salehin et al., 2004; Cardenas et al., 2004; Revelli et al., 2008; Cardenas, 2008, 2009a,b; Boano et al., 2006; Stonedahl et al., 2010; Boano et al., 2009, 2010; Brookfield and Sudicky, 2013; Gomez-Velez et al., 2014, 2015; see also Table S1 by Balbarini et al., I). Hyporheic processes occur in a zone adjacent to the stream where groundwater and stream water mixes before entering the stream. Thus, hyporheic flow processes cannot describe the groundwater flow paths in the aquifer and the transport of contaminants to streams. When dealing with contaminant plumes discharging to streams, the reach scale (10-200 m) is often the appropriate study scale (Harvey and Bencala, 1993; Conant et al., 2004; Anibas et al., 2012; Weatherill et al., 2014).

Examples of modelling studies investigating the variability of the groundwater flow and of the discharge to streams at different scales are summarized in Table 1. Few studies have looked at meandering streams, with most focusing instead on straight streams. However, meander bends can greatly affect groundwater flow and the spatial distribution of groundwater discharge to streams (Modica et al., 1998; Diem et al., 2014; Krause et al., 2014; Boano et al., 2014; Balbarini et al., I and III).

In this chapter, the effects of stream meanders on groundwater flow paths at the reach scale and on groundwater discharge to streams are discussed. The effects of stream meanders are considered in relation to other factors affecting groundwater-stream exchanges: the hydraulic gradient in the aquifer and in the stream, the groundwater flow direction, and the presence of low permeability layers.

|                    | Stream                                 | Study   | D   | Method  | Aim   | Results on the spatial variability  |
|--------------------|--|---|-----|---|---|---|
|                    | Meander                                | Modica et<br>al., 1998                            | 3-D | Steady-state groundwater flow model with stream interaction   | Source area of groundwater dis-<br>charging to stream and estimate<br>its age   | Groundwater that flows in the stream banks<br>originates near the stream, groundwater that<br>flows in the stream channel originates in dis-<br>tant areas.                   |
| Catchment<br>scale | Straight                               | Aisopou<br>et al.,<br>2015                        | 2-D | Groundwater flow and transport model with stream interaction and pumping system   | Effect of pumping on pesticide transport in groundwater   | Groundwater coming from one side, enters the stream at both sides with under-stream paths   |
|                    | Straight                               | Larkin<br>and<br>Sharp,<br>1992                   | 3-D | Steady state groundwater flow with stream interaction   | Effect of stream channel slope,<br>penetration, and hydraulic param-<br>eters on the relative magnitude of<br>base- and under-flow          | Underflow is highest for high channel slope,<br>low sinuosity, high width-to-depth ratio, and low<br>penetration.   |
|                    | Straight                               | Derx et<br>al., 2010                              | 3-D | Transient groundwater flow and transport with stream interaction  | Mixing processes in the aquifer at<br>riverbanks, short-term change of<br>groundwater discharge due to<br>changes in the stream water level | Spatial discharge variability in straight stream due to changes in the hydraulic gradient.  |
|                    | Straight                               | Guay et<br>al., 2013                              | 3-D | Groundwater flow model in FEFLOW<br>with infiltration from HELP; CAUCHY<br>coupling a diffusion wave surface rout-<br>ing and Richards equation | Comparison of fully integrated<br>models (CATHY) and sequential<br>models (HELP + FEFLOW)   | Groundwater flows concentrically to the stream.   |
| Reach<br>scale     | Straight                               | Miracap-<br>illo and<br>More-<br>Seytoux,<br>2014 | 2-D | The analytical values for the one-sided<br>dimensionless conductance are com-<br>pared with a numerical groundwater<br>model                    | Analytical approach to character-<br>ize local flow exchange conduct-<br>ance and boundary condition be-<br>tween a stream and an aquifer   | Groundwater flows below the stream and<br>enters the stream to the opposite side because<br>different horizontal gradients imposed by<br>boundari conditions                  |
|                    | Meander                                | Balbarini<br>et al., I                            | 3-D | Groundwater flow model implementing<br>a coordinate transformation method by<br>Boon et al. (2017) in COMSOL                                    | Effect of meander bends on the groundwater flow and discharge to streams  | Groundwater flow paths and the spatial<br>variability of the discharge to streams are<br>affected by meander bend geometry,<br>groundwater flow direction, hydrualic gradient |
|                    | Meander                                | Balbarini<br>et al., III                          | 3-D | Groundwater flow model implementing<br>a coordinate transformation method by<br>Boon et al. (2017) in COMSOL                                    | Effect of layered aquifer on groundwater flow and discharge to a meandering stream  | Groundwater flow paths and the origin of<br>groundwater discharging to a meandering<br>stream are affected by low permeability layers<br>in the aquifer                       |
| Local scale        | Straight<br>reach,<br>meander<br>river | Munz et<br>al., 2011                              | 3-D | Transient groundwater flow model in contact with a stream, modelled using MODFLOW River Package   | Identifying groundwater-surface<br>water exchange flow patterns and<br>quantifying fluxes in a small-<br>stream reach                       | Particularly at the beginning of peak flow<br>conditions, head gradients are likely to cause<br>substantial increase in surface water infiltration<br>into the streambed.     |

Table 1: Examples of modelling studies analyzing the spatial variability of groundwater flow and discharge to streams. D stands for dimension.

# 3.1 Spatial variability of the groundwater discharge to meandering streams

Groundwater discharge to streams changes along meander bends. At the Grindsted stream site, the horizontal groundwater discharge at the upper edge of the stream-aquifer interface is shown in Figure 2. Details on the 3D groundwater flow model simulating groundwater flow to Grindsted stream (see Figure 2) and to sinusoidal streams are provided by Balbarini et al. (I and III). These studies concluded that groundwater discharge is highest on the outside of meander bends and is lowest on the inside of the meander bends. The effect of meander bends on the spatial variability of groundwater discharge increases with the sinuosity, which depends on the amplitude and on the wavelength of the meanders (Balbarini et al., I).



Figure 2: Simulated groundwater discharge (blue arrows) to Grindsted stream at the upper edge of the stream-aquifer interface. The upper left figure shows the location of the model domain (black lines) at the Grindsted stream site. The upper right figure shows the grid, the boundary conditions, and the model size. Modified figure from Balbarini et al., I.

The effect of meander bends on contaminant discharge to streams has implications for the transport of contaminant plumes to streams and on the distribution of contaminant concentrations near streams. High concentrations of contaminants at the outer parts of meander bends are explained by the model results and are confirmed by observations at meander bends at the Tern river (Weatherill et al., 2014) and at the Grindsted stream site (Rønde et al., VII; Sonne et al., 2017).

Stream meanders are not the only factor affecting the discharge of groundwater and of contaminant plumes to streams. The spatial variability of the groundwater discharge is also affected by the groundwater flow direction (Balbarini et al., I) and by the distribution of hydraulic conductivity in the streambed (Kalbus et al., 2009; Krause et al., 2012; Brookfield and Sudicky, 2013; Poulsen et al., 2015) and in the aquifer (Balbarini et al., I and III). The magnitude of the groundwater discharge to streams increases with the hydraulic conductivity and with the magnitude of the hydraulic gradient in the aquifer (Balbarini et al., I).

#### 3.2 Groundwater flow paths to meandering streams

Groundwater flow paths to meandering streams change greatly with depth. (Harvey and Bencala, 1993; Modica et al., 1998; Flipo et al., 2014; Balbarini et al., I and III). Thus, these sites must be characterized using 3D field and modelling tools.

In straight streams, groundwater enters the stream at the bank closer to the provenience of the streamlines (Guay et al., 2013; Balbarini et al., I). At meander bends pointing north, groundwater originating north enters the stream both at the north and at the south banks by flowing beneath the stream (Figure 3). Flow paths are reversed for meandering bends pointing north (Balbarini et al., I). This effect is caused by the difference in hydraulic gradients at the two sides of the stream near meander bends. Different head gradients in an aquifer between the two sides of a stream caused by pumping wells or by boundary conditions can also result in similar groundwater flow paths (Miracapillo and Morel-Seytoux, 2014; Aisopou et al., 2015; Balbarini et al, I).

Groundwater discharging at the upper edge of a stream bank originates from the upper part of the aquifer (Figure 3), while groundwater discharging at the centre of the stream originates from the deeper part of the aquifer (Modica et al., 1998; Balbarini et al., I and III). The effect of stream channel geometry on the groundwater flow paths decreases with the depth of the aquifer. In a sandy aquifer, at large depths groundwater flows horizontally to the stream and then downgradient parallel to the stream flow (Balbarini et al., I). This effect may be enhanced by the presence of low permeability layers in the aquifers (Balbarini et al., III). This is shown in Figure 3 by the different groundwater flow paths to Grindsted stream in the shallow unconfined aquifer compared to the deep confined aquifer.



Figure 3: Groundwater flow paths (red lines) and equipotential lines (blue lines) in a cross section cutting thought a meander bend pointing north. The two close ups on the right shows groundwater flow paths in plan view in the confined and unconfined aquifers discharging to Grindsted stream. The upper left figure shows the location of the model domain (black lines) and the cross section (red dashed line) at the site. Modified figure from Balbarini et al. (I and III).

# 3.3 Implications of groundwater flow paths to meandering streams on the migration of contaminant plumes

Since groundwater flow paths to meandering streams are depth dependent, especially in layered aquifers, the migration of contaminant plumes to streams may be as well. At the Grindsted stream site, the distribution of 48 pharmaceutical compounds in groundwater and in the hyporheic zone was analyzed by principal component analysis and hierarchical cluster analysis (Balbarini et al., III).

The different distribution of pharmaceutical compounds in the shallow unconfined aquifer and in the deep confined aquifer suggests the presence of different plumes originating from the old factory site. Simulated groundwater flow paths can explain the different distributions of pharmaceuticals in the two aquifers (Figure 4).

The plume in the unconfined aquifer with high concentrations of pharmaceuticals, chlorinated ethenes (mainly *cis*-DCE and vinyl chloride) and petroleum hydrocarbons (mainly benzene) enters the stream on a short stretch within the middle of the model domain. This is supported by stream water samples (Rønde et al., VII; Balbarini et al., III; Sonne et al., 2017). Differently, in the confined aquifer, groundwater flow paths parallel to the stream may result in the migration of the contaminant plume downstream the model domain. This is confirmed by the presence of several peaks in stream water samples of pharmaceuticals on a 2 km stretch The results suggest a potential risk of contamination of the deep aquifer downstream the study area, especially for persistent and semi-persistent compounds, such as the pharmaceuticals..



Figure 4: In a) PCA using pharmaceutical compounds found in groundwater samples collected in the unconfined and confined aquifer and at stations in the hyporheic zone. The colored circle indicate clusters that differ significantly from each other (p<0.05). The clustering was found by HCA (SIMPROF). The location of the groundwater and hyporheic zone samples is shown in b) for the unconfined aquifer and in c) for the confined aquifer. In b) and c) the model domain (black line), the groundwater flow paths (red lines) and the equipotential lines (blue lines) are shown.

# 4 Mapping the distribution of contaminant concentrations by DCIP

The surface DCIP method has increasingly been used to characterize lithological stratification and hydrogeological properties, such as permeability and water content (e.g. Rubin and Hubbard, 2005; Slater et al., 2007; Weller et al., 2010; Gazoty et al., 2012b; Weller et al., 2015; Binley et al., 2015; Fiandaca et al., V; Maurya et al., VI).

At contaminated sites, DCIP method has been applied for contaminant source characterization. The method has been used to detect the presence of pools of mobile phase or residuals of non-aqueous phase liquids, such as petroleum hydrocarbons, (DeRyck et al., 1993; Yang et al., 2007; Flores Orozco, et al., 2012; Johansson et al., 2015) and to map waste distribution at landfills (Chambers et al., 2006; Gazoty et al., 2012a; Frid et al., 2017).

DCIP is also a useful tool for contaminant plume investigation. However, the applicability of DCIP surveys for contaminant plumes can be more challenging than at contaminant sources because contaminant concentrations in plumes are often much lower. In this chapter, an overview of applications of DCIP for contaminated plume investigations is provided. Then, the imaged bulk EC from DCIP is compared with the concentration of inorganic and organic contaminants at the Grindsted stream and landfill sites.

#### 4.1 Contaminant plumes detected by DCIP

DCIP response is affected by the EC of both groundwater and soil surface (e.g. Ntarlagiannis et al., 2016; Maurya et al., VI). Water EC depends on the concentration of ions in water (Appelo and Postma, 2005) and is proportionate to the bulk EC (Archie, 1942). Surface EC depends on the surface area of the material and on the distribution of the pore size (e.g. Weller et al., 2013; Ntarlagiannis et al., 2016). The presence of contaminant plumes can affect both the bulk EC and the surface EC.

In Table 2, examples of bulk EC imaged by DCIP applied at contaminant plume investigations are collected. Contaminant plumes, and especially landfill leachate plumes, are characterized by high concentrations of inorganic species (Christensen et al., 2001). Thus, several studies have successfully applied DCIP to localize leachate plumes (e.g. Abu-Zeid et al., 2004; Chambers et al., 2006; Rucker et al., 2009; Maurya et al., IV; Balbarini et al., II).

Contaminant plumes can have high concentrations of organic carbon, depending on the composition of the contaminant source. Microbial biodegradation of organic carbon affects the distribution of organic and redox species. In a laboratory column experiment, Aal et al. (2004) observed an increase in the concentration of ions and thus water EC due to microbial biodegradation, which could be detected by DCIP. DCIP has also been used at the field scale to localize areas with pronounced microbial degradation processes (e.g. Atekwana et al., 2005; Atekwana and Atekwana et al., 2010; Vaudelet et al., 2011).

Microbial biodegradation was also observed to affect the surface EC due to biofilm formation, increasing in cell population, and mineral precipitates (e.g. Allen et al., 207; Atekwana and Slater, 2009; Aal et al., 2004; Williams et al., 2009; Personna et al., 2013). At the studied sites at Grindsted, iron precipitates are not considered a controlling factor of the DCIP signal and the presence of biofilm is unlikely due to low microbial densities in a contaminant plume (Balbarini et al., II). Under these assumptions, the focus of this study has been only on the effects of contaminant plume on the bulk EC imaged by DCIP.

| Process<br>affecting the im-<br>aged bulk EC | Study                          | Findings   |  |  |
|--|--------------------------------|--|--|--|
|  | Abu-Zeid et al.,<br>2004       | Identification of leachate plumes characterized by high<br>concentrations of inorganic species, such as dissolved iron<br>and aluminum, migrating from a landfill site.  |  |  |
|  | Rucker et al.,<br>2009         | Identification of a leachate plume with high concentrations<br>of inorganic species, including radiological and heavy met-<br>als, from a nuclear waste disposal site.   |  |  |
| Landfill leachate<br>plume                   | Chambers et al.,<br>2006       | Identification of a potential zone of leachate migration from<br>the landfill. Chemical analysis on samples collected in the<br>zone are not reported.   |  |  |
|  | Maurya et al., IV              | Correlations of imaged bulk EC from DCIP with water EC<br>and ionic strength from groundwater samples collected<br>downstream Grindsted landfill site.   |  |  |
|  | Balbarini et al., II           | Correlation of imaged bulk EC from DCIP with water EC<br>and with inorganic species, such as chloride, and selected<br>pharmaceutical compounds. The correlations are site spe-<br>cific for Grindsted landfill site.  |  |  |
|  | Aal et al., 2004               | In a column test, increases in bulk EC over time reflects in-<br>creases in water EC. The test showed also increases of<br>calcium and microbial population numbers as well as de-<br>creases in nitrate, sulfate, and total hydrocarbon. These<br>temporal changes are due to microbial biodegradation of<br>hydrocarbons: benzene, toluene, ethylbenzene, and xy-<br>lene.                                     |  |  |
|  | Atekwana et al.,<br>2005       | Identification of areas with high bulk EC, high concentra-<br>tions of total dissolved solids, of dissolved inorganic car-<br>bon, of major ions (e.g. calcium and alkalinity) and redox<br>sensitive parameters. These effects were related to the mi-<br>crobial degradation of petroleum hydrocarbons.  |  |  |
| Microbial<br>biodegradation                  | Atekwana and<br>Atekwana, 2010 | Identification of areas with high bulk EC, high concentra-<br>tions of dissolved water EC, iron and calcium, and low ni-<br>trate and sulfate. These effects are related to the microbi<br>degradation of contaminant hydrocarbons. Difference elec<br>trical responses can be obtained due to microbial activity<br>from different areas in the plume.  |  |  |
|  | Vaudelet et al.,<br>2011       | Identification of an area with high bulk EC linked to high<br>water EC. In the same area, high concentrations of total<br>organic carbon and chlorinated ethenes, and low concen-<br>trations of nitrate and sulfate were found. This can be ex-<br>plained by microbial biodegradation of dissolved organic<br>carbon, including contaminant hydrocarbons, and anaero-<br>bic reduction of chlorinated ethenes. |  |  |
|  | Balbarini et al., II           | Correlation of imaged bulk EC from DCIP with water EC<br>and with inorganic and organic compounds (benzene, <i>cis</i> -<br>DCE, vinyl chloride). The correlations are site specific for<br>Grindsted stream site.   |  |  |

Table 2: Examples of applications of bulk EC imaged by DCIP for describing the distribution of contaminants in groundwater plumes.

# 4.2 Linking contaminant concentrations with the imaged bulk EC by DCIP

The effects of contaminant plumes on the bulk EC (see Section 4.1) indicate that DCIP can provide information on the distribution of contaminants in groundwater. However, the applicability of DCIP is limited by the chemical composition and the transport processes of the plume. A conceptual model of the possible links between bulk EC and the distribution of concentrations of organic and inorganic contaminants in plumes is shown in Figure 5.



Figure 5: Conceptual model of the correlation between bulk EC from DCIP, water EC conductivity and inorganic and organic contaminants. Direct correlations are indicated by bulk blue arrows and indirect correlations are indicated by green dotted arrows. XOCs indicates xenobiotic organic compounds, DOC indicates dissolved organic carbon. Modified figure from Balbarini et al. (II)

The conceptual model was applied at Grindsted landfill and Grindsted stream sites to investigate the use of bulk EC for describing the distribution of selected groundwater contaminants. At Grindsted landfill (Figure 6a), the bulk EC could describe the distribution of the ionic strength (Figure 6b), of chloride (not shown), and of sulfonamides and barbiturates (Figure 6c) (Maurya et al., IV; Balbarini et al., II).



Figure 6: Locations of the DCIP profiles (orange lines) and multilevel sampling wells (black dots) are shown in a) for the landfill site. The bulk electrical resistivity and the ionic strength from water samples (black bars) are shown in b), legend shown in d), for the profile parallel to the groundwater flow direction indicated by the black line in a). The correlation between the water electrical conductivity (EC) and the concentration of sulfonamides and barbiturates are shown in a log-log plot in c). Modified figure from Balbarini et al (II) and Maurya et al (IV).

At the Grindsted stream, a correlation could be established between the contaminant plume in the unconfined aquifer discharging to Grindsted stream and the water EC, ionic strength, and redox sensitive species, such as dissolved iron (Balbarini et al., II). High concentrations of dissolved iron, low sulfate concentrations, and the presence of methane indicate strongly reducing conditions due to pronounced microbial activity (Christensen et al., 2000). A correlation was found between water EC and benzene, a biodegradable XOCs released from the contaminant source.

Chlorinated ethenes can take part in reductive dechlorination, where the parent compounds (tetrachloroethene and trichloroethene) are transformed to daughter products, mainly *cis*-DCE and vinyl chloride (Badin et al., 2016; Chambon et al., 2012).Generation of VC from *cis*-DCE takes place under strongly reducing conditions (iron reducing to methanogenic), such as those in the contaminant plume at the stream site. Since water EC can describe the distribution of redox sensitive compounds, and since redox conditions can describe the distribution of chlorinated ethenes, an indirect link between EC and daughter products can be established. At the Grindsted stream site, the water EC could thereby describe the concentration of *cis*-DCE and vinyl chloride in the unconfined aquifer (Figure 7).

The correlations established between the bulk EC (or water EC) and the concentrations of inorganic and organic compounds are indirect and may change in different areas of the same site (Atekwana and Atekwana, 2010). At the Grindsted stream site, the correlations established at the contaminant plume discharging to the stream could not be applied in the deeper part of the of the contaminant plume (Figure 7).

The distribution of pharmaceutical compounds was used to analyze the composition of the contaminant plume. The pharmaceutical compounds are semi persistent and present in the contaminant plume originating from the former factory site. Principal component analysis and hierarchical cluster analysis performed on groundwater samples indicate that the distribution of these compounds in the plume discharging to the stream is statistically different from the plume in the confined aquifer. Even within the confined aquifer, water samples collected in the area marked by the black box (Figure 7) show different compositions (Balbarini et al., II). This indicates that areas with different chemical characteristics exist within the plume at Grindsted stream site. Thus, the correlations between the bulk EC and the contaminants can be applied only at specific areas of the plume as discussed above (Figure 7). This limits the applicability of the DCIP survey for delineating the contaminant plume.

The correlation could successfully be used to determine the contaminant mass discharge of chlorinated ethenes and benzene of the plume in the unconfined aquifer discharging to the stream (see Section 5). However, it was not possible to apply the DCIP survey to delineate the contaminant plume in the confined aquifer. Additional boreholes in this area may help identify and describe the transport paths of the contaminant plume in the confined aquifer and the potential link to DCIP.



Figure 7: Correlation between the water EC, vinyl chloride (VC), *cis*-DCE, and benzene in an area of the unconfined aquifer, marked by the red box, and in an area of the confined aquifer, marked by the black box, at the Grindsted stream site. The map shows Grindsted town with the factory site (brown), located north of the stream site, and the landfill site (dark red) located south of the stream. The equipotential lines [m asl] are indicated by the blue lines.

# 5 A tool for contaminant mass discharge quantification that combines DCIP and contaminant concentrations

The contaminant mass discharge is a key parameter for the risk assessment of contaminated sites and contaminant plumes (Einarson and Mackay, 2001; Kübert and Finkel, 2006; Basu et al., 2006; Cai et al., 2001; Troldborg et al., 2012; Balbarini et al., II; Rønde et al., VII). It is defined as the total mass of contaminants passing per unit time through a control plane that is perpendicular to the groundwater flow direction and encompasses the plume (Basu et al., 2006; Troldborg et al., 2010).

A common method relies on multilevel wells installed on the control plane to collect contaminant concentrations and hydrological data. The control plane is divided into *n* sections of area  $(A_n)$  at which a value of the contaminant concentration  $(C_n)$  and a value of groundwater discharge normal to the plane  $(q_n)$  are assigned. The contaminant mass discharge *CMD* [kg/y] can be calculated as described in equation 1 (Mackay et al., 2012; Li and Abriola, 2009; Kübert and Finkel, 2006; Balbarini et al., II; Rønde et al., VII).

$$CMD = \sum_{n=1}^{N} C_n \cdot q_n \cdot A_n \tag{1}$$

The contaminant concentration and the groundwater discharge do not need to be sampled at each section n. Statistical tools, such as ordinary kriging, can be used to predict the value of a target variable (e.g. the concentration of a selected contaminant) at an unknown location (e.g. the centre of section n) by using the weighted average of the observations.

The error in the contaminant mass discharge estimation depends on the density of the sampling points as well as on the heterogeneity of both the flow and the contaminant concentration fields (Kübert and Finkel, 2006; Troldborg et al., 2012). At large contaminated sites, installing a sufficient number of sampling points to describe the variability the concentration field and of the flow field is often not possible (Troldborg et al., 2010).

In order to tackle the limited number of groundwater samples, surface DCIP can be a useful tool to interpolate between the point measurements (Rubin and Hubbard, 2005, Balbarini et al., II). A geophysics based method for modelling the concentration field for contaminant mass discharge estimation was deve-

loped. In this chapter, the geophysics based method is described. Then, the method is compared with traditional methods for contaminant mass discharge. Finally, the use of a geophysics for modelling the flow field is discussed.

#### 5.1 The geophysics based method

The geophysics based method analyses both the imaged bulk EC determined by DCIP and water samples to describe the contaminant concentration field. This method uses regression kriging to assign the contaminant concentration value to each section of the control plane. In regression kriging, the weighted average of auxiliary variables (e.g. the bulk DCIP) is used to predict the target variable (e.g. the concentration of a selected contaminant) (Hengl et al., 2009; Hengl et al., 2007; McBratney et al., 2003; Odeh et al., 1995; Matheron et al., 1973). Additional details about the implementation of the method are provided by Balbarini et al. (II).

The geophysics based method can be applied only for contaminants whose distribution can be directly or indirectly linked to the distribution of water EC. The correlations are site specific and depend on the chemical composition of the plume and on the contaminant transport processes. At the Grindsted stream site, it could be applied for benzene, vinyl chloride, and *cis*-DCE; at the Grindsted landfill site, the method could be applied for sulfonamides and barbiturates (Balbarini et al., II). However, at the Grindsted landfill site a correlation could not be established for some contaminants, such as benzene or chlorinated ethenes, which are found at low concentrations in the leachate plume.

In Figure 8, the distributions of contaminant concentration obtained by combining contaminant concentrations and DCIP are shown for selected compounds at the Grindsted stream and at the Grindsted landfill site. The distributions of contaminant concentration are used to estimate the contaminant mass discharge in Section 5.3.



Figure 8: Locations of the control planes (red dashed lines), DCIP profiles (orange dotted lines), and multilevel sampling wells (black dots) are shown in a) for the landfill site and c) for the stream site. The distribution of sulfonamides determined by the geophysics based method along the control plane at the landfill site is shown in b); the distribution of vinyl chloride determined by the geophysics based method at the stream site is shown in d). Modified Figure from Balbarini et al. (II).

# 5.2 The geophysics based method versus the contaminant concentration based method

In Table 3, the estimated contaminant mass discharge for selected contaminants at the Grindsted stream and at the Grindsted landfill sites are shown. Two methods are compared: a contaminant concentration based method and the geophysics based method. Both methods apply equation 1 and assume a constant groundwater flow velocity of 14.6 m/y at the landfill site and 106 m/y at the stream site (Balbarini et al., II). In the contaminant concentration method, the concentration field is modelled by kriging the contaminant concentration data (Rønde et al., VII; Balbarini et al., II). In the geophysics based method, the concentration field is modelled by combining contaminant concentration data and DCIP surveys (see Section 5.1).

Table 3: Estimated contaminant mass discharges in kg/y for selected contaminants at the Grindsted stream and at the Grindsted landfill sites (see Figure 8 for the location of the control planes and of the data points). The contaminant mass discharge is estimated by two methods: the first interpolated water sample measurements through kriging and the second combined water samples with DCIP data through regression kriging. The assumed groundwater flow is 106 m/y at the stream and 14.6 m/y at the landfill. Source Balbarini et al. (II).

|                       |                 | Contaminant concentra-<br>tion based method [kg/y] | Geophysics<br>based method<br>[kg/y] |
|-----------------------|-----------------|--|--------------------------------------|
| Grindsted<br>landfill | Sulfonamides    | 750  | 1,848                                |
|                       | Barbiturates    | 88   | 112                                  |
| Grindsted stream      | Vinyl chloride  | 48   | 49                                   |
|                       | <i>cis</i> -DCE | 51   | 52                                   |
|                       | Benzene         | 12   | 11                                   |

For all contaminants, the difference between the two methods is larger at the landfill site compared to the stream site. This can be explained by the sample density at the two site:  $0.06 \text{ samples/m}^2$  at the stream site versus only  $0.0004 \text{ samples/m}^2$  at the landfill site. The relative contaminant mass discharge error is inversely proportional to the sample density.

In Table 4, examples of relative contaminant mass discharge errors and sample densities of studies calculating the contaminant mass discharge using contaminant concentration based methods and the geophysical based method are shown. The relative error requires the "true" value of the total contaminant mass discharge to be calculated. The "true" value is usually not known at field sites. Instead, common practice is to calculate the relative mass discharge uncertainty as the standard deviation divided by the mean. In Balbarini et al. (II), the contaminant discharge calculated using all concentrations is assumed to be the "true" value. The calculations employing all contaminant concentrations at the Grindsted stream site and at the Grindsted landfill site (shown in table 3) are not included in table 4, since no uncertainty/error was calculated.

Table 4: Comparison of sample densities and relative contaminant mass discharge errors and uncertainties from studies applying contaminant concentration based methods and the geophysical based method for calculating the contaminant mass discharge. Only the sample densities applied in the stochastic simulation are included in the table. The error/uncertainty could not be calculated for the contaminant mass discharge employing all site observations of contaminant concentration. Modified table from Troldborg et al. (2012), Troldborg (2010), and Balbarini et al. (II).

| Study                         |                               | Sample<br>density<br>[sam-<br>ples/m <sup>2</sup> ] | Area of the<br>control<br>plane [m <sup>2</sup> ] | Relative error<br>of the mass<br>discharge [%] | Relative<br>uncertainty of<br>the mass<br>discharge [%] |
|-------------------------------|-------------------------------|---|---|--|---|
| Kübert and Finkel             | , 2006                        | 1.07  | 60  | 15   | -   |
|                               |                               | 1.00  | 80  | 40   | -   |
|                               |                               | 1.00  | 80  | 100  | -   |
| Li et al., 2007               |                               | 0.12  | 77.3  | 20   | -   |
|                               |                               | 0.32  | 77.3  | 10   | -   |
| Scwede and Cirpk              | a, 2010                       | 0.08  | 120   | 76   | 81  |
|                               |                               | 0.08  | 120   | 80   | 2   |
| Troldborg et al., 2           | 010                           | 0.02  | 1450  | -  | 68  |
| Cai et al., 2011              |                               | 3.50  | 16  | -  | 9   |
|                               |                               | 0.63  | 77.7  | -  | 19  |
| Beland-Pelletier et al., 2011 |                               | 0.63  | 126   | -  | 67  |
| Troldborg et al., 2012        |                               | 0.32  | 380   | -  | 43  |
|                               |                               | 0.05  | 380   | -  | 74  |
|                               | Concentration<br>based method | 0.055   | 960   | 2  | 6   |
|                               |                               | 0.045   | 960   | 6  | 12  |
|                               |                               | 0.035   | 960   | 13   | 18  |
|                               |                               | 0.025   | 960   | 21   | 31  |
| Balbarini et al., Il          |                               | 0.015   | 960   | 25   | 51  |
|                               | Geophysics<br>based method    | 0.055   | 960   | 0.2  | 6   |
|                               |                               | 0.045   | 960   | 4  | 12  |
|                               |                               | 0.035   | 960   | 11   | 19  |
|                               |                               | 0.025   | 960   | 18   | 31  |
|                               |                               | 0.015   | 960   | 19   | 52  |

When examining all studies shown in table 4, a correlation between the sample density and the relative error/uncertainty cannot be found. This can be explained by the dependence of the error/uncertainty on both the sample density

and the level of heterogeneity in the flow and concentration fields (Kümbert and Finkel, 2006; Troldborg et al., 2012). Different studies may have different level of heterogeneities. Furthermore, Balbarini et al. (II) and Cai et al. (2011) did not account for the heterogeneity of the flow field, which may result in lower relative errors and uncertainties compared to other studies. Balbarini et al. (II) calculated the error by assuming the contaminant mass discharge estimated using the contaminant concentration method including all available samples as the "true" value. This may result in low relative errors, especially for the contaminant concentration based method.

When comparing the contaminant concentration based method and the geophysics based method, the relative error and uncertainty increase with the sample density. The geophysics based method show lower mass discharge errors and uncertainties at all sample densities compared to the contaminant concentration based method. The difference between the mass discharge error calculated using the geophysics based method and the concentration based method increases when decreasing the sample density. This indicates that the geophysics based method may be valuable at large contaminated sites, such as the landfill site, where the sample density is usually low due to drilling costs.

## 5.3 DCIP as a tool to model the hydraulic conductivity field

The flow field for contaminant mass discharge calculations can be determined by assigning a hydraulic conductivity and a hydraulic gradient value to each part of the cross sectional area. The flow is then calculated using Darcy's law. Surface DCIP surveys can provide information on the hydraulic properties of the soil, including the hydraulic conductivity (e.g. Slater et al., 2007; Weller et al., 2015, Fiandaca et al., V; Maurya et al., VI). At the Grindsted stream and at the Grindsted landfill sites, the hydraulic permeability, and thus the hydraulic conductivity, were estimated by DCIP using an empirical equation derived by Weller et al. (2015). In Figure 9, the vertical variability of the hydraulic permeability at three boreholes located at the investigated sites are shown. The DCIP surveys were acquired using a logging-while-drilling technique (El-log). Hydraulic conductivities were measured by slug tests and grain size analysis (Fiandaca et al, V).



Figure 9: a) Location of the El-logs (E1-E3, black stars) at the Grindsted stream and landfill (dark red) sites. Next to each El-log, three boreholes for collecting soil samples and performing hydraulic tests are installed (Bh1-Bh3). Next to E1, a sediment core (Sc1) was collected. The vertical variability of the permeability estimated by geophysics (black line), grain size analysis (red dots), and slug tests (blue dots) are shown in b). The geological log is shown next to each permeability profile.

The hydraulic permeability estimated by the El-log can match the hydraulic permeability estimated by slug tests and grain size analysis to within one order of magnitude. When employing surface DCIP, thin low permeability layers embedded in thick high permeability layers cannot be detected by the method due to lack of resolution. Thin high permeability layers embedded in low permeability layers can also not be detected. The permeability is also underestimated near the boundaries between high permeability layers and low permeability layer, because of the smoothness constraint applied in the inversion procedure (Maurya et al., VI). These limitations meant that the hydraulic permeability estimated by surface DCIP could not be applied for contaminant mass discharge estimations. The El-log results showed the potential of DCIP for permeability estimation. Future developments of surface DCIP collection and inversion techniques may improve the permeability estimation.

## 6 Conclusions

The aim of this PhD thesis was to develop tools for contaminant plume investigation that integrate geological, hydrogeological, contaminant concentrations, and geophysical data. The major conclusions of this study are:

- A 3D geological model developed at a field site showed that surface DCIP can describe the continuity and thickness of low permeability layers between borehole logs. DCIP could discriminate between the effects of clayey layers and high concentrations of ionic compounds in the contaminant plume (Maurya et al., VI);
- 3D groundwater flow models were developed simulating groundwater flow to sinuous and meandering streams. Comparison of the scenarios showed that meander bends affect groundwater flow paths and the spatial variability of groundwater discharge to streams. The effect of meanders increases with the sinuosity and depends on the orientation of meander bends relative to groundwater flow (Balbarini et al., I);
- The developed groundwater flow models showed groundwater flow to meandering streams depends on the properties of the aquifer, such as the aquifer thickness. Deep groundwater may flow below the stream to enter through the opposite bank to its origin. The presence of low permeability layers in the aquifer may enhance this effect. (Balbarini et al., I and III);
- The distribution of pharmaceutical compounds in the unconfined and confined aquifer indicated the transport of contaminants to meandering streams require 3D analysis. A join interpretation of groundwater flow paths and of contaminant concentrations in groundwater, hyporheic zone and stream water could provide insight on the discharge of contaminants to the stream. Pharmaceutical compounds were found to pose a potential risk for the deep confined aquifer (>30-50 m below ground surface) and for the stream along a 2 km stretch.
- Analysis of concentrations of inorganic and organic compounds at two field sites indicated that the imaged bulk EC by DCIP could describe changes in water EC. DCIP surveys could map high electrically conductive contaminant plumes, such as leachate plumes. Bulk EC could describe the distribution of selected conservative ions (e.g. chloride) and low degradable organic compounds (e.g. sulfonamides and barbiturates), which have similar transport paths compared to the conservative ions (Maurya et al, IV; Balbarini et al., II);

- Microbial biodegradation cause changes in the redox conditions and the distribution of ionic species, which have been linked with the DCIP anomalies by previous studies. In this study, bulk EC imaged by DCIP could be correlated with concentrations of redox sensitive species. When such a link can be established, imaged bulk EC could describe the distribution of contaminants involved in the degradation (e.g. organic carbon and hydrocarbons) and contaminants whose presence depends on the redox conditions (e.g. daughter products of chlorinated solvents) (Balbarini et al., II);
- Comparison of two field sites showed that the correlations between the bulk EC imaged by DCIP and selected inorganic species and organic contaminants are site specific. The correlations may change at the same site depending on the composition of the contaminant plume and the transport processes (Balbarini et al., II);
- A contaminant mass discharge method which combines DCIP surveys with contaminant concentration data was developed. The method can estimate the contaminant mass discharge by a lower error compared to traditional methods applying only contaminant concentrations. The method is limited by the possibility of establishing a link between the bulk EC imaged by DCIP and the distribution of concentrations of selected contaminants. The novel method can be beneficial at large contaminated sites where a high sample density is costly (Balbarini et al., II; Rønde et al., VII);
- An empirical equation for calculating hydraulic conductivity by DCIP surveys was tested at two field sites. When DCIP surveys were performed by logging-while-drilling technology, the geophysics based hydraulic conductivity could describe hydraulic conductivities within one order of magnitude compared to the value determined by slug tests and grain size analysis. Surface DCIP surveys were limited by the lack of resolution of thin layers and near boundaries between layers with different permeability (Fiandaca et al., V).

These findings allow the number of drillings required for contaminant plume investigations to be reduced, thus decreasing the costs of risk assessment.

## 7 Perspectives

This study presented a few applications of DCIP geophysical methods for investigation of contaminant plumes. However, describing and predicting the contaminant plume transport is challenging. It relies on both determination of the groundwater flow field and plume mapping. The effects on the electrical signal of soil properties and of ionic compounds can be similar; thus, disentangling the two effects on the geophysical signal can be difficult. In addition, organic contaminants are not directly linked to the geophysical signal and their indirect cause and effect relationship can be challenging to explain. Even though we have shown that the methods are promising, the applicability of geophysics for contaminant plume investigations is still limited. Here are some ideas for future research in order to extend the use of geophysical methods for contaminant plume investigations:

- Investigate how the link between DCIP and selected organic and inorganic compounds changes within a contaminant plume. The correlations between DCIP and selected contaminants was found to change within the same contaminant plume. This may be explained by transport processes taking place in the contaminant plumes. The development of contaminant transport models which can explain how the distribution of inorganic and organic species changes over time and space in the plume could help understanding the changes in the link with DCIP. A combined approach of contaminant transport models and DCIP surveys could allow describing the distribution of contaminants by DCIP at different areas of the plume.
- Investigate the applicability of DCIP at contaminated sites characterized by highly heterogeneous geology. The Grindsted landfill site is characterized by a mildly heterogeneous geology. Thus, the effects of contaminant plumes on the DCIP signal could be analyzed without the disturbance of the geological heterogeneity. At the Grindsted stream site, which has a more heterogeneous geology, disentangling the effects of the geology and contaminant plumes has been more challenging (Maurya et al., VI). The challenges relied on the effects of heterogeneity on the geophysical signal as well as on the transport and thus the distribution of contaminants. Even though the two studied sites has different degree of heterogeneity, the geology is similar. Thus, it would be interesting to test and compare the tools developed in this study between sites with different geologies.

- Mapping the distribution of hydraulic conductivity by surface DCIP. The empirical correlation developed by Weller et al. (2015) can describe the distribution of hydraulic conductivity. This could be successfully applied when using logging-while-drilling DCIP surveys (Fiandaca et al., V), but not at surface DCIP surveys. Methods for collecting and inverting the surface DCIP data could be developed in order to solve some of the issues which limited the application of surface DCIP for hydraulic conductivity mapping. This would be beneficial at large sites where few hydraulic tests and hydraulic conductivity values are available.
- Extend the analysis of the effects on meander bends on groundwater flow to streams with seasonally dependent stream-aquifer interactions and to streams with heterogeneous streambeds. The analysis on groundwater flow to meandering streams was performed on gaining streams. However, streams may change between gaining and losing conditions depending on the stretch of the stream and on the period of the year. Future analysis on groundwater flow to meandering streams could investigate how groundwater flow is affected by the alternation of gaining and losing conditions. This may require to extend the investigation to a different study site than Grindsted stream. Furthermore, the analysis performed by Balbarini et al. (I and III) did not accounted for streambed heterogeneity, which is a known factor affecting the stream-aquifer interaction. Future studies could investigate the combined effect of meanders bends and streambed heterogeneity to groundwater flow to meandering streams.
- Develop modelling tools that integrates other geophysical methods than DCIP for contaminant plume investigations. This study has focused only on DCIP geophysical methods. However, other methods were found to be promising for contaminant plume investigations. Among these, the self potential method could describe redox zonation (Heenan et al., 2017). In this study, the bulk EC imaged by DCIP could be linked to redox sensitive parameters and organic contaminants taking part on or whose presence depends on redox processes. Future research could investigate the use of self potential at the studied sites and how the results compare with the ones obtained by DCIP methods.

#### 8 References

- Aal, G. Z. A., Atekwana, E. A., Slater, L. D., & Atekwana, E. A. (2004). Effects of microbial processes on electrolytic and interfacial electrical properties of unconsolidated sediments. Geophysical Research Letters, 31(12), L12505 1–4, L12505–4. doi:10.1029/2004GL020030
- Abu-Zeid, N., Bianchini, G., Santarato, G., & Vaccaro, C. (2004). Geochemical characterisation and geophysical mapping of Landfill leachates: the Marozzo canal case study (NE Italy). Environmental Geology, 45(4), 439–447. doi:10.1007/s00254-003-0895-x
- Aisopou, A., Binning, P. J., Albrechtsen, H.-J., & Bjerg, P. L. (2015). Modeling the Factors Impacting Pesticide Concentrations in Groundwater Wells. Ground Water, 53(5), 722– 736. doi:10.1111/gwat.12264
- Allen, J. P., Atekwana, E. A., Atekwana, E. A., Duris, J. W., Werkema, D. D., & Rossbach, S. (2007). The microbial community structure in petroleum-contaminated sediments corresponds to geophysical signatures. Applied and Environmental Microbiology, 73(9), 2860–2870. doi:10.1128/AEM.01752-06
- Anibas, C., Verbeiren, B., Buis, K., Chormanski, J., De Doncker, L., Okruszko, T., ... Batelaan, O. (2012). A hierarchical approach on groundwater-surface water interaction in wetlands along the upper Biebrza River, Poland. Hydrology and Earth System Sciences, 16(7), 2329–2346. doi:10.5194/hess-16-2329-2012
- Appelo, C. A. J., & Postma, D. J. (2005). Geochemistry, groundwater and pollution. Balkema Publishers, A.A. / Taylor & Francis The Netherlands.
- Archie, G. E. (1942), The effect of temperature on the density and electrical resistivity of sodium chloride solutions, Amer. Instr. Mining Metallurgical and Petroleum Engineers, 146, 54-62.
- Atekwana, E. A., Atekwana, E., Legall, F. D., & Krishnamurthy, R. V. (2005). Biodegradation and mineral weathering controls on bulk electrical conductivity in a shallow hydrocarbon contaminated aquifer. Journal of Contaminant Hydrology, 80(3-4), 149–167. doi:10.1016/j.jconhyd.2005.06.009
- Atekwana, E. A., & Atekwana, E. A. (2010). Geophysical Signatures of Microbial Activity at Hydrocarbon Contaminated Sites: A Review. Surveys in Geophysics, 31(2), 247–283. doi:10.1007/s10712-009-9089-8
- Badin, A., Broholm, M. M., Jacobsen, C. S., Palau, J., Dennis, P., & Hunkeler, D. (2016). Identification of abiotic and biotic reductive dechlorination in a chlorinated ethene plume after thermal source remediation by means of isotopic and molecular biology tools. Journal of Contaminant Hydrology, 192, 1–19. doi:10.1016/j.jconhyd.2016.05.003
- Basu, N. B., Rao, P. S. C., Poyer, I. C., Annable, M. D., & Hatfield, K. (2006). Flux-based assessment at a manufacturing site contaminated with trichloroethylene. Journal of Contaminant Hydrology, 86(1-2), 105–127. doi:10.1016/j.jconhyd.2006.02.011

- Beland-Pelletier, C., Fraser, M., Barker, J., & Ptak, T. (2011). Estimating contaminant mass discharge: A field comparison of the multilevel point measurement and the integral pumping investigation approaches and their uncertainties. Journal of Contaminant Hydrology, 122(1-4), 63–75. doi:10.1016/j.jconhyd.2010.11.004
- Binley, A., Ullah, S., Heathwaite, A. L., Heppell, C., Byrne, P., Lansdown, K., ... Zhang, H. (2013). Revealing the spatial variability of water fluxes at the groundwater-surface water interface. Water Resources Research, 49(7), 3978–3992. doi:10.1002/wrcr.20214
- Binley, A. (2015). DC electrical methods. In G. Schubert (Ed.), Treatise on geophysics. (2nd ed., Vol. 11, pp. 233-259). Elsevier. doi: 10.1016/B978-0-444-53802-4.00192-5
- Bjerg, P. L., Rügge, K., Pedersen, J. K., & Christensen, T. H. (1995). Distribution of Redox-Sensitive Groundwater Quality Parameters Downgradient of a Landfill (Grindsted, Denmark). Environmental Science and Technology (Washington), 29(5), 1387–1394. doi:10.1021/es00005a035
- Boano, F., Camporeale, C., Revelli, R., & Ridolfi, L. (2006). Sinuosity-driven hyporheic exchange in meandering rivers. Geophysical Research Letters, 33(18), L18406. doi:10.1029/2006GL027630
- Boano, F., Revelli, R., & Ridolfi, L. (2009). Quantifying the impact of groundwater discharge on the surface-subsurface exchange. Hydrological Processes, 23(15), 2108–2116. doi:10.1002/hyp.7278
- Boano, F., Harvey, J. W., Marion, A., Packman, A. I., Revelli, R., Ridolfi, L., & Woerman,
  A. (2014). Hyporheic flow and transport processes: Mechanisms, models, and biogeochemical implications. Reviews of Geophysics, 52(4), 603–679. doi:10.1002/2012RG000417
- Boon, W. M., Balbarini, N., Binning, P. J., & Nordbotten, J. M. (2017). Efficient water table evolution discretization using domain transformation. Computational Geosciences, 21(1), 3–11. doi:10.1007/s10596-016-9597-9
- Brookfield, A.E., Sudicky, E.A., 2013. Implications of Hyporheic Flow on Temperature-Based Estimates of Groundwater/Surface Water Interactions. J. Hydrol. Eng. 18 (10), 1250–1261.
- Brooks, M. C., Wood, A. L., Annable, M. D., Hatfield, K., Cho, J., Holbert, C., ... Smith, R. E. (2008). Changes in contaminant mass discharge from DNAPL source mass depletion: Evaluation at two field sites. Journal of Contaminant Hydrology, 102(1-2), 140– 153. doi:10.1016/j.jconhyd.2008.05.008
- Cai, Z., Wilson, R. D., Cardiff, M. A., & Kitanidis, P. K. (2011). Increasing Confidence in Mass Discharge Estimates Using Geostatistical Methods. Ground Water, 49(2), 197–208. doi:10.1111/j.1745-6584.2010.00709.x
- Cardenas, M. B., Wilson, J. L., & Zlotnik, V. A. (2004). Impact of heterogeneity, bed forms, and stream curvature on subchannel hyporheic exchange. Water Resources Research, 40(8), W083071–W0830713, W083071–W0830713. doi:10.1029/2004WR003008

- Cardenas, M. B. (2008). The effect of river bend morphology on flow and timescales of surface water-groundwater exchange across pointbars. Journal of Hydrology, 362(1-2), 134–141. doi:10.1016/j.jhydrol.2008.08.018
- Cardenas, M. B. (2009a). Stream-aquifer interactions and hyporheic exchange in gaining and losing sinuous streams. Water Resources Research, 45(6), W06429. doi:10.1029/2008WR007651
- Cardenas, M. B. (2009b). A model for lateral hyporheic flow based on valley slope and channel sinuosity. Water Resources Research, 45(1), W01501. doi:10.1029/2008WR007442
- Chambers, J. E., Kuras, O., Meldrum, P. I., Ogilvy, R. D., & Hollands, J. (2006). Electrical resistivity tomography applied to geologic, hydrogeologic, and engineering investigations at a former waste-disposal site. Geophysics, 71(6), B231–B239. doi:10.1190/1.2360184
- Chambon, J. C. C., Bjerg, P. L., Scheutz, C., Bælum, J., Jakobsen, R., & Binning, P. J. (2013). Review of reactive kinetic models describing reductive dechlorination of chlorinated ethenes in soil and groundwater. Biotechnology and Bioengineering (Print), 110(1), 1–23. doi:10.1002/bit.24714
- Christensen, T. H., Bjerg, P. L., Banwarth, S. A., Jakobsen, R., Heron, G., & Albrechtsen, H.-J. (2000). Characterization of redox conditions in groundwater contaminant plumes. Journal of Contaminant Hydrology, 45(3-4), 165–241. doi:10.1016/S0169-7722(00)00109-1
- Christensen, T. H., Kjeldsen, P., Bjerg, P. L., Jensen, D. L., Christensen, J. B., Baun, A., ... Heron, G. (2001). Biogeochemistry of landfill leachate plumes. Applied Geochemistry, 16(7-8), 659–718. doi:10.1016/S0883-2927(00)00082-2
- Cey, E. E., Rudolph, D. L., Parkin, G. W., & Aravena, R. (1998). Quantifying groundwater discharge to a small perennial stream in southern Ontario, Canada. Journal of Hydrology, 210(1-4), 21–37. doi:10.1016/S0022-1694(98)00172-3
- Conant, B., Cherry, J. A., & Gillham, R. W. (2004). A PCE groundwater plume discharging to a river: influence of the streambed and near-river zone on contaminant distributions. Journal of Contaminant Hydrology, 73(1-4), 249–279. doi:10.1016/j.jconhyd.2004.04.001
- Danish EPA (1998), Prøvetagning og analyse a fjord, Vejledning fra Miljøstyrelsen nr. 13 [Sampling and analysis of soil, guidance nr. 13]. Danish Ministry of the Environment, Danish Environmental Protection Agency, In Danish, <u>http://www2.mst.dk/udgiv/Pub-likationer/1998/87-7909-142-3/pdf/87-7909-142-3.PDF</u>.
- Danish EPA (2000), Kortlægning af forurenede arealer, Vejledning fra Miljøstyrelsen, nr. 8 [Mapping of contaminated areas, guidance nr. 8], Danish Ministry of the Environment, Danish Environmental Protection Agency, In Danish, <u>http://ww2.mst.dk/udgiv/publikationer/2000/87-7944-331-1/pdf/87-7944-331-1.pdf</u>.

- DeRyck, S. M., Redman, J. D., & Annan, A. P. (1993). Geophysical monitoring of a controlled kerosene spill. In Symposium on the Application of Geophysics to Engineering and Environmental Problems 1993 (pp. 5-19). Society of Exploration Geophysicists.
- Derx, J., Blaschke, A. P., & Bloeschl, G. (2010). Three-dimensional flow patterns at the river-aquifer interface a case study at the Danube. Advances in Water Resources, 33(11), 1375–1387. doi:10.1016/j.advwatres.2010.04.013
- Diem, S., Renard, P., & Schirmer, M. (2014). Assessing the effect of different river water level interpolation schemes on modeled groundwater residence times. Journal of Hydrology, 510, 393–402. doi:10.1016/j.jhydrol.2013.12.049
- Döberl, G., D. Müller, T. Dörri, & M. Kästner (2012), Guideline. In m. Kästener, M. Braeckevelt, G. D"berl, G. Cassiani, M. P. Papini, C. Leven-Pfister, & D. Van Ree (ed) Model-driven soil probing, site assessment and evaluation, guidance on technologies. Sapienza Università Editrice, Rome, Italy, Pages 1-16.
- European Water Framework Directive (2000), Directive 2000/60/ec of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy, Official Journal of the European Communities. L 327/1-72.
- European Commission (2012), The implementation of the Soil Thematic Strategy and ongoing activities, Report from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, 52012DC0046.
- Einarson, M. D., & Mackay, D. M. (2001). Predicting impacts of groundwater contamination. Environmental Science and Technology, 35(3), 66A–73A.
- Orozco, A. F., Kemna, A., Oberdoerster, C., Zschornack, L., Leven, C., Dietrich, P., & Weiss, H. (2012). Delineation of subsurface hydrocarbon contamination at a former hydrogenation plant using spectral induced polarization imaging. Journal of Contaminant Hydrology, 136, 131–144. doi:10.1016/j.jconhyd.2012.06.001
- Frid, V., Sharabi, I., Frid, M., & Averbakh, A. (2017). Leachate detection via statistical analysis of electrical resistivity and induced polarization data at a waste disposal site (Northern Israel). Environmental Earth Sciences, 76(6), 233. doi:10.1007/s12665-017-6554-4
- Fernando, H.J.S., (2013), Handbook of Environmental Fluid Dynamics, vol. 2. CRC Press. Chapter 2, Pages 19–30.
- Flipo, N., Mouhri, A., Labarthe, B., Biancamaria, S., Riviere, A., & Weill, P., (2014), Continental hydrosystem modelling: the concept of nested stream-aquifer interfaces. Hydrol. Earth Syst. Sci. 18, 3121–3149. <u>http://dx.doi.org/10.5194/hess-18-3121-2014</u>.
- Gazoty, A., Fiandaca, G., Pedersen, J., Auken, E., & Christiansen, A. V. (2012a). Mapping of landfills using time-domain spectral induced polarization data: the Eskelund case study. Near Surface Geophysics, 10(6), 575–586. doi:10.3997/1873-0604.2012046

- Gazoty, A., Fiandaca, G., Pedersen, J., Auken, E., Christiansen, A. V., & Pedersen, J. K. (2012b). Application of time domain induced polarization to the mapping of lithotypes in a landfill site. Hydrology and Earth System Sciences Discussions, 9(1), 983–1011. doi:10.5194/hessd-9-983-2012
- Guay, C., Nastev, M., Paniconi, C., & Sulis, M. (2013). Comparison of two modeling approaches for groundwater-surface water interactions. Hydrological Processes, 27(16), 2258–2270. doi:10.1002/hyp.9323
- Gomez-Velez, J. D., Krause, S., & Wilson, J. L. (2014). Effect of low-permeability layers on spatial patterns of hyporheic exchange and groundwater upwelling. Water Resources Research, 50(6), 5196–5215. doi:10.1002/2013WR015054
- Gomez-Velez, J. D., Harvey, J. W., Cardenas, M. B., & Kiel, B. (2015). Denitrification in the Mississippi River network controlled by flow through river bedforms. Nature Geoscience, 8(12), 941–U75. doi:10.1038/NGEO2567
- HARVEY, J. W., & BENCALA, K. E. (1993). THE EFFECT OF STREAMBED TOPOG-RAPHY ON SURFACE-SUBSURFACE WATER EXCHANGE IN MOUNTAIN CATCHMENTS. Water Resources Research, 29(1), 89–98.
- Heenan, J. W., Ntarlagiannis, D., Slater, L. D., Beaver, C. L., Rossbach, S., Revil, A., ... Bekins, B. (2017). Field-scale observations of a transient geobattery resulting from natural attenuation of a crude oil spill. Journal of Geophysical Research-Biogeosciences, 122(4), 918–929. doi:10.1002/2016JG003596
- Hengl, T., G. B. M., Heuvelink, & D. G. Rossiter (2007), About regression-kringing: From equations to case studies, Computer & Geosciences, 33, Pages, 1301-1315, doi:10.1016/j.cageo.2007.05.001.
- Hengl, T. (2009), A Practical Guide to Geostatistical Mapping, EUR 22904 EN Scientific and Technical Research series report published by Office for Official Publications of the European Communities, ISBN: 978-92-79-06904-8.
- Heron, G., Bjerg, P. L., Gravesen, P., Ludvigsen, L., & Christensen, T. H. (1998). Geology and sediment geochemistry of a landfill leachate contaminated aquifer (Grindsted, Denmark). Journal of Contaminant Hydrology, 29, 301–317
- Holm, J. V., Rügge, K., Bjerg, P. L., & Christensen, T. H. (1995). Occurrence and Distribution of Pharmaceutical Organic Compounds in the Groundwater Downgradient of a Landfill (Grindsted, Denmark). Environmental Science and Technology (Washington), 29(5), 1415–1420.
- Johansson, S., Fiandaca, G., & Dahlin, T. (2015). Influence of non-aqueous phase liquid configuration on induced polarization parameters: Conceptual models applied to a timedomain field case study. Journal of Applied Geophysics, 123, 295–309. doi:10.1016/j.jappgeo.2015.08.010
- Kalbus, E., Schmidt, C., Molson, J. W., Reinstorf, F., & Schirmer, M. (2009). Influence of aquifer and streambed heterogeneity on the distribution of groundwater discharge. Hydrology and Earth System Sciences, 13(1), 69–77. doi:10.5194/hess-13-69-2009

- Kjeldsen, P., Bjerg, P. L., Rügge, K., Christensen, T. H., & Pedersen, J. K. (1998a). Characterization of an old municipal landfill (Grindsted, Denmark) as a groundwater pollution source. Waste Management and Research, 16(1), 14–22. doi:10.1177/0734242X9801600103
- Kjeldsen, P., Grundtvig, A., Winther, P., & Andersen, J. S. (1998b). Characterization of an old municipal landfill (Grindsted, Denmark) as a groundwater pollution source. Waste Management and Research, 16(1), 3–13. doi:10.1177/0734242X9801600102
- Krause, S., Bronstert, A., & Zehe, E. (2007). Groundwater-surface water interactions in a North German lowland floodplain - Implications for the river discharge dynamics and riparian water balance. Journal of Hydrology, 347(3-4), 404–417. doi:10.1016/j.jhydrol.2007.09.028
- Krause, S., Blume, T., & Cassidy, N. J. (2012). Investigating patterns and controls of groundwater up-welling in a lowland river by combining fibre-optic distributed temperature sensing with observations of vertical head gradients. Hydrology and Earth System Sciences Discussions, 9(1), 337–378. doi:10.5194/hessd-9-337-2012
- Krause, S., Boano, F., Cuthbert, M. O., Fleckenstein, J. H., & Lewandowski, J. (2014). Understanding process dynamics at aquifer-surface water interfaces: An introduction to the special section on new modeling approaches and novel experimental technologies. Water Resources Research, 50(2), 1847–1855. doi:10.1002/2013WR014755
- Kubert, M., & Finkel, M. (2006). Contaminant mass discharge estimation in groundwater based on multi-level point measurements: A numerical evaluation of expected errors. Journal of Contaminant Hydrology, 84(1-2), 55–80. doi:10.1016/j.jconhyd.2005.12.003
- LARKIN, R. G., & SHARP, J. M. (1992). ON THE RELATIONSHIP BETWEEN RIVER-BASIN GEOMORPHOLOGY, AQUIFER HYDRAULICS, AND GROUNDWATER-FLOW DIRECTION IN ALLUVIAL AQUIFERS. Geological Society of America Bulletin, 104(12), 1608–1620.
- Li, K. B., Goovaerts, P., & Abriola, L. M. (2007). A geostatistical approach for quantification of contaminant mass discharge uncertainty using multilevel sampler measurements. Water Resources Research, 43(6), W06436. doi:10.1029/2006WR005427
- Li, K. B., & Abriola, L. M. (2009). A multistage multicriteria spatial sampling strategy for estimating contaminant mass discharge and its uncertainty. Water Resources Research, 45(6), W06407. doi:10.1029/2008WR007362
- McBratney, A. B., Santos, M. L. M., & Minasny, B. (2003). On digital soil mapping. Geoderma, 117(1-2), 3–52. doi:10.1016/S0016-7061(03)00223-4
- Mackay, D. M., Einarson, M. D., Kaiser, P. M., Nozawa-Inoue, M., Goyal, S., Chakraborty, I., ... Scow, K. M. (2012). Mass Discharge in a Tracer Plume: Evaluation of the Theissen Polygon Method. Ground Water, 50(6), 895–907. doi:10.1111/j.1745-6584.2012.00912.
- Matheron, G. (1973). The intrinsic random functions and their applications. Advances in Applied Probability, 5(3), 439–68, 439–468. doi:10.2307/1425829

- Miracapillo, C., & Morel-Seytoux, H. J. (2014). Analytical solutions for stream-aquifer flow exchange under varying head asymmetry and river penetration: Comparison to numerical solutions and use in regional groundwater models. Water Resources Research, 50(9), 7430–7444. doi:10.1002/2014WR015456
- Modica, E., Burton, H. T., & Plummer, L. N. (1998). Evaluating the source and residence times of groundwater seepage to streams, New Jersey Coastal Plain. Water Resources Research, 34(11), 2797–2810. doi:10.1029/98WR02472, 10.1029/98WR02472
- Munz, M., Krause, S., Tecklenburg, C., & Binley, A. (2011). Reducing monitoring gaps at the aquifer-river interface by modelling groundwater-surface water exchange flow patterns. Hydrological Processes, 25(23), 3547–3562. doi:10.1002/hyp.8080
- Nielsen, M. A. (2015). The Feasibility of Tree Coring as a Screening Tool for Selected Contaminants in the Subsurface. Technical University of Denmark, DTU Environment.
- NIRAS A/S (2009) (in Danish). Overview report of chemicals used at the old Grindsted factory "Grindstedværket" and their potential threat to the environment (Redegørelse overanvendte kemikalier på Grindstedværket og deres potentielle trussel i forhold til miljøet). Technical Report no.1, Region Syddanmark, Kolding.
- Ntarlagiannis, D., Robinson, J., Soupios, P., & Slater, L. (2016). Field-scale electrical geophysics over an olive oil mill waste deposition site: Evaluating the information content of resistivity versus induced polarization (IP) images for delineating the spatial extent of organic contamination. Journal of Applied Geophysics, 135, 418–426. doi:10.1016/j.jappgeo.2016.01.017
- ODEH, I. O. A., MCBRATNEY, A. B., & CHITTLEBOROUGH, D. J. (1995). FURTHER RESULTS ON PREDICTION OF SOIL PROPERTIES FROM TERRAIN ATTRIBUTES
  HETEROTOPIC COKRIGING AND REGRESSION-KRIGING. Geoderma, 67(3-4), 215–226. doi:10.1016/0016-7061(95)00007-B
- Personna, Y. R., Slater, L., Ntarlagiannis, D., Werkema, D., & Szabo, Z. (2013). Complex resistivity signatures of ethanol biodegradation in porous media. Journal of Contaminant Hydrology, 153, 37–50. doi:10.1016/j.jconhyd.2013.07.005
- Poulsen, J. R., Sebok, E., Duque, C., Tetzlaff, D., & Engesgaard, P. K. (2015). Detecting groundwater discharge dynamics from point-to-catchment scale in a lowland stream: combining hydraulic and tracer methods. Hydrology and Earth System Sciences, 19(4), 1871–1886. doi:10.5194/hess-19-1871-2015
- Rasmussen, J. J., McKnight, U. S., Sonne, A. T., Wiberg-Larsen, P., & Bjerg, P. L. (2016). Legacy of a Chemical Factory Site: Contaminated Groundwater Impacts Stream Macroinvertebrates. Archives of Environmental Contamination and Toxicology, 70(2), 219–230. doi:10.1007/s00244-015-0211-2
- Revelli, R., Boano, F., Camporeale, C., & Ridolfi, L. (2008). Intra-meander hyporheic flow in alluvial rivers. Water Resources Research, 44(12), W12428. doi:10.1029/2008WR007081

- Roy, J. W., & Bickerton, G. (2012). Toxic Groundwater Contaminants: An Overlooked Contributor to Urban Stream Syndrome? Environmental Science and Technology, 46(2), 729– 736. doi:10.1021/es2034137
- Rubin, Y. and S. S. Hubbard (2005), Hydrogeophysics, Springer, ISBN-10 1-4020-3101-7.
- Rucker, D. F., Levitt, M. T., & Greenwood, W. J. (2009). Three-dimensional electrical resistivity model of a nuclear waste disposal site. Journal of Applied Geophysics, 69(3-4), 150–164. doi:10.1016/j.jappgeo.2009.09.001
- Rügge, K., Bjerg, P. L., & Christensen, T. H. (1995). Distribution of Organic Compounds from Municipal Solid Waste in the Groundwater Downgradient of a Landfill (Grindsted, Denmark). Environmental Science and Technology (Washington), 29, 1395–1400.
- Salehin, M., Packman, A. I., & Paradis, M. (2004). Hyporheic exchange with heterogeneous streambeds: Laboratory experiments and modeling. Water Resources Research, 40(11), W1150401–W1150416, W1150401–W1150416. doi:10.1029/2003WR002567
- Schwede, R. L., & Cirpka, O. A. (2010). Stochastic evaluation of mass discharge from pointlike concentration measurements. Journal of Contaminant Hydrology, 111(1-4), 36–47. doi:10.1016/j.jconhyd.2009.10.011
- Slater, L. (2007). Near surface electrical characterization of hydraulic conductivity: From petrophysical properties to aquifer geometries - A review. Surveys in Geophysics, 28(2-3), 169–197. doi:10.1007/s10712-007-9022-y
- Sonne, A. T., McKnight, U. S., Rønde, V., & Bjerg, P. L. (2017). Assessing the chemical contamination dynamics in a mixed land use stream system. Water Research, 125, 141– 151. doi:10.1016/j.watres.2017.08.031
- Stonedahl, S. H., J. W. Harvey, A. Wörman, M. Salehin, and A. I. Packman (2010), A multiscale model for integrating hyporheic exchange from ripples to meanders, Water Resour. Res., 46, W12539, doi:10.1029/2009WR008865
- Swartjes, F. E. (2011), Dealing with Contaminated Sites, Springer, doi:10.1007/978-90-481-9757-6.
- Troldborg, M. (2010). Risk assessment models and uncertainty estimation of groundwater contamination from point sources. Technical University of Denmark (DTU).
- Troldborg, M., Nowak, W., Tuxen, N., Bjerg, P. L., Helmig, R., & Binning, P. J. (2010).
  Uncertainty evaluation of mass discharge estimates from a contaminated site using a fully
  Bayesian framework. Water Resources Research, 46(1), W12552.
  doi:10.1029/2010WR009227
- Troldborg, M., Nowak, W., Lange, I. V., Pompeia Ramos dos Santos, M. C., Binning, P. J., & Bjerg, P. L. (2012). Application of Bayesian geostatistics for evaluation of mass discharge uncertainty at contaminated sites. Water Resources Research, 48(9), W09535. doi:10.1029/2011WR011785
- Vaudelet, P., Schmutz, M., Pessel, M., Franceschi, M., Guerin, R., Atteia, O., ... Begassat, P. (2011). Mapping of contaminant plumes with geoelectrical methods. A case study in

urban context. Journal of Applied Geophysics, 75(4), 738–751. doi:10.1016/j.jappgeo.2011.09.023.

- Weller, A., Slater, L., Nordsiek, S., & Ntarlagiannis, D. (2010). On the estimation of specific surface per unit pore volume from induced polarization: A robust empirical relation fits multiple data sets. Geophysics, 75(4), WA105–WA112. doi:10.1190/1.3471577
- Weller, A., Slater, L., & Nordsiek, S. (2013). On the relationship between induced polarization and surface conductivity: Implications for petrophysical interpretation of electrical measurements. Geophysics, 78(5), D315–D325. doi:10.1190/GEO2013-0076.1
- Weller, A., Slater, L., Binley, A., Nordsiek, S., & Xu, S. (2015). Permeability prediction based on induced polarization: Insights from measurements on sandstone and unconsolidated samples spanning a wide permeability range. Geophysics, 80(2), D161–D173. doi:10.1190/GEO2014-0368.1
- WHO (2013), Contaminated sites and health, Report of two WHO workshops: Syracuse, Italy, 18 November 2011 and Catania, Italy, 21-22 June 2012, World health Organization, Regional office for Europe.
- Weatherill, J., Krause, S., Voyce, K., Drijfhout, F., Levy, A., & Cassidy, N. (2014). Nested monitoring approaches to delineate groundwater trichloroethene discharge to a UK lowland stream at multiple spatial scales. Journal of Contaminant Hydrology, 158, 38–54. doi:10.1016/j.jconhyd.2013.12.001
- Williams, K. H., Kemna, A., Wilkins, M. J., Druhan, J., Arntzen, E., N'Guessan, A. L., ... Banfield, J. F. (2009). Geophysical Monitoring of Coupled Microbial and Geochemical Processes During Stimulated Subsurface Bioremediation. Environmental Science and Technology, 43(17), 6717–6723. doi:10.1021/es900855j.
- Wroblicky, G. J., Campana, M. E., Valett, H. M., & Dahm, C. N. (1998). Seasonal variation in surface-subsurface water exchange and lateral hyporheic area of two stream-aquifer systems. Water Resources Research, 34(3), 317–328.
- Yang, C.-H., Yu, C.-Y., & Su, S.-W. (2007). High resistivities associated with a newly formed LNAPL plume imaged by geoelectric techniques - A case study. Journal of the Chinese Institute of Engineers, 30(1), 53–62. doi:10.1080/02533839.2007.9671230

In this online version of the thesis, **paper I-VII** 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 Bygningstorvet 115 2800 Kgs. Lyngby Denmark

info@env.dtu.dk.

The Department of Environmental Engineering (DTU Environment) conducts science based engineering research within six sections: Water Resources Engineering, Water Technology, Urban Water Systems, Residual Resource Engineering, Environmental Chemistry and Atmospheric Environment.

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.

**Department of Environmental Engineering** Technical University of Denmark

DTU Environment Bygningstorvet, building 115 2800 Kgs. Lyngby Tlf. +45 4525 1600 Fax +45 4593 2850

www.env.dtu.dk