



Risk assessment of chlorinated ethene plumes impacting streams: contaminant mass discharge, eld methods and attenuation

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Risk assessment of chlorinated ethene plumes impacting streams: contaminant mass discharge, field methods and attenuation



Vinni Rønde

PhD Thesis
June 2019

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DTU Environment
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Technical University of Denmark

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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>.

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Preface

This PhD thesis is based on research conducted from September 2014 to May 2019 at the Department of Environmental Engineering, Technical University of Denmark (DTU) with Professor Poul L. Bjerg (DTU) as the main supervisor and Associate Professor Ursula S. McKnight (DTU) as co-supervisor.

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In the first part of the thesis, the findings of the research are put into context in an introductory review, while the second part consists of the papers listed below. These papers will be referred to in the text by their paper number written with the Roman numerals **I-V**. Since paper IV does not deal with conditions at the groundwater-surface water interface, it will play a minor role in the introductory review. However, it is still included in the thesis, as it serves as background for paper III.

- I** **Rønede, V.**, McKnight, U. S., Sonne, A. T., Balbarini, N., Devlin, J. F., & Bjerg, P. L. (2017). Contaminant mass discharge to streams: Comparing direct groundwater velocity measurements and multi-level groundwater sampling with an in-stream approach. *Journal of Contaminant Hydrology*, 206, 43-54.
- II** **Rønede, V.**, McKnight, U. S., Annable, M., Ottosen, C., Broholm, M., Devlin, J. F. & Bjerg, P. L. Conceptualising attenuation of chlorinated ethene plumes discharging to streams: perspectives for risk assessment. *Manuscript*.
- III** Balbarini, N., **Rønede, V.**, Maurya, P., Fiandaca, G., Møller, I., Klint, K. E., Christiansen, A. V., Binning, P. J., & Bjerg, P. L. (2018). Geophysics based contaminant mass discharge quantification downgradient of a landfill and a former pharmaceutical factory. *Water Resources Research*, 54, 5436-5456.

- IV** Maurya, P. K., **Rønede, V. K.**, Fiandaca, G., Balbarini, N., Auken, E., Bjerg, P. L., & Christiansen, A. V. (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*, 138, 1-8.
- V** Sonne, A. T., McKnight, U. S., **Rønede, V.**, & Bjerg, P. L. (2017). Assessing the chemical contamination dynamics in a mixed land use stream system. *Water Research*, 125, 141-151.

In this online version of the thesis, paper **I-V** 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 concluded during this PhD study:

Ottosen, C. B., **Rønede, V.**, Trapp, S., Bjerg, P. L., & Broholm, M. M. (2018). Phytoscreening for Vinyl Chloride in Groundwater Discharging to a Stream. *Groundwater Monitoring & Remediation*, 38(1), 66-74.

Maurya, P. K., Balbarini, N., Møller, I., **Rønede, V.**, Christiansen, A. V., Bjerg, P. L., Auken, E., & Fiandaca, G. (2018). Subsurface imaging of water electrical conductivity, hydraulic permeability and lithology at contaminated sites by induced polarization. *Geophysical Journal International*, 213(2), 770-785.

Balbarini, N., Frederiksen, M., **Rønede, V.**, Møller, I. B., Sonne, A. T., McKnight, U. S., Pedersen, J. K., Binning, J. P., & Bjerg, P. L. (2019). Assessing the transport of pharmaceutical compounds in a layered aquifer discharging to a stream. *Groundwater*, in press.

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“Find a group of people who challenge and inspire you, spend a lot of time with them, and it will change your life.” – Amy Poehler

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Summary

Contaminated sites across the world are a major threat to human health and the environment. Contaminants from contaminated sites can migrate through aquifers and discharge to streams, leading to decreased surface water quality and ecosystem health. The vast number of sites makes clean-up of all economically infeasible; hence, risk assessment is used to prioritise the sites that pose a risk.

When assessing the risk posed to streams, contaminant mass discharge (CMD) is a key parameter. CMD is defined as the contaminant mass passing through a hypothetical control plane per time. Near streams, the CMD approach has several applications due to the possibility to obtain both subsurface and in-stream estimates. However, the advantage of the CMD approach near streams has not yet been fully explored.

It is not trivial to measure the CMD near streams due to large spatial variations in contaminant concentrations and hydraulic conductivities, as well as the temporally varying multi-directional groundwater flow. Field tools that can overcome the challenges related to such variabilities are required. The point velocity probe (PVP) and the novel sediment bed passive flux meter (SBPFM) provide direct measurements of seepage velocity and contaminant flux, respectively, and are promising tools for CMD quantification near streams.

Chlorinated ethenes are a key contaminant group. After release to the environment, chlorinated ethenes may undergo natural attenuation. This can reduce contaminant mass, but can also lead to the formation of more harmful substances, such as vinyl chloride. Conditions beneath streams can be more favourable for natural attenuation than conditions in aquifers. Nevertheless, risk assessment is challenged by the variation in attenuation observed near streams; some literature studies observe extensive attenuation, while others observe inconsistent attenuation.

The aim of the thesis is to improve risk assessment of contaminated sites and plumes impacting streams. This was done by exploring the advantage of the CMD approach near streams, evaluating different field methods for CMD quantification, and quantifying and conceptualising near-stream attenuation of chlorinated ethenes. The Grindsted Stream site was used as a field study site.

Detailed field investigations was conducted to quantify subsurface and in-stream CMDs of chlorinated ethenes. These estimates were shown to have several applications. In-stream CMD discharges along a stretch of Grindsted

Stream were used to identify unknown and/or main pathways and sources. Subsurface CMDs can inversely be used to predict stream concentrations, which can support the identification and prioritisation of known contaminated sites.

Contaminant mass balance analyses were conducted at the reach scale by comparing total CMDs, as well as CMD-based molar ratios of individual chlorinated ethenes at several subsurface and in-stream transects. Such analyses showed to be capable of improving the conceptual understanding of the system with respect to temporal characteristics of the sources, seasonal trends in stream concentrations, key pathways, and dominant attenuation processes. This level of conceptual understanding is crucial for the design of field campaigns for conservative risk assessment, identification of receptors at risk, and selecting remedial methods. Finally, mass balance analyses can be used to quantify the combined and sometimes even the distinct attenuation processes by assessing mass loss/gain or shift in molar ratios.

Several field methods for CMD quantification exist. Darcy's law-based methods are commonly applied; however, the multi-directional groundwater flow field near streams may decrease the quality of results based on Darcy's law. PVP-based and SBPFMs-based methods were applied at the Grindsted Stream site. The PVPs were capable of measuring the magnitudes and directions of both horizontal and vertical groundwater flow at the stream bank that could be used to estimate CMD. SBPFMs deployed in a transect in the streambed yielded averaged flux concentrations and specific discharges comparable to results from water samples and various methods for groundwater flow quantification, respectively. DCIP geophysical measurements were additionally applied. DCIP data could improve the description of the concentration distribution – especially for low sampling densities, that are common at large sites – and thus decreased the uncertainty of CMD estimates. Based on a comparison of selected field methods, it was concluded that no single method for CMD quantification near streams is always more advantageous than other methods. The choice of method should rather be based on the purpose and scope of the investigation as well as specific site characteristics.

Attenuation is commonly assessed by applying the multiple line of evidence approach. This approach integrates multidisciplinary methods to increase confidence in the interpretation of results and observations at field sites. The ma-

majority of the field studies assessing near-stream attenuation of chlorinated ethenes have advanced process understanding. Such knowledge is important for risk assessment, however it cannot stand alone. From a risk assessment perspective, quantifying the effect of the attenuation by applying the CMD approach, as well as developing holistic conceptual models are additionally required.

By applying the CMD approach at the Grindsted Stream site, it was found that limited near-stream attenuation of chlorinated ethenes takes place. Volatilisation was identified as the only important attenuation processes removing chlorinated ethenes from the stream, however, the rate of removal is slow. Consequently, the vinyl chloride concentration exceeds the environmental quality criteria for several kilometres, hence Grindsted Stream is at risk.

Based on experiences from the Grindsted Stream site and literature case studies, a set of holistic conceptual models were developed. These models show the near-stream attenuation behaviour for discharging chlorinated ethene plumes for various scenarios. In essence, they illustrate that the attenuation – and thus the influence on the surface water quality – depends on the hydrogeology, biogeochemistry and stream characteristics. If favourable conditions for attenuation are only present in parts of the plume discharge zone, a patchy attenuation behaviour will be expected. Moreover, the models identify some key parameters, which – in addition to the CMD – can support reliable risk assessment. These include: geological heterogeneity, seepage velocity, redox conditions, key microorganisms and content of organic carbon in sediments.

In conclusion, this PhD thesis has demonstrated the advantages of the CMD approach near streams, compared a selection of field methods for CMD quantification, as well as quantified and conceptualised near-stream attenuation of chlorinated ethenes. This can improve risk assessment and thus strengthen the foundation on which prioritisation of remedial efforts is based. Ultimately, this can support efforts to ensure good surface water quality.

Dansk sammenfatning

Forurenede grunde udgør en trussel mod miljøet og menneskers sundhed. Forureningsstoffer fra forurenede grunde kan transporteres med grundvandet og udsive til vandløb, med forringet kvalitet af overfladevand og økosystemer til følge. Et stort antal af forurenede grunde gør oprensning af dem alle økonomisk urealistisk, hvorfor risikovurdering benyttes til at prioritere de grunde, der udgør en risiko.

Forureningsflux er en central parameter i risikovurdering i forhold til vandløb. Forureningsflux er defineret som massen af forureningsstoffer, der passerer et fiktivt kontrolplan per tid. Forureningsflux har som metode mange anvendelser nær vandløb, bl.a. på grund af muligheden for at beregne estimater i både grundvandet og i selve vandløbet. Dog er fordelene ved at anvende forureningsflux nær vandløb endnu ikke undersøgt til bunds.

Det er langt fra trivielt at måle forureningsflux nær vandløb. Dette skyldes betydelige rumlige variationer af forureningskoncentrationer og hydraulisk ledningsevne, samt store rumlige og tidslige variationer af grundvandshastighed og strømningsretning. Det er nødvendigt at finde feltmetoder, der kan løse udfordringerne relateret til sådanne variationer. PVP'en (point velocity probe) kan måle grundvandshastighed direkte, mens SBPFM'en (sediment bed passive flux meter) kan måle forureningsflux. Disse metoder er interessante i forhold til kvantificering af forureningsflux nær vandløb.

Klorerede ethener er blandt nogle af de forureningsstoffer, der vækker størst bekymring. Klorerede ethener kan nedbrydes og transporteres i miljøet. Betingelser under et vandløb kan være mere favorable for sådanne processer end betingelserne i et grundvandsmagasin. Dog er risikovurdering udfordret af de mange forskellige observationer af å-nære transport- og nedbrydningsprocesser (attenuation), der er rapporteret i litteraturen. Nogle studier har for eksempel observeret omfattende nedbrydning, mens andre studier har observeret nedbrydning i begrænset omfang.

Formålet med denne ph.d.-afhandling er at forbedre risikovurdering af forurenede grunde, der påvirker vandløb. De specifikke formål var at undersøge fordelene ved kvantificering af forureningsflux nær vandløb, sammenligne udvalgte feltmetoder for dens bestemmelse, samt kvantificere og konceptualisere å-nære transport- og nedbrydningsprocesser for klorerede ethener. Grindsted Å blev anvendt som feltlokalitet.

Detaljerede feltundersøgelser blev udført for at kvantificere fluxen af klorede ethener i undergrunden og i vandløbet. Estimerne viste sig at have flere anvendelser. På en strækning langs Grindsted Å kunne forureningsfluxen i vandløbet anvendes til at identificere vigtige, eventuelt ukendte kilder og transportveje. Estimer af forureningsflux i undergrunden kan omvendt anvendes til bestemmelse af fuldt opblandede overfladevandskoncentrationer, som kan benyttes til identificering og prioritering af kortlagte forureninger.

Analyse af massebalancer blev udført ved sammenligning af total forureningsflux samt molefraktioner af klorede ethener i flere transekter i undergrunden og i vandløbet. Analyserne viste sig at forbedre den konceptuelle forståelse af systemet angående tidlig variation i kilden, sæsonprægede tendenser i overfladevandskoncentrationer, vigtige transportveje, samt dominerende transport- og nedbrydningsprocesser. Konceptuel forståelse på et sådant niveau er afgørende for design af feltkampagner med henblik på konservativ risikovurdering, identificering af receptorer forbundet med risiko, samt valg af oprensningstype. Desuden kan massebalancer anvendes til kvantificering af den samlede effekt af transport- og nedbrydningsprocesser. Sommetider kan individuelle processer endda kvantificeres.

Der findes adskillige feltmetoder til kvantificering af forureningsflux. Metoder baseret på Darcys lov bliver ofte benyttet til trods for at komplekse strømningsforhold nær vandløb øger usikkerheden af resultaterne. Metoder baseret på PVP'er samt SBPFM'er blev anvendt ved Grindsted Å. PVP'erne målte grundvandshastighed og strømningsretning på åbrinken, som i kombination med grundvandskoncentrationer blev benyttet til bestemmelse af forureningsflux. SBPFM'er, installeret i et transekt i åbunden, målte forureningsflux og Darcyflux. Flux-vægtede gennemsnitskoncentrationer samt værdier for Darcyflux var sammenlignelige med resultater fra vandprøver og diverse metoder for kvantificering af grundvandshastighed.

Endvidere blev DCIP geofysiske målinger udført. DCIP data viste sig at kunne forbedre beskrivelsen af koncentrationsdistributionen – særligt når densiteten af målepunkter var lav, som ofte er tilfældet på store lokaliteter – og kunne således mindske usikkerheden af forureningsfluxen. På baggrund af en sammenligning af udvalgte feltmetoder, kunne det konkluderes, at ingen metode altid var mere fordelagtig end de andre metoder til å-nær forureningsfluxbestemmelse. Valg af metode bør basere sig på undersøgelsens formål og ramme, samt lokalitetsspecifikke karakteristika.

Transport- og nedbrydningsprocesser bliver ofte karakteriseret ved benyttelse et såkaldt "multiple line of evidence"-koncept. Konceptet kombinerer multidisciplinære metoder for at øge pålideligheden af datafortolkningen. Størstedelen af feltstudier, der karakteriserer transport- og nedbrydningsprocesser, har fokuseret på at fremme vores procesforståelse. Sådanne bidrag er vigtige for risikovurdering, men kan ikke stå alene. Fra et risikovurderingsperspektiv, er kvantificering af processernes effekt, dvs. bestemmelse af forureningsflux, samt udformning af holistiske konceptuelle modeller ligeledes nødvendig.

Bestemmelser af forureningsflux ved Grindsted Å viste at å-nære transport- og nedbrydningsprocesser finder sted i begrænset omfang. Afdampning blev identificeret som eneste proces af betydning for masse reduktion, men foregår langsomt. Som resultat heraf, overskrider koncentrationen af vinylklorid kriteriet for overfladevandskvalitet i en strækning på flere kilometer. Den undersøgte forureningsfane udgør således en risiko for Grindsted Å.

På baggrund af feltlokaliteten ved Grindsted Å samt andre lokaliteter beskrevet i litteraturen, blev et sæt holistiske konceptuelle modeller udformet. Modellerne illustrerer effekten af å-nære transport- og nedbrydningsprocesser for klorerede ethener for forskellige scenarier. Essensen er, at processerne – og dermed effekten på overfladevandskvaliteten – afhænger af hydrogeologiske- og biogeokemiske forhold, samt vandløbskarakteristika. Nedbrydning og sorption vil være begrænset til de områder, hvor forholdene for disse processer er gunstige. Således kan rumlige variationer forekomme. Endvidere, identificerer de konceptuelle modeller flere centrale måleparametre, som – i kombination med forureningsflux – kan bidrage til pålidelig risikovurdering. Centrale parametre inkluderer: geologisk heterogenitet, grundvandshastighed, redox forhold, relevante mikroorganismer samt indhold af organisk karbon i sedimentet.

Samlet set har denne ph.d.-afhandling demonstreret en række fordele ved bestemmelse af forureningsflux nær vandløb, sammenlignet et udvalg af feltmetoder til kvantificering af forureningsflux, samt kvantificeret og konceptualiseret å-nære transport- og nedbrydningsprocesser for klorerede ethener. Dette kan styrke anvendelsen af forureningsflux nær vandløb, forbedre risikovurdering og således styrke det fundament hvorpå prioriteringen af ressourcer til oprensning baserer sig. Ultimativt kan resultaterne fra ph.d.-afhandlingen understøtte valg af tiltag, der kan forbedre kvaliteten af overfladevand.

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1 Introduction

1.1 Background and motivation

Contaminated sites across the world are a major threat to humans and the environment and thus a global environmental concern. Plumes from contaminated sites may migrate through aquifers and eventually discharge to hydraulically connected streams, leading to decreased surface water quality and ecosystem health (McKnight et al., 2012). In the EU, more than 650,000 sites are registered as potentially contaminated (JCR, 2018), and in Denmark this number is more than 35,000 (Danske Regioner, 2017). The vast number of sites makes clean-up of all sites unrealistic in terms of economic resources. Therefore, risk assessment is used to prioritise between sites, so those posing the highest risk can be remediated (Einarson and Mackay, 2001).

The main focus in risk assessment of contaminated sites has been on groundwater protection since concerns on water quality gained strength in the 1970s and 80s. In Denmark, the emphasis on groundwater may be related to the fact that drinking water resources almost exclusively are based on groundwater (IWA, 2014). However, in 2000, the EU Water Framework Directive (WFD) (Directive 2000/60/EC) was issued. This directive requires member states to aim to achieve good chemical status in both groundwater and surface water bodies. Consequently, the focus of regulatory agencies has now been extended to also include surface water quality. The WFD includes various deadlines for development and revision of action plans, and allows for a maximum deadline extension until 2027.

Chlorinated solvents are some of the compounds causing most concern. They originate from industry, where they are used in e.g. dry-cleaning, metal degreasing and the production of pharmaceuticals (Chambon et al., 2013). After release to the environment via leaching from underground storage tanks, accidental spills, and waste disposals, they may undergo natural attenuation, such as sorption, degradation, dilution, mixing and volatilisation. In risk assessment, this potential is crucial: natural attenuation can result in reduced concentrations and thus reduced risk, but degradation of chlorinated solvents may lead to the formation of lesser chlorinated ethenes – such as vinyl chloride, a known carcinogen – and thus enhanced risk.

When assessing the risk posed to streams, it is therefore essential to answer the following questions:

- 1) How much contaminant mass is discharging to the stream?
- 2) How do the contaminants attenuate as they migrate from the bank to the stream and in the stream water?

The first question can be answered by measuring the contaminant mass discharge (mass per time). This is defined as the total contaminant mass per unit of time passing through a control plane that is oriented perpendicular to the groundwater flow, and that extends over the full width and depth of the plume (Basu et al., 2006; ITRC, 2010). A growing consensus exists among scientists, practitioners and regulatory agencies to use the contaminant mass discharge as an alternative or supplement to traditional concentration-based risk assessment (Basu et al., 2006).

Close to streams, the contaminant mass discharge is especially useful, because it can be used to predict stream concentrations, and vice versa, stream concentrations can be used to estimate a so-called in-stream contaminant mass discharge. However, only few studies have set up reach scale contaminant mass balances, combining in-stream and subsurface estimates of contaminant mass discharge (Chapman et al., 2007; Courbet et al., 2011). Hence, the advantages of applying the contaminant mass discharge approach near streams has not yet been fully explored.

The most common method used for contaminant mass discharge estimation is the control plane approach, where multi-level concentration data and specific discharge, commonly obtained from Darcy's law, are integrated (Barbaro and Neupane, 2006; Béland-Pelletier et al., 2011; Bockelmann et al., 2003; Kübert and Finkel, 2006; Troldborg et al., 2012). However, it is not trivial to measure the contaminant mass discharge for several reasons. Contaminant concentrations in plumes are typically characterised by high spatial variability, as is the hydraulic conductivity of the subsurface. The challenge is even greater at the groundwater-surface water interface, due to a multi-directional groundwater flow field with large temporal and spatial variability in hydraulic gradients, velocities and flow directions (Karan et al., 2014; Kasahara and Hill, 2007; Keery et al., 2007; Storey, 2003; Wroblicky et al., 1998).

The complex hydrogeology close to groundwater-surface water interfaces calls for field tools that can overcome the challenges related to the large spatial and temporal variations. Alternative field tools promising for contaminant mass

discharge estimation close to streams includes the point velocity probe (PVP) and the sediment bed passive flux meter (SBPFM), each having distinct advantages. The PVP can directly measure the horizontal and vertical seepage velocities at the centimetre scale without estimates of hydraulic conductivity (Labaky et al., 2007). The SBPFM can measure streambed contaminant fluxes over a given time period without the need for additional water sampling (Layton et al., 2017). Moreover, a potential exists for geophysical methods to improve the quality of contaminant mass discharge estimates (Chambers et al., 2006).

The second question deals with the attenuation contaminant compounds are undergoing as they move from the bank to the stream and in the stream. Conditions beneath streams can be more favourable for natural attenuation than conditions in aquifers (Weatherill et al., 2018). This may be related to mixing and exchange of groundwater and surface water in the saturated zone adjacent to streams, commonly referred to as the hyporheic zone (Anibas et al., 2016; Tonina and Buffington, 2007). For instance, infiltration of dissolved oxygen-rich or dissolved organic carbon-rich surface water may facilitate microbial metabolism and thus degradation of contaminants (Boano et al., 2014; Freitas et al., 2015; Sauvage et al., 2018; Weatherill et al., 2018). Nevertheless, risk assessment is challenged by the various attenuation behaviours observed near streams: some studies observe enhanced attenuation of chlorinated ethenes (e.g. Conant et al., 2004; Lorah and Olsen, 1999; Şimşir et al., 2017), while others observe a patchy attenuation (e.g. Weatherill et al., 2014).

1.2 Aim and research objectives

The aim of the thesis is to improve risk assessment of contaminated sites and plumes impacting streams by providing insight into contaminant mass discharge, field methods and attenuation. This can strengthen the foundation for prioritisation of remedial efforts to ensure surface water protection. Specific objectives are to:

- 1) Explore the advantages of contaminant mass discharge in the assessment of risk posed to streams **(I, II, V)**
- 2) Evaluate different field methods, including the point velocity probe (PVP) and streambed passive flux meter (SBPFM) for contaminant mass discharge estimation **(I, II, III, IV)**
- 3) Quantify and conceptualise chlorinated ethene attenuation near streams **(I, II, V)**

1.3 Thesis outline

Different approaches to assess the risk of contaminated groundwater are presented in Chapter 2, serving as background for the following chapters. To fulfil the presented objectives, field investigations were undertaken at Grindsted Stream site. The field site is described in Chapter 3. Chapter 4 explores the advantages of applying the contaminant mass discharge approach near streams by exemplifying various applications of it, and Chapter 5 evaluates selected field methods for contaminant mass discharge quantification. Chapter 6 quantifies and conceptualises near-stream attenuation of chlorinated ethenes, and discusses the implications for risk assessment. Finally, the main conclusions are presented in Chapter 7 and put in perspective by identifying future research needs in Chapter 8.

2 Approaches to assess risk of groundwater contamination

Contaminated sites may pose a risk if toxic contaminants reach a given receptor (e.g. drinking water resources, streams, ecosystems or humans). The term “risk” can be defined as the combination of the probability of a hazardous event to occur and the severity of the corresponding consequences (e.g. Critto and Suter II, 2009). The objective of risk assessment of contaminated sites is to quantify risks posed to humans and ecosystems by data collection and interpretation, in order to support risk management in the selection of the most appropriate regulatory action.

Since a contaminated site only poses a risk to a given receptor if a complete pathway between the source and the receptor exists, a source-pathway-receptor concept is commonly used (Ferguson et al., 1998; McKnight et al., 2010; Verreydt et al., 2012). This concept takes into account all three components by characterizing the source and the potential pathways between the source and potential receptors, such as surface water.

2.1 Point of compliance

Most commonly, risk assessment of contaminated sites is concentration-driven, and hence an outcome of risk assessment is often the prediction or measurement of contaminant concentrations in a specific point, termed the “point of compliance” (ITRC, 2010; US EPA, 2004). The measured concentrations in this point must comply with agreed upon maximum concentration levels (e.g. environmental quality criteria) in order to pose no risk.

No universal location of the point of compliance exists, but common locations include the source zone, beneath the source zone at the groundwater table or in groundwater, and in groundwater beyond the source zone. The US EPA (2004) defines the location of the point of compliance depending on future land-use. For example, in case groundwater should return to its “maximum beneficial use”, the location of the point of compliance is throughout the volume of contaminated groundwater, which principally means “everywhere”.

Some advantages of the point of compliance approach are that it is inexpensive compared to more extended field investigations and relatively straightforward because concentration levels above the set quality criteria are indicative of a risk. However, the approach has several drawbacks:

- 1) If concentrations in the point of compliance exceed the quality criteria, it may only occur in a very small volume of the aquifer and/or be present in a zone with little groundwater movement implying low or no risk. Conversely, concentrations complying with quality criteria could misleadingly indicate low or no risk.
- 2) The chosen point of compliance may be located outside of an existing hotspot, leading to underestimated risk.
- 3) Groundwater concentrations alone cannot predict surface water concentrations resulting from plume discharge and therefore the point of compliance approach does not allow for comparison of sites impacting surface water (Verreydt et al., 2012).

2.2 Contaminant mass discharge

Another approach is to use the contaminant mass discharge, which is a more quantitative method to assess risk. It is generally defined as:

$$CMD = c \cdot Q \quad (1)$$

where CMD (mass/time) is the contaminant mass discharge, c (mass/volume) is the contaminant concentration and Q (volume/time) is the volumetric discharge (of e.g. recharge, infiltration, groundwater, a stream, etc.). In the subsurface, the contaminant mass discharge is defined as the total contaminant mass passing through a control plane that extends over the entire width and depth of a plume and is oriented perpendicular (normal) to the groundwater flow direction (Basu et al., 2006; ITRC, 2010; Rønde et al., I). Notably, if the control plane is not placed perpendicular to the flow, correction for the deviating angle should be made (Rønde et al., I). Several measurement and interpretation methods for quantification of contaminant mass discharge exist (see Chapter 5). The most common approach utilizes multi-level concentration data and specific discharge in a control plane as illustrated in Figure 1.

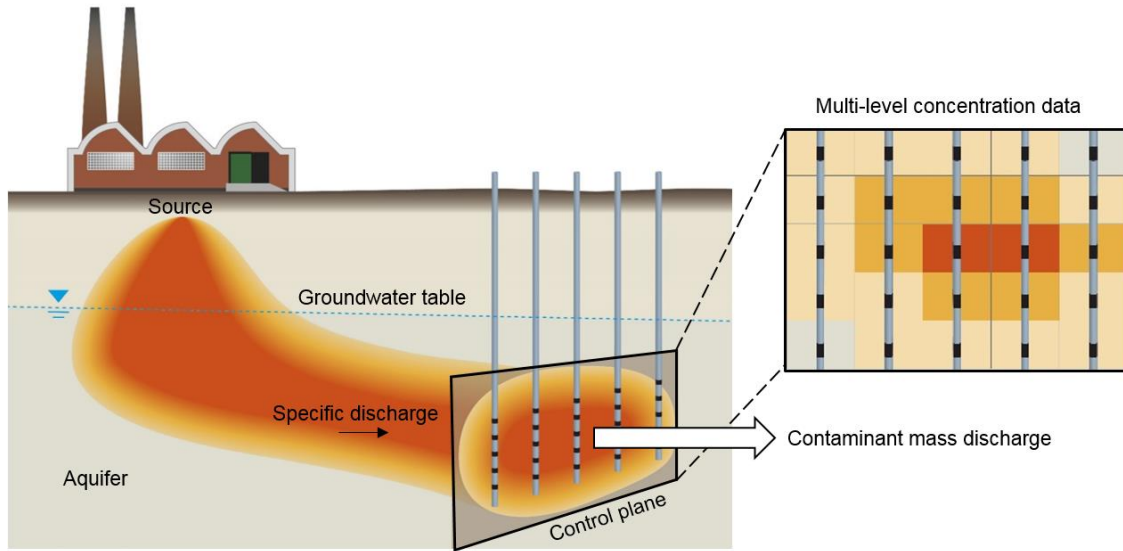


Figure 1: Graphical representation of contaminant mass discharge through a control plane with a multi-level sampling network. To the right, the control plane has been divided into 5x5 sub-sections. The figure is a modified version of two figures outlined by Poul L. Bjerg with inspiration from the literature (the graphics were made by the former graphics department at DTU Environment).

The basic formula to calculate the contaminant mass discharge (*CMD*) from such data is:

$$CMD = \sum_{i=1}^N c_i q_i A_i \quad (2)$$

where c_i and q_i are the contaminant concentration and the specific discharge, respectively, measured in the i^{th} sub-section, A_i is the area of the i^{th} sub-section and N is the total number of sub-sections in the control plane. However, depending on the measured parameters, variations of this formula exist. Typically, the specific discharge is indirectly estimated from Darcy's law and q can thus be substituted with the hydraulic conductivity (K) multiplied by the hydraulic gradient (dh/dx):

$$CMD = \sum_{i=1}^N c_i \left(K \frac{dh}{dx} \right)_i A_i \quad (3)$$

An average value for $K \cdot dh/dx$ is often used for the entire control plane. Alternatively, the specific discharge can be calculated from direct measurements of seepage velocity (v) and the porosity (n), yielding the formula:

$$CMD = \sum_{i=1}^N c_i v_i n_i A_i \quad (4)$$

Another possibility is to measure the contaminant flux (J ; mass/area/time) directly and thus substitute $c \cdot q$ with J :

$$CMD = \sum_{i=1}^N J_i A_i \quad (5)$$

In case of vertical plume migration, such as discharge to a stream through the streambed, it is also possible to place the control plane in the horizontal plane. In this case, multiple data points in the xy -plane, rather than multi-level data, are required. This changes the selection of available tools for measurement of water and contaminant fluxes (Chapter 5).

If stream concentrations are above the quantification level, a so-called in-stream approach can be used to calculate the contaminant mass discharge in the stream itself (Aisopou et al., 2015; Rønde et al., **I**):

$$CMD_{mix} = c_{mix} Q_{mix} \quad (6)$$

where c_{mix} and Q_{mix} are the concentration and stream discharge, respectively, at the point of fully mixed conditions. This point is defined as the location downstream of the discharging contaminant plume where the stream concentrations in a transverse transect across the stream vary no more than 5% with respect to the mean value within the transect (Fischer et al., 1979).

Although the contaminant mass discharge approach has some advantages over the point of compliance approach for comparison and prioritisation purposes, it is associated with some noteworthy challenges, including:

- 1) The assessment of the magnitude of contaminant mass discharge estimates is site specific. Therefore, in order to relate the contaminant mass discharge to a concentration (Equation 1), knowledge on specific receptors, such as stream discharge or groundwater abstraction rates, is required, or alternatively, a standardised ranking system must be defined, which relies on e.g. dilution in fictive/future groundwater abstraction rates (Hadley et al., 2015).
- 2) No standardised method for quantification of the contaminant mass discharge exists, hence the large selection of available field tools makes the decision about which to use difficult.

- 3) Relatively high uncertainty is associated with contaminant mass discharge estimates. Understanding these uncertainties is crucial when designing field investigations and evaluating obtained results (Section 5.6).
- 4) Relative to concentrations-based risk assessment, field investigations are associated with high costs, as an increased number of sampling points are required to delineate the plume and to reflect the spatial distribution of contaminants.

Altogether, the contaminant mass discharge is a valuable metric to use in risk assessment. Especially near streams, it is beneficial due to its many applications, as described in Chapter 4. However, a need exists to overcome some of the challenges mentioned in this section. Points 2-4 listed above are further addressed in Chapter 5.

3 Field site: Grindsted Stream

Grindsted Stream served as the study site for the conducted research (Figure 2). Two contaminated sites, Grindsted landfill (not shown in Figure 2) and Grindsted factory site, are located south and north of the stream, respectively. However, only the factory site has been shown to impact the stream (Sonne et al., V).

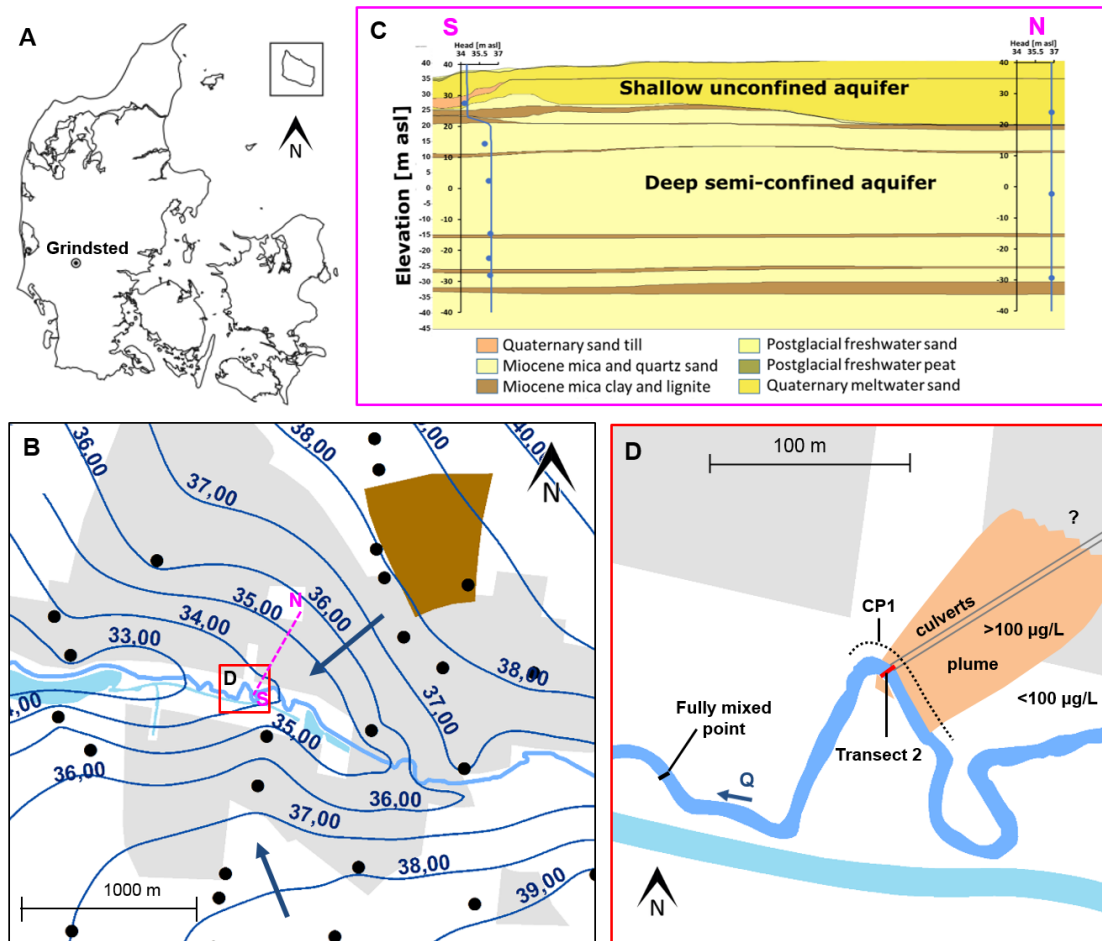


Figure 2: A) The location of Grindsted on a map of Denmark. B) Map showing Grindsted Stream (light blue curvature), Grindsted factory site (brown area), the locations of the focus area (red rectangle), and a geological transect S-N (dashed magenta line). Dark blue lines and values show the groundwater equipotential lines in meters above sea level (m asl), while the arrows indicate the flow direction. C) Geological profile of transect S-N. Modified by the author from Balbarini et al. (2019). D) Enlarged map of the focus area, showing a discharging contaminant plume (outline = 100 µg/L contour for vinyl chloride at 31 m asl (± 0.5 m)), the location of two culverts, two studied transects: CP1 (dotted curvature) and Transect 2 (red line), and the fully mixed point. Modified by the author from Rønne et al. (I).

The Grindsted Stream site is located in the Region of Southern Denmark (Figure 2). Flowing westward through Grindsted town, the stream drains a catchment of 200 km². It is 8-12 m wide and 1-2.5 m deep and has an annual average discharge of ca. 2000 L/s (Figure 3). The average annual rainfall in the area is 800 mm/y (DMI, 2016). Groundwater flows towards the stream as indicated by the groundwater equipotential lines in Figure 2B (Balbarini et al., 2017; Rønde et al., I).

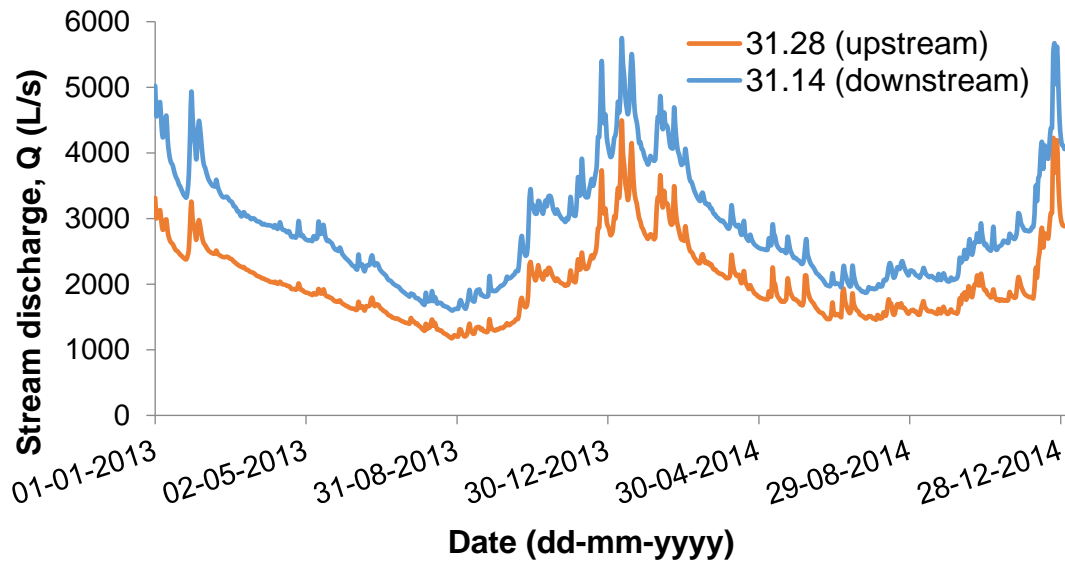


Figure 3: Stream discharge in Grindsted Stream measured at two gauging stations located up- and downstream of the study area. Modified by the author from Rønde et al. (I).

The geology in the area is presented in Figure 2C. It is comprised of a 10-12 m thick Quaternary layer, of which the upper ca. 2 m are dominated by post-glacial freshwater peat. The underlying layer consists mainly of Quaternary meltwater sand. A Miocene layer, characterized by mica clay and lignite successions and mica and quartz sand, underlies the Quaternary layer (Balbarini et al., III; Maurya et al., 2018).

The stream is impacted by a plume from a former pharmaceutical factory (Grindstedværket) located 1.5 km north of the stream. The factory was active from 1914-1999, and during that period large quantities of chemicals were deposited at the factory site. Consequently, xenobiotic compounds have been detected in the groundwater and in the stream (Rasmussen et al., 2016; Rønde et al., I; Sonne et al., V). These compounds include pharmaceuticals, such as barbiturates and sulphonamides, BTEX compounds (benzene, toluene, ethylbenzene and xylenes) and chlorinated ethenes (tetrachloroethene, PCE; trichloroethene, TCE; DCE dichloroethene; and vinyl chloride).

4 Contaminant mass discharge near streams

The contaminant mass discharge approach is generally valuable when assessing the risk of contaminant sources or plumes, however, it is especially beneficial near streams. To fully benefit from the method, it is essential to recognise the information hidden in contaminant mass discharge estimates and to understand how this information can be extracted and used near streams. By illuminating and discussing some of the applications of the contaminant mass discharge approach, this chapter explores its advantages near streams. Estimation of source life times, definition of clean-up criteria (Hadley et al., 2015), and prediction and evaluation of remedial effect (Horst et al., 2017) are outside the scope of this thesis.

Examples of applications of the contaminant mass discharge approach near streams are provided in Table 1.

Table 1: Examples of applications of the contaminant mass discharge close to streams. Note that some studies are listed multiple times, as they fall into several application categories.

Application	Reference	Objective / approach
Prediction/ assessment of surface water quality	Aisopou et al., 2015	Predict stream concentrations within the mixing zone (including maximum concentration) and at the fully mixed point from a model that considers dilution and volatilisation
	Ellis and Rivett, 2007	Obtain and compare volatile organic compound (VOC)-fluxes estimated in the streambed and in the stream by various methods
Source identify cation/prioritisation	Sonne et al., V	Distinguish sources with high and low impact on a mixed land use stream system by calculating the in-stream contaminant mass discharges along a stream reach
	VMR, 2019	Identifying contaminated sites that potentially pose a risk to surface water by applying a screening tool based on Equation 6
	Ellis, 2002	Identify contaminant plumes discharging to a river by calculating the in-stream contaminant mass discharges along a river reach
Assessment of natural attenuation / potential for MNA*	Courbet et al., 2011	Demonstrate the existence and effectiveness of biodegradation of chlorinated solvents and thus potential for MNA by comparing the contaminant mass discharge at the river bank and in the river
	Chapman et al., 2007	Identify and quantify the natural attenuation processes in a TCE plume discharging to a pond, tributary streams and ultimately a river by comparing the contaminant mass discharge in transects located at different distances from the river
	Rønne et al., II	Assess the natural attenuation (and potential for remediation by MNA) of a chlorinated ethene plume discharging to a stream by comparing flux-based compound ratios at the stream bank, below the stream and at the fully mixed point in the stream
	LaSage et al., 2008	Assess the natural attenuation of TCE by comparing in-stream contaminant mass discharges at different points for TCE, taking advantage of a linear relationship between concentrations of TCE and a non-volatile co-contaminant in discharging groundwater
	Sonne et al., V	Quantify the volatilisation of vinyl chloride and cis-DCE by comparing in-stream contaminant mass discharges at different points, taking advantage of the presence of non-volatile pharmaceutical compounds
Improvement of conceptual understanding	Rønne et al., I	Assess whether all mass in the chlorinated ethene plume delineated at the stream bank has been accounted for by comparing the contaminant mass discharge at the stream bank and in the stream at the mixing point
	Milosevic et al., 2012	Assess whether all contaminant mass (chloride, sodium, ammonium, DOC, phenoxy acids) has been accounted for by comparing the extrapolated contaminant mass discharges in the streambed with in-stream estimates

Evaluation of field tools	Rønne et al., I	Evaluate direct velocity measurements from PVPs, combined with multi-level groundwater sampling to quantify contaminant mass discharge to a stream by comparing contaminant mass discharges estimated based on Darcy's law and PVP data
	Rønne et al., II	Evaluate SBPFMs for quantification of contaminant mass discharge to a stream by comparing 1) groundwater velocities derived from SBPFMs with results from other methods, and 2) flux averaged concentrations from SBPFMs with concentrations measured in water samples
	Cremeans et al., 2018	Validate the streambed point velocity probe (SBPVP) to quantify groundwater-surface water interactions by comparing contaminant mass discharges estimated based on Darcy's law, PVP data and SBPVP data
	Balbarini et al., III	Describe the distribution of contaminant concentration by integrating geophysical and chemical data using regression kriging

*Monitored natural attenuation.

4.1 Prediction of stream water quality and source identification/prioritisation

An application of the contaminant mass discharge approach near streams is the prediction of stream concentrations. This has been done by e.g. Aisopou et al. (2015), who simulated stream concentrations in the mixing zone and in the fully mixed point, while taking dilution and volatilisation into account. The simulated stream concentrations can be used to assess the risk posed to a particular stream, but can also be used to identify, compare and prioritise known contaminated sites and plumes for remedial action.

This has in fact been done by the Danish regions. They used the contaminant mass discharge approach to predict stream concentrations and could thereby identify contaminated sites that potentially posed a risk to surface water (VMR, 2019). They used a screening tool, which utilizes information about the contaminated sites, including potentially contaminating industries that have operated at the locality in the past. The screening tool is based on Equation 6, and similarly to the model developed by Aisopou et al. (2015), it dilutes the estimated subsurface contaminant mass discharge into selected surface water bodies. Mixing and volatilisation are not taken into account. Surface water within a defined distance from the source was considered (250 m for chlorinated solvents), and the potential for impact on approximately 19,000 km streams, 650 lakes and 7,300 km shoreline were evaluated. The investigations, which ended in December 2018, found that 1,234 out of ca. 36,000 mapped contaminated sites pose a potential risk for the aquatic environment in streams, lakes or the

sea. This example shows how the contaminant mass discharge approach has been implemented into the Danish national risk assessment and management strategy.

Rather than predicting stream concentrations from subsurface estimates of contaminant mass discharge, identification and prioritisation of sites can also be done via estimation of the in-stream contaminant mass discharge along a stream reach. In-streams contaminant mass discharge peaks can then help in identifying the locations of discharge zones of contaminated groundwater, and contaminant sources (Ellis, 2002; Sonne et al., **V**).

4.2 Improvement of conceptual understanding

When the contaminant mass discharge is quantified in both the subsurface and in the stream, a comparison of the two estimates can be used to improve conceptual understanding. For example, Milosevic et al. (2012) compared a rough estimate of contaminant mass discharge through the streambed in a small stream downgradient of a landfill with in-stream estimates. Due to the larger in-stream estimate for several contaminants, they concluded that contaminants may enter the stream through routes other than the streambed. Section 4.1 discussed the application of the contaminant mass discharge approach for identification of sources. This example shows that it also can be used for contaminant pathway identification.

In an extensive field study at the Grindsted Stream site, Rønne et al. (**I**) measured completely mixed stream concentrations of chlorinated ethenes and corresponding stream discharge at different times, representing various flow conditions (see location of the fully mixed point in Figure 2D). The contaminant mass discharge (CMD_{mix}) was then obtained by plotting c_{mix} versus $1/Q_{mix}$ and then fitting Equation 6 to the data (Figure 4). Figure 4 adds to our conceptual understanding by showing that the contaminant plume discharging to Grindsted Stream is a relatively constant source. Groundwater concentration measurements could also have been used to assess the characteristics in terms of temporal variations of the plume. However, evidence of a constant source based on concentration data would not be as strong due to the high concentration gradients that exist within the plume. Additionally, we can learn from Figure 4 that concentrations are lowest at low-flow conditions; hence, the risk is highest during summer (Figure 3).

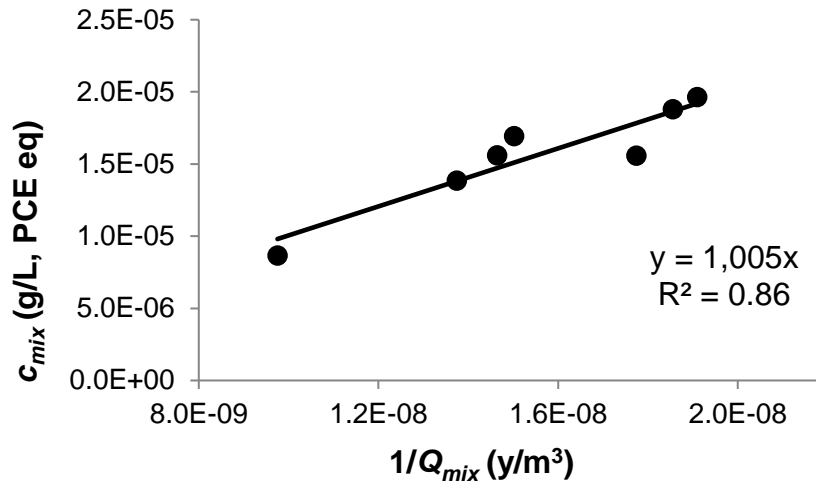


Figure 4: c_{mix} versus $1/Q_{mix}$ for the sum of chlorinated ethenes. The slope reflects the contaminant mass discharge, according to Equation 6. Modified by the author from (Rønne et al., I).

The contaminant contribution from groundwater (CMD_{GW}) was calculated from CMD_{mix} by subtracting the contaminant mass entering the stream through two culverts ($CMD_{culverts}$), and upstream of the investigated plume ($CMD_{upstream}$) (Table 2). The culverts was found to contribute to CMD_{mix} by 28%. Moreover, the degree of dechlorination was highest for the culvert input and lowest for the subsurface estimates (Table 2). The magnitudes of the different inputs and their different chemical compositions improved our conceptual understanding by identifying the culverts as an important pathway, and by indicating that the discharging water from the culverts originates from another source than the groundwater plume surrounding them.

The contaminant mass discharge at the stream bank was calculated in a control plane, CP1, from multi-level concentration data and specific discharge estimated by either Darcy's law ($CMD_{CP,Darcy}$) or PVP data ($CMD_{CP,PVPmean}$ and $CMD_{CP,PVPvary}$). Figure 5 shows the distribution of vinyl chloride concentrations obtained from water samples and interpolated by ordinary kriging, and the specific discharge obtained from PVP data.

A contaminant mass balance analysis showed that the in-stream estimate, i.e. CMD_{GW} , was higher than the subsurface estimates (Table 2). This added to our conceptual understanding by suggesting that not all mass has been accounted

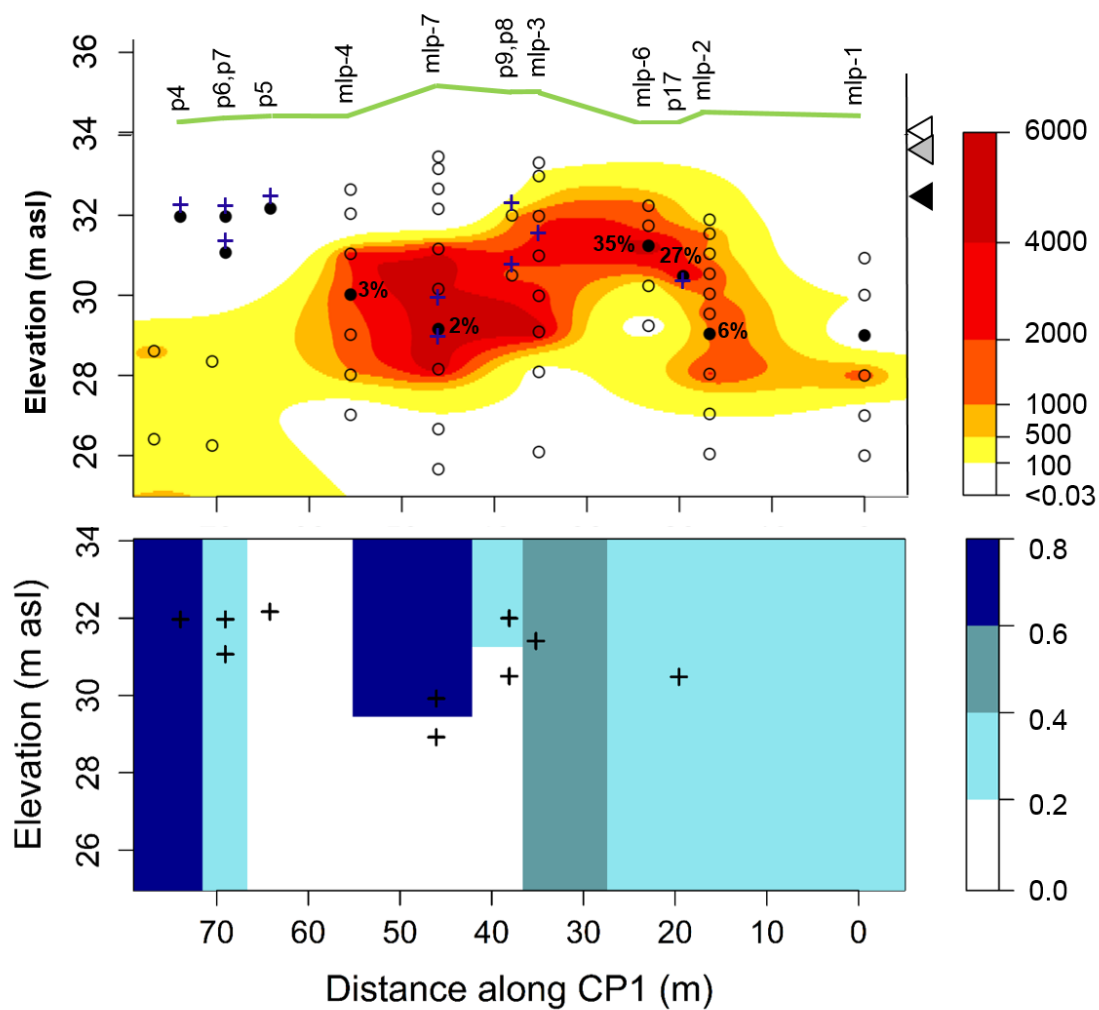


Figure 5: A) The vinyl chloride concentration ($\mu\text{g/L}$) in the control plane, CP1, at the bank, used in the calculation of the contaminant mass discharge. Open and filled circles represents concentration data sampled once or twice. For duplicated samples, the deviation from the mean is given in percentage. The white, grey and black triangles indicate the groundwater table, the stream stage and the streambed elevation, respectively. The green curvature represents the terrain. B) The specific discharge (m/d) in CP1 obtained from PVP data, assuming a porosity of 0.37. The black crosses indicate locations of PVPs. Modified by the author from Rønne et al. (I).

for, and hence that either contaminant mass bypassed the control plane or unidentified zones characterised by high concentrations or fast flow existed within the control plane. In this context, uncertainties of contaminant mass discharge estimates are crucial, see Section 5.6. The conducted mass balance analyses could additionally improve the conceptual understanding of chlorinated ethene attenuation at the Grindsted Stream site, which is further discussed in Section 194.3.

Table 2: Comparison of contaminant mass discharge in Grindsted Stream and at the bank. Modified by the author from Rønede et al. (I).

	IN-STREAM				STREAM BANK		
	CMD_{mix}	$CMD_{upstream}$	$CMD_{culverts}$	CMD_{GW}	$CMD_{CP,Darcy}$	$CMD_{CP,PV}^{Pmean}$	$CMD_{CP,PV}^{Pvary}$
Total chlorinated ethenes, CE (kg/y, PCE eq.)	1005	170	277	558	372	204	269
PCE (kg/y)	11.8	2.1	5.5	4.2	0.1	0.0	0.0
TCE (kg/y)	3.6	1.0	0.9	1.7	0.1	0.1	0.0
<i>cis</i> -DCE (kg/y)	200	37	40	123	82	45	65
Vinyl chloride, VC (kg/y)	235	38	74	123	77	42	54
Degree of dechlorination*	0.64	0.63	0.66	0.63	0.60	0.60	0.61

*= $(n_{TCE}+2 \cdot n_{DCE}+3 \cdot n_{VC}+4 \cdot n_{ethene+ethane})/(4 \cdot (n_{CE}+n_{ethene+ethane}))$, where n_i is the molar mass discharge of i (Bjerg et al., 2006). Ethene and ethane was not included in the calculation due to lack of data.

4.3 Quantification of attenuation processes

After release to the environment, chlorinated ethenes may undergo various natural attenuation processes, including sorption, degradation, dilution, mixing and volatilisation.

One of the few studies that have combined in-stream estimates of contaminant mass discharge with subsurface estimates to quantify attenuation was conducted by Rønede et al. (II) at the Grindsted Stream site. This study quantified the contaminant mass discharge at the stream bank, beneath the stream and in the stream by various field methods and set up a mass balance (Figure 6). It was found that the chlorinated ethene composition in the contaminant mass discharge estimates were almost constant from the bank to the fully mixed point. This finding combined with the comparison of total chlorinated ethene mass discharges displayed in Table 2 indicated that limited degradation and volatilisation took place between the bank and the fully mixed point. Reductive dechlorination processes likely take place from the bank to the stream to some extent (Rønede et al., II), but the combined effect of attenuation is minor from a risk assessment perspective.

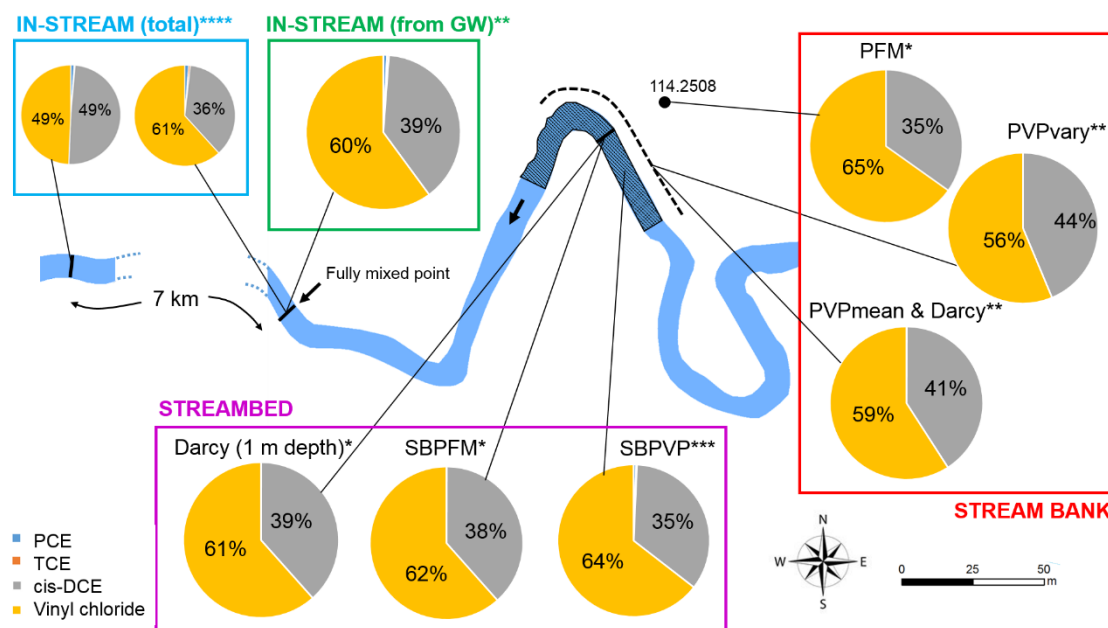


Figure 6: Molar ratios of chlorinated ethenes along the plume pathway at Grindsted Stream site. Data originate from Rønne et al. (II) (*), Rønne et al. (I) (**), Cremeans and Devlin (2017) (***), and Sonne et al. (V) (****). The figure is from Rønne et al. (II).

A few other studies have taken advantage of the possibility to compare subsurface and in-stream contaminant mass discharge estimates. Chapman et al. (2007) compared the contaminant mass discharge in streams and through subsurface transects to assess attenuation of a plume intersected by a pond and several streams before discharging to a river. Moreover, Courbet et al. (2011) assessed the potential for MNA by comparing the contaminant mass discharge at the river bank and in the river.

The in-stream contaminant mass discharge can also be estimated and compared at several locations along the stream in order to quantify the in-stream attenuation of contaminants. For example, Sonne et al. (V) quantified the total mass loss of chlorinated ethenes between the point of fully mixed conditions and a point 7 km further downstream. The increase in stream discharge between the two locations was determined from the dilution of non-volatile, persistent pharmaceutical compounds. The total mass losses were 35-64% for cis-DCE and 60-85% for vinyl chloride. This could be ascribed to volatilisation, as lack of degradation was verified by CSIA. The decrease in the vinyl chloride molar fraction between the two points (Figure 6) is expected, as vinyl chloride is more

volatile than cis-DCE. A similar approach was undertaken by LaSage et al. (2008), who estimated the volatilisation of TCE.

The mass balance analyses conducted at the Grindsted Stream site from the bank to 7 km downstream from the fully mixed point links back to Section 4.2, because it shows how the contaminant mass discharge approach can improve our conceptual understanding of near-stream attenuation. Figure 6 shows that attenuation processes that do not remove contaminant mass, such as mixing and dilution by stream water, are the only important once at the scale of several hundred meters. At the kilometre scale, volatilisation also becomes important, but the rate of chlorinated ethene removal is slow.

4.4 Implications for risk assessment

Subsurface estimates of contaminant mass discharging to streams can be used to predict contaminant concentrations in surface water. This is useful, as the predicted stream concentrations can be compared to existing surface water quality criteria in order to assess the risk associated with individual contaminants (Newell et al., 2011; Verreydt et al., 2012). This approach allows for identification and prioritisation of known sources and plumes posing a risk to streams on a regional or national scale. Notably, large temporal variations are associated with stream discharge, resulting in temporal variations in stream concentrations (Sonne et al., **V**). A conservative assessment should therefore in general be based on low flow conditions. Moreover, one should keep in mind that local stream water concentrations likely exceed the fully mixed concentration (Aisopou et al., 2015; Rønde et al., **I**, **II**). In addition, contaminated groundwater often passes through the streambed before being diluted, and may thus harm vulnerable aquatic organisms living within the streambed (Sonne et al., 2018; Verreydt et al., 2012).

For mixed land use stream systems, where many (unknown) sources impact streams, the in-stream contaminant mass discharge may be more useful than sub-surface estimates for identification of sources and pathways (Sonne et al., **V**).

Contaminant mass balance analysis at the reach scale can help in improving the conceptual understanding of a system regarding source characteristics in terms of temporal variability, seasonal trends in stream concentrations, key pathways and dominant attenuation processes. Such conceptual understandings are crucial. For example, knowledge on temporal source characteristics, and seasonal trends can support the design of field campaigns by ensuring that data

are collected at the appropriate time to allow for conservative risk assessment. Furthermore, understanding the key pathways for major sources and the dominant attenuation processes can help in supporting design of field campaigns, help in identifying receptors at risk, and may direct decisions about remedial methods to ensure targeted clean-up.

The contaminant mass discharge approach can also be used to quantify the effect of the combined attenuation processes on mass loss/gain or shift in molar ratios of individual compounds. This is crucial in risk assessment, because the final conclusion about risk is dependent on the reduction of total contaminant mass and formation of degradation products. It may even be possible to quantify individual attenuation processes, when applying the contaminant mass discharge approach in combination with other methods or when the level of conceptual understanding of the system is high,. This can have implications for specific receptors and may also support decision on remedial methods.

5 Evaluation of methods for contaminant mass discharge estimation

The contaminant mass discharge can be estimated from data collected in a control plane. Typically, approaches for subsurface estimates are divided into two groups: the integral and the point-scale approach (Kübert and Finkel, 2006). The integral approach utilizes data from pumping tests (e.g. Béland-Pelletier et al., 2011; additional references are provided in Table 3), while the point-scale approach integrates multiple data points, as illustrated in Figure 1.

Many different field tools can be used for the point-scale approach. Table 3 gives an overview of methods and examples of references applying these. Common methods for quantification of groundwater flow and/or groundwater-surface water interactions include Darcy's law-based methods, natural gradient tracer tests, heat tracer methods and seepage meter tests. More recently developed methods include the point velocity probe (PVP), the streambed point velocity probe (SBPVP) and the high resolution passive profiler (HRPP). Contaminant concentrations are most commonly measured in collected water samples but can also be measured using passive samplers (Table 3). In addition, geophysical measurements have recently been used to improve the description of concentration distributions in the control plane (Balbarini et al., **III**).

Rather than combining concentration data and specific discharge (Equation 2), the contaminant flux can be measured and used to calculate the contaminant mass discharge from Equation 5. The contaminant flux can be measured directly by the passive flux meter (PFM) or the newly developed sediment bed passive flux meter (SBPFM) (Table 3).

Finally, and in addition to the subsurface approaches, the contaminant mass discharge can be determined in the stream by the so-called in-stream approach (Rønde et al., **I**) as outlined in Section 2.2.

This chapter describes the Darcy's law-based methods, as well as more recently developed and less explored methods for contaminant mass discharge quantification. Descriptions of the remaining methods can be found in reviews (e.g. Kalbus et al., 2006).

Table 3: Methods used for subsurface contaminant mass discharge estimation.

Method	Measured parameters	Spatial measuring scale (m)	Examples of references
Integral pump test	Q, c	$10 - >10^2$	Bauer et al., 2004; Bayer-Raich et al., 2006; Béland-Pelletier et al., 2011; Bockelmann et al., 2003; Goltz et al., 2009; Herold et al., 2009; Jarsjö et al., 2005; Zeru and Schäfer 2005
Darcy's law-based method	$K, dh/dx$	$10 - >10^5$	Cremeans et al., 2018; Ellis and Rivett, 2007; Kalbus et al., 2006; Rønne et al., I
Seepage meter*	q, c	$10^{-1} - 1$	Fryar et al., 2000; Lee, 1977; Milosevic et al., 2012; Rosenberry, 2008
Natural gradient tracer test	v	$10 - >10^5$	Freeze and Cherry, 1979; Kalbus et al., 2006; Mutz and Rohde, 2003; Niemann and Rovey, 2000
Heat tracer methods*	v	$10^{-2} - 1$	Blume et al., 2013; Kalbus et al., 2006; Keery et al., 2007; Schmidt et al., 2006, 2007; Sebok et al., 2015
Point velocity probe (PVP)	v	$10^{-2} - 10^{-1}$	Devlin, 2016; Devlin et al., 2012, 2009; Kempf et al., 2013; Labaky et al., 2009, 2007; Rønne et al., I; Schillig et al., 2014, 2011
Streambed point velocity probe (SBPVP)*	v	$10^{-2} - 10^{-1}$	Cremeans et al., 2018; Cremeans and Devlin, 2017
High resolution passive profiler (HRPP)	v	$10^{-2} - >10^{-1}$	Schneider et al., 2019
Water samples from monitoring wells	c	$10^{-1} - 1$	Kalbus et al., 2006; Rønne et al., I
Passive samplers	c	$10^{-2} - 1$	Kalbus et al., 2006; Namiesnik et al., 2005; Verreydt et al., 2010
Passive flux meter (PFM)	J, q	$10^{-1} - 1$	Annable et al., 2005; Basu et al., 2008, 2006; Klammler et al., 2012; Rønne et al., II; Verreydt et al., 2015
Sediment bed passive flux meter (SBPFM)*	J, q	$10^{-1} - 1$	Layton et al., 2017; Rønne et al., II

*Developed for lakes/streambeds.

5.1 Darcy's law-based methods

Darcy's law-based methods use measurements of the hydraulic conductivity and hydraulic gradient to estimate the contaminant mass discharge (Equation 3). The hydraulic conductivity can be estimated by numerous methods at various scales, including pumping tests (e.g. Niemann and Rovey, 2000; Rovey and Cherkauer, 1995), slug tests (e.g. Bouwer and Rice, 1976; Hinsby et al., 1992), permeameter tests (e.g. Chen, 2000; Freeze and Cherry, 1979), grain size analysis (e.g. Kalbus et al., 2006), hydraulic profiling tool (HPT) tests

(e.g. Horst et al., 2017) and geophysical measurements (Maurya et al., 2018). Details on these methods are outside the scope of this thesis and the reader should refer to the references provided in this section for further information.

It is challenging to obtain reliable estimates of the hydraulic conductivity. The reasons are that values can vary several orders of magnitude over small distances and because results are highly dependent on the spatial measuring scale, making it difficult to determine the appropriate size for a representative element volume (Rovey and Cherkauer, 1995).

The hydraulic gradient is typically obtained from hydraulic head measurements at three or more locations. However, at small scales or when the hydraulic gradient is small, even minor measurement errors may adversely impact the results. This can lead to erroneous conclusions about flow directions (Labaky et al., 2007; Silliman and Mantz, 2000).

Moreover, when using Darcy's law, it is often assumed that the flow lines are perpendicular to the hydraulic head isopotential lines, which is true for isotropic conditions, i.e. the hydraulic conductivity is constant in all directions. However, conditions are in fact anisotropic at most locations. This is usually not an issue for horizontal groundwater flow, but can be a problem near streams. Close to groundwater-surface water interfaces, the flow is frequently non-horizontal and crosses various geological layers. Consequently, flow lines are likely to be non-perpendicular to isopotential lines of hydraulic head.

For anisotropic conditions, flow lines can instead be obtained by transforming the coordinate system of the flow net, drawing the flow lines as for isotropic conditions, and then inverting the coordinate system back to the original. When the vertical hydraulic conductivity (K_v) is lower than the horizontal (K_h), the z-axis is expanded by a factor equal to $K_x^{0.5}/K_h^{0.5}$ before the flow lines are drawn (Sarsby, 2013). Incorrect assumptions of isotropy can lead to erroneous corrections for the angle between the flow direction and the control plane in contaminant mass discharge calculations.

The issues discussed in this section make Darcy's law-based methods less suitable for depiction of velocity near streams. Hence, alternative or supplementary methods are sought, including methods for direct measurements of seepage velocity and contaminant flux.

5.2 Direct measurement of seepage velocity

The point velocity probe (PVP), developed by Labaky et al. (2007), can measure seepage velocity directly at the centimetre scale in non-cohesive sediments. When corrected for the porosity and combined with contaminant concentration data, PVP data can be used to calculate the contaminant mass discharge (Equation 4) (Rønne et al., I). Near streams, where the flow field is often multi-directional with large spatial variations (Karan et al., 2014; Kasahara and Hill, 2007; Keery et al., 2007; Storey, 2003; Wroblicky et al., 1998), this method may be advantageous to others, as the seepage velocity can be determined in both the horizontal and vertical directions. An additional feature of the PVP is that it does not require estimations of hydraulic conductivity (Schillig, 2012). This is a major advantage as reliable estimates of hydraulic conductivity are difficult to obtain (Section 5.1) (Rovey and Cherkauer, 1995).

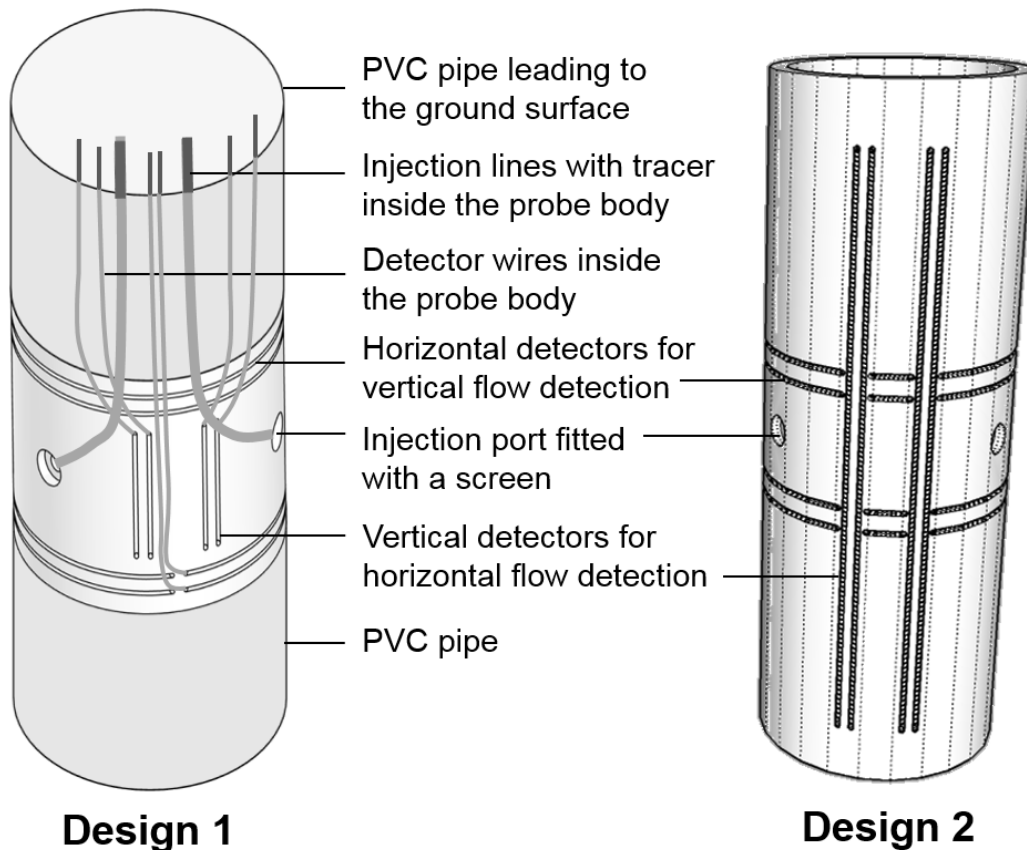


Figure 7: Schematic overview of two different PVP designs: the regular 3-port design (design 1), and a design developed for locations with steep vertical flow. Both designs are equipped with 3 injection ports and 8 detector pairs; however, only 2 ports and 4 detectors are visible on the schematic. (Rønne et al., I).

The PVP consists of a cylindrical probe with detectors on the outside (Figure 7) and is permanently installed in a borehole exclusively dedicated to this purpose. Measurements are based on small-scale tracer tests, conducted by injecting a saline tracer through an the injection ports. The PVP may be equipped with three injection ports to ensure that at least one is appropriately oriented to measure seepage velocity at locations where the flow direction is unknown (Gibson and Devlin, 2018). As the tracer flows around the probe, it passes by the detectors, which are connected to a datalogger recording the resistivity. The resulting tracer breakthrough curves can be used to estimate the direction and magnitude of groundwater flow (Rønne, 2014; Schillig, 2012) with an average error of $\pm 15\%$ in magnitude and $\pm 9^\circ$ in direction based on 17 laboratory tests (Gibson and Devlin, 2018).

The first study to use the PVP close to surface water was Kempf et al. (2013), who compared different field methods in an area influenced by tidal effects, however, the aim was not in particular to quantify groundwater-surface water interactions. Using the PVP for this purpose was investigated by Rønne et al. (I). This study measured the seepage velocity and flow direction with several PVPs installed along the bank of Grindsted Stream with the aim of quantifying the contaminant mass discharge. Figure 8 shows horizontal and vertical flow directions obtained from PVPs. Groundwater was flowing towards the stream mostly with an upward direction. Contaminant mass discharge estimates using PVP data were comparable to estimates obtained from Darcy's law (Table 2), indicating that PVPs yield reliable results at the groundwater-surface water interface.

Interpretation of PVP data can be challenging, however, if the shape of the tracer breakthrough curves deviates too much from the shape expected based on the advection-dispersion equation. Such deviations can be caused by injection of air bubbles through the injection port during an experiment (Schillig et al., 2011). Moreover, verification of no flow remains a challenge for the PVP, as no detector response, using any of the ports, could be caused by either no or very slow groundwater flow, or a damaged PVP. Other challenges associated with the PVP are the disturbance of the subsurface during PVP installation and practical issues related to installation at great depths.

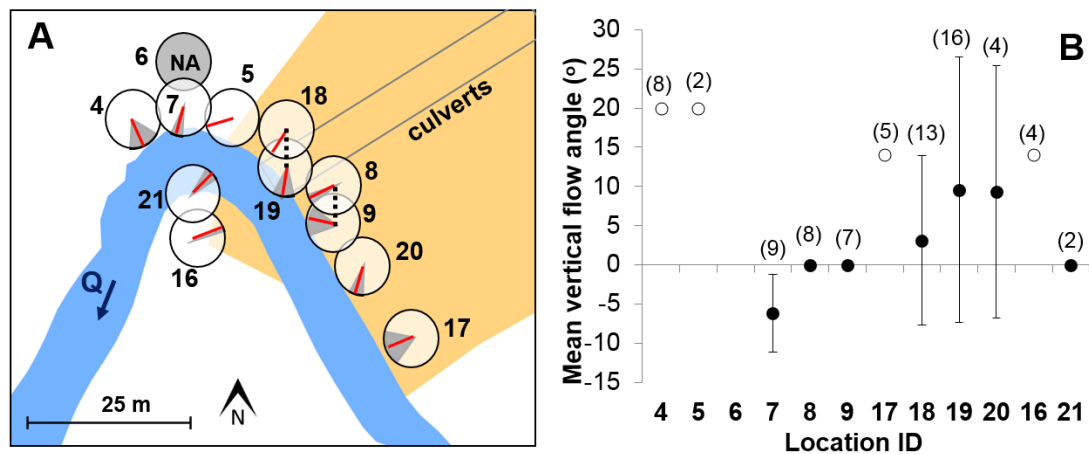


Figure 8: Groundwater flow directions at the Grindsted Stream site obtained by PVPs. A) PVP locations (white circles), Horizontal directions (red lines) and standard deviations (grey zone). The numbers are location ID. B) Vertical flow angles. The error bars indicate the standard deviation. The numbers in parentheses are the number of successfully conducted tests. Open data points indicate that the flow angle exceeded the maximum angle (critical angle) that could possibly be measured by the PVP. Maximum (and minimum) critical angles are dependent on vertical detector length and distance between injection ports and horizontal detectors (Figure 7). Modified by the author from Rønde et al. (I).

The PVP is unfortunately not commercially available at this point in time. However, it can be constructed from a few pieces printed by a 3-D printer and additional inexpensive materials (Rønde, 2014; Walter and Devlin, 2017).

An alternative version of the PVP, termed the streambed point velocity probe (SBPVP), was developed by Cremeans and Devlin (2017). It works on the same principle as the regular PVP, but measures the vertical seepage velocity in the streambed during temporary deployment at ca. 10 cm depth. The average error of $\pm 3\%$ was found based on 90 laboratory tests (Cremeans and Devlin, 2017). Cremeans et al. (2018) used the SBPVP to quantify the contaminant mass discharge through the streambed of Grindsted Stream, which compared well to estimates at the streambank obtained by Rønde et al. (I). As with the regular PVP, the SBPVP is currently not commercially available.

The high resolution passive profiler (HRPP) is another tool for direct measurements of seepage velocity, which has recently been developed by Schneider et al. (2019). In this method, a passive measurement of seepage velocity is obtained from the mass transfer rates of conservative tracers across the membrane used to separate the HRPP reservoirs from the soil matrix (i.e. mass transfer of Br^- from the HRPP to groundwater, and Cl^- from groundwater into the HRPP).

A simplified version of the HRPP, designed to exclusively measure seepage velocity, has been tested in the laboratory, while the fully equipped HRPP is claimed to be capable of measuring contaminant concentrations and microbial community structures (Schneider et al., 2019). This would allow for calculation of time integrated contaminant fluxes and assessment of the degradation potential. However, before the application of the device has been tested in the field, it is difficult to evaluate the method.

5.3 Passive contaminant flux measurements

The passive flux meter (PFM) can measure the contaminant flux (mass/area/time) directly, as well as the magnitude of the horizontal specific discharge in porous media (Annable et al., 2005; Hatfield et al., 2004; Klammler et al., 2012). When multiplied with the area of a control plane, the contaminant mass discharge can be calculated from Equation 5. This is a major advantage of the PFM, as the contaminant flux can be measured with a single device with no additional requirements for concentration data.

The PFM contains a sorbent of granular activated carbon (GAC) mixed with residence tracers with various known retardation factors. During deployment in the screened part of a borehole, the residence tracers gradually wash out of the PFM, while contaminants sorb to the GAC. The length of deployment period depends on prior knowledge of specific discharge and contaminant concentration levels. After retrieval, the GAC is analysed for tracers, to obtain specific discharge, and contaminants, to obtain contaminant flux. Results are then corrected by a convergence/divergence factor, which depends on the difference in hydraulic conductivities between the PFM and the aquifer (Annable et al., 2005), as well the filter pack around the screen (Verreydt et al., 2015).

Detectable contaminants include chlorinated ethenes, brominated ethenes (e.g. tetrabromoethane, TBA; tribromoethene, TBE; methyl tert-butyl ether, MTBE), perchlorate, arsenic, chromate, uranium, phosphate and nitrogen, and recently also chromium(VI) and low partitioning compounds, such as Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,4-dioxane (Haluska et al., 2018).

Various versions of the PFM have been developed, including one that measures the flow direction (Klammler et al., 2007). However, for this purpose, the assumption that advective transport dominates over diffusion is critical and hence reliable flow directions cannot be measured for slow groundwater flow. Other PFM versions include a fractured rock PFM (FRPFM) for contaminant flux measurements in fractured media (Klammler et al., 2016), a hyporheic PFM

(HPFM) for quantification of horizontal hyporheic flow (Kunz et al., 2017b, 2017a) as well as a sediment bed PFM (SBPFM) to quantify the vertical contaminant flux through streambeds (Layton et al., 2017; Rønne et al., **II**). The latter is especially useful for quantifying the contaminant mass discharge to streams. While regular PFMs can be purchased from Enviroflux, the SBPFM is not currently commercially available. However, construction is simple, inexpensive and can be completed in the field in ca. 10 min.

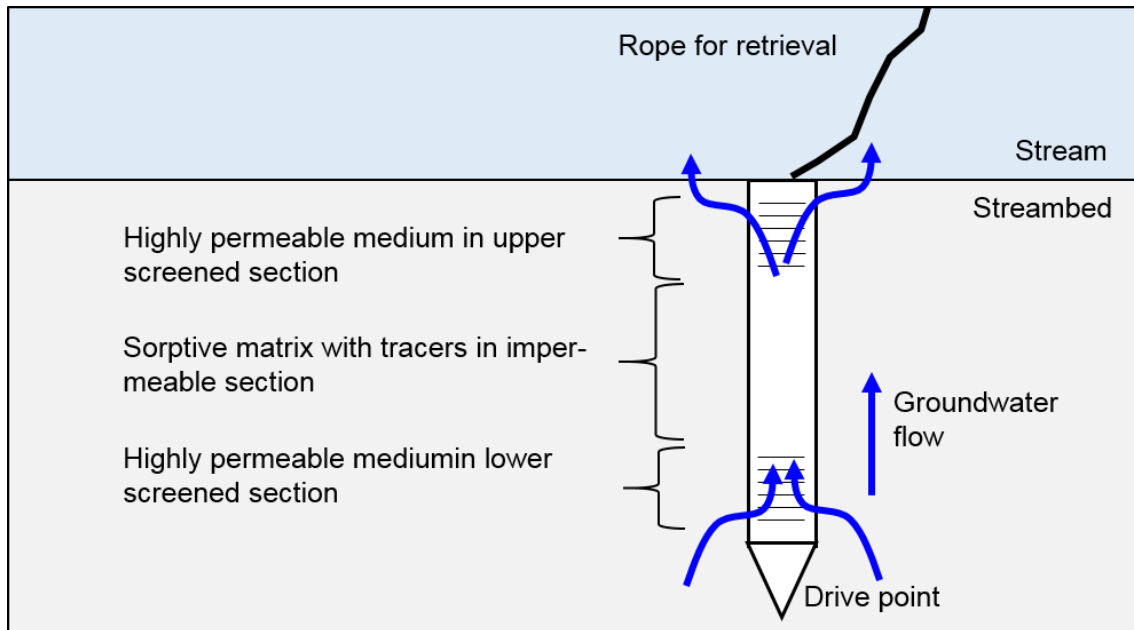


Figure 9: Schematic of the SBPFM. Blue arrows indicate groundwater flow.

The SBPFM consist of a tube of e.g. 70 cm length with two screened sections and a drive-point bottom (Figure 9). The screened sections contain a highly permeable medium, such as coarse sand, and allow for water inflow (lower section) and outflow (upper section) (Layton et al., 2017). The resulting flow pattern makes the calculation of the convergence/divergence factor different compared to the regular PFM. Besides this, the principles for the two devices are the same, and hence the solid pipe section of the SBPFM contains GAC mixed with several residence tracers as the regular PFM (Annable et al., 2005). Deployment is conducted by sliding an SBPFM into a guide tube (placed and held at the top of the streambed) and hammering it into the (non-cohesive) streambed by a rod (Rønne et al., **II**).

Rønne et al. (**II**) deployed several SBPFM in a transect across Grindsted Stream to measure the mass flux of chlorinated ethenes. The spatial distribution

of flux averaged concentrations (mass/volume) calculated from measured contaminant fluxes and specific discharges were similar to that obtained by analysis of collected water samples, however, the absolute values obtained from SBPFMs were in general higher.

5.4 Support from geophysics

Non-invasive geophysical methods can provide valuable information of the subsurface regarding the geology and groundwater composition. For instance, the direct current (DC) and induced polarisation (IP) methods can be used to image the resistivity (or electrical conductivity) and chargeability of the subsurface, respectively. The imaged resistivity is a combination of the electrical conductivity of the overall geologic formation (σ_{bulk}) and the pore water electrical conductivity (σ_{w}). For example, water saturated sand and clay are associated with low and high σ_{bulk} , respectively. σ_{w} increases with increasing ionic strength and is thus related to ion concentrations (Maurya et al., **IV**).

Ionic species, such as chloride, calcium, sodium and hydrogen carbonate, are often present in plumes from landfills (Christensen et al., 2001; Maurya et al., **IV**). The resulting difference in electrical conductivity between the plume and pristine aquifer makes the DC method able to map inorganic plumes, provided that the geology is known (Maurya et al., **IV**). At sites with relatively homogeneous geology, σ_{bulk} approximately reflects σ_{w} , and DC may thus be used to map inorganic contamination.

The use of non-invasive geophysical methods for mapping inorganic contaminant plumes are not new in particular (Chambers et al., 2006; Maurya et al., **IV**), however, mapping of organic contaminants, which are not electrically charged, is novel. This was done by Balbarini et al. (**III**), who used DC and IP in combination (DCIP). They found that the distribution of σ_{bulk} was similar to that of pharmaceuticals at Grindsted landfill, and to that of benzene and chlorinated ethenes at Grindsted Stream site. The recognition of the reasons for the similarities in distribution is crucial: since organic compounds do not contribute to the σ_{w} , their presence in areas of increased σ_{w} is either related to source characteristics, i.e. organic and inorganic contamination are located in the same areas, or degradation of the organic contaminants that may change the general water chemistry. For example, the degradation of BTEX com-

pounds can result in the formation of dissolved ferrous iron, leading to an increase in ionic strength. Application of the method is therefore highly site specific.

Balbarini et al. (III) used imaged σ_{bulk} from DCIP measurements to support the description of contaminant concentration distributions in a control plane. This was done through regression kriging of contaminant concentrations with σ_{bulk} as the dependent variable at both Grindsted landfill and Grindsted Stream site. An uncertainty analysis of contaminant mass discharge estimates obtained from the geophysics-supported concentration field and a concentration field based on water samples alone showed that DCIP data could decrease the uncertainty. Additionally, Balbarini et al. (III) showed that support from geophysical measurements are especially beneficial for a low sampling density of concentration data. The method is thus mainly suitable for large relatively homogeneous sites, where high sampling densities are infeasible.

5.5 The in-stream approach

The in-stream contaminant mass discharge can be calculated from stream concentrations and stream discharge in the fully mixed point (Equation 6). The fully mixed point can be found by assessing the variability in stream contaminant concentrations within multiple control planes across the stream. If the mixing in the transverse direction is slower than the vertical mixing, as is often the case for wide rivers, it is sufficient to assess the variability in the transverse direction (Aisopou et al., 2015; Rønde et al., I).

When the fully mixed point has been determined, the fully mixed concentrations and corresponding stream discharge are measured. Stream discharge may be measured directly or derived from rating curves, i.e. relationship between stream stage and discharge, and estimates are associated with some uncertainty. Preferably, concentrations and discharge are measured at various flow conditions in order to confirm a linear relationship between c_{mix} and $1/Q_{\text{mix}}$, which exists if the contaminant mass discharge is constant in time (Figure 4). In that case, the mass discharge is equal to the slope. Depending on the specific purpose, it might be necessary to correct CMD_{mix} for contaminant mass entering the stream through routes other than groundwater, such as drain pipes, or upstream of the investigated plume (Section 4.2).

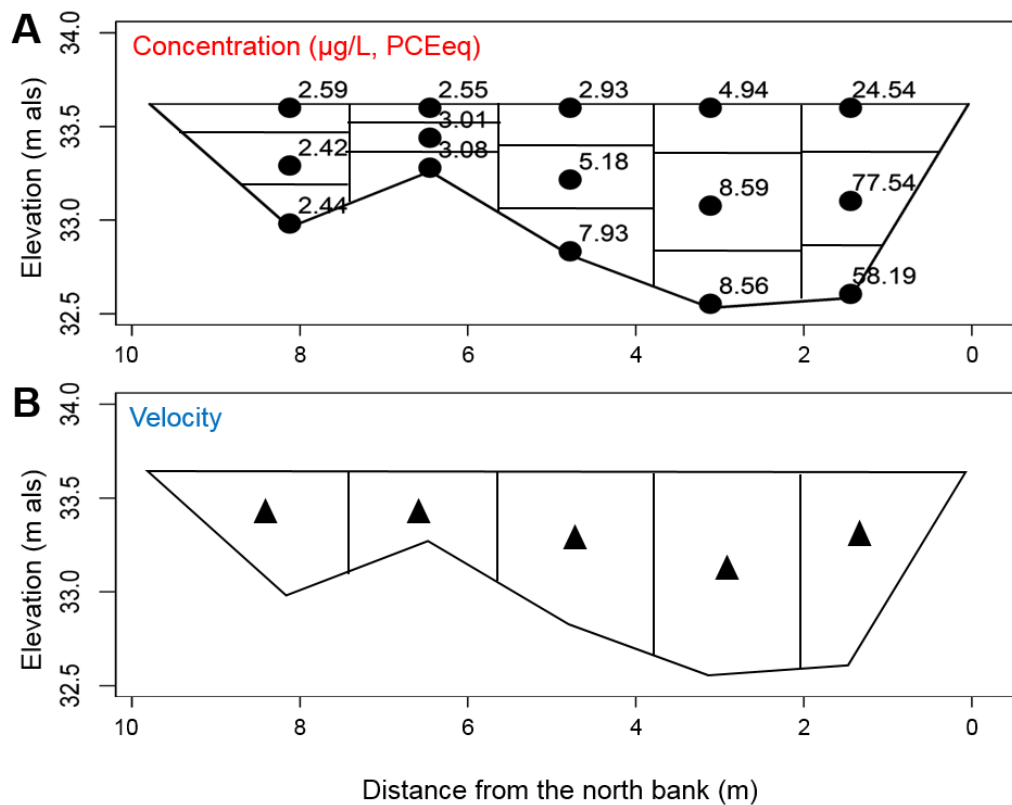


Figure 10: A) Total chlorinated ethene concentration in Transect 2 (Figure 2D), representing highly unmixed conditions. B) Example of measuring point locations for stream velocity in the same transect, required to estimate the in-stream contaminant mass discharge at unmixed conditions. Modified by the author from (Rønde et al., II).

In principle, the in-stream contaminant mass discharge can also be determined in a transect upstream of the fully mixed point. However, determination of concentration and stream velocity would be required in several points within the transect similarly to the point-scale approach, in order to calculate the contaminant mass discharge (Figure 10).

The in-stream contaminant mass discharge is a spatially integrated measurement, hence the uncertainty of estimates is generally expected to be lower than subsurface estimates (Rønde et al., I). Moreover, it is an inexpensive approach as surface water sampling and stream discharge measurements are associated with low costs compared to sub-surface investigations. However, it naturally requires that stream concentrations are above quantification limits, making it inapplicable at sites where dilution by stream water renders stream concentrations negligible (e.g. Hamonts et al., 2009; Şimşir et al., 2017).

5.6 Uncertainty of contaminant mass discharge

Uncertainty in contaminant mass discharge estimates is of great practical importance because it influences the results of subsequent assessment (Kübert and Finkel, 2006). The aim of this section is not to quantify or in detail describe uncertainties of estimates, but rather to highlight the importance of considering the uncertainty. Uncertainties of contaminant mass discharge estimates can be ascribed to 1) uncertainties resulting from interpolation in the control plane, 2) insufficient sampling density, and 3) uncertainties in the actual data used in the calculations. For the in-stream approach at fully mixed conditions, only point 3 is relevant.

When performing interpolation, introduction of uncertainty is unavoidable. However, geostatistical methods, i.e. kriging, for description of a variable in space hold an advantage over others, such as the Thiessen polygon method, due to the possibility to quantify the uncertainty (Cai et al., 2011).

Using such statistical methods, the uncertainty related to sampling density has been extensively investigated (e.g. Balbarini et al., **III**; Kübert and Finkel, 2006; Troldborg et al., 2012, 2010). Generally, these studies found that the uncertainty of estimates increase with increasing geological heterogeneity and decreasing sampling density. Depending on the purpose of investigation, higher or lower sampling density may be desired to obtain a certain quality of results or to decrease drilling costs.

Uncertainties in individual parameters may be related to sampling or analysis procedures. Due to their cause, such uncertainties are typically assumed to be spatially uncorrelated and display as a nugget variance component in the data variogram on which kriging is based (Klammler et al., 2012). Nevertheless, they do influence the uncertainty of the contaminant mass discharge estimates.

For the Darcy's law-based methods, reliable estimates of the hydraulic conductivity are often the greatest challenge, as uncertainties of at least one order of magnitude can be expected (Rovey and Cherkauer, 1995). These errors are severe as they propagate directly into mass discharge estimates (Equation 3). Therefore, when evaluating Darcy's law-based estimates, the high uncertainty of the hydraulic conductivity is essential to consider. In addition, the common assumption of isotropy may lead to increased uncertainty for anisotropic conditions (Section 5.1).

The uncertainty in estimates based on direct measurements of seepage velocity is expected to be relatively lower, since the porosity (which usually only varies

between 0.2-0.5 (Schneider et al., 2019)) is the only geological parameter used in the contaminant mass discharge calculation (Equation 4).

Contaminant mass discharge estimates based on direct contaminant flux measurements (Equation 5) are, as Darcy's law-based estimates, influenced by errors in the hydraulic conductivity. Yet, the impact is lower, given the definitions of the convergence/divergence factor for the PFM (Annable et al., 2005) and SBPFM (Layton et al., 2017).

In summary, uncertainties need to be considered when evaluating contaminant mass discharge estimates and designing field campaigns. Otherwise, incorrect conclusions may be drawn, and wasted resources may be put, for example, into refining the quality of estimates even when it is clear that no risk exists, or into field campaigns incorrectly designed to yield estimates of insufficient accuracy.

5.7 Comparison of field methods

Each of the methods for contaminant mass discharge quantification, described in this chapter, is associated with some advantages as well as some challenges. No single method is always more advantageous than others, and the choice of field method should therefore be based on considerations regarding the following:

- Purpose of the investigation and thus desired outcome, regarding aquifer/streambed estimates, time integrated results/snapshot, uncertainty level, etc.
- Resources available, including economic resources, timeframe and expertise.
- Specific site characteristics, including geology, plume depth, scale of the investigation, type of contamination, available borehole infrastructure, knowledge on flow direction etc.
-

For determination of the groundwater flow direction at the small scale, PVPs seem to be the most accurate method. However, a high sampling density of parameters of less accuracy may nevertheless yield better mass discharge estimates than a few points of high accuracy. Therefore, if boreholes are already available at a site, Darcy's law or PFMs might be preferred over PVPs. On the other hand, the PVP may be a suitable choice for a site with a shallow plume and unknown or spatially variable groundwater flow direction.

Support from geophysical measurements are especially useful at large sites, where high accuracy is required. If the average contaminant mass discharge over a period of time is desired, the PFM/SBPFM could be the appropriate choice. Time integrated estimates may be especially relevant in streambeds, where magnitude of flow is highly variable in time. Finally, the in-stream approach is inexpensive and it is therefore recommended to apply this approach before beginning expensive subsurface investigations.

The selected methods for contaminant mass discharge quantification discussed in this chapter are compared in Table 4. As mentioned in Section 2.2, a standardised method for quantification of the contaminant mass discharge is lacking. Hence, the comparison made in this chapter may in its place provide guidance on which field method to use for a given purpose. Since the contaminant mass discharge approach is a valuable tool in risk assessment, such guidance can improve risk assessment of contaminated sites impacting streams.

Table 4: Comparison of selected methods for contaminant mass discharge quantification, including the main advantages and challenges. AQ = applicable in the aquifer. SB = applicable in the streambed. SW = applicable in the stream water.

Method	AQ/SB/SW	Advantages	Challenges
Subsurface point-scale approach	AQ/SB	Spatial information is gained; minimal waste is generated	High sampling density required to decrease uncertainty; risk of missing high contaminant flux zones; uncertainty introduced by interpolation
- Darcy's law	AQ/SB	Borehole infrastructure is often already present	Requires hydraulic conductivity estimates; high uncertainty when distances between hydraulic head measurements are short; snapshot in time; challenging for anisotropic conditions
- Direct seepage velocity (PVPs)	AQ	Accurate quantification of both the horizontal and vertical velocity component; no requirement for hydraulic conductivity and gradient estimates	Not currently commercially available; snapshot in time; separate borehole needed; cannot be used in cohesive sediments; difficult to install at large depths
- Direct seepage velocity (SBPVPs)	SB	Accurate quantification of vertical seepage velocity in streambeds; no requirement for hydraulic conductivity and gradient estimates	Not currently commercially available; snapshot in time; cannot be used in cohesive sediments
- Passive flux (PFMs)	AQ	Direct measurements of contaminant flux, i.e. water sampling not required; infrastructure is often already present; yields time integrated results	Requires estimates of the hydraulic conductivity; assumes horizontal flow; sensitive to vertical flow
- Passive flux (SBPFMs)	SB	Direct measurements of streambed contaminant flux, i.e. water sampling not required; yields time integrated results; quick and inexpensive to construct	Requires estimates of the hydraulic conductivity; hyporheic flow may influence results
- Support from geophysics	AQ	Can improve descriptions of concentration distributions; non-invasive; high data resolution makes it beneficial at large scales	Relies on (site specific) conceptual links between imaged bulk electrical conductivity and contaminant concentrations; interpretation challenging in heterogeneous settings
In-stream approach	SW	Inexpensive, relative to subsurface estimates; yields spatially integrated results	Only applicable if stream concentrations are above quantification limits; attenuation processes (e.g. volatilisation) must be considered depending on purpose.

6 Near-stream attenuation of chlorinated ethenes

Chlorinated ethenes may undergo various natural attenuation processes in the environment as mentioned in Section 4.3. In the past 15 years, the investigation of chlorinated ethene attenuation near streams has intensified. A driving factor for such investigations is the recognition of the need to ensure surface water quality by regulatory directives such as the EU WFD (Section 1.1). Compared to conditions in aquifers, the environment beneath streams can be more favourable for natural attenuation (Weatherill et al., 2018). This could be due to the frequently organic matter-rich fluvial sediments, which have been linked to enhanced microbial activity (Weatherill et al., 2018), and due to exchange flow between groundwater and surface water in the saturated soil matrix surrounding the stream, as illustrated in Figure 11. The zone in which such exchange flow takes place is commonly termed the hyporheic zone (Anibas et al., 2016; Tonina and Buffington, 2007).

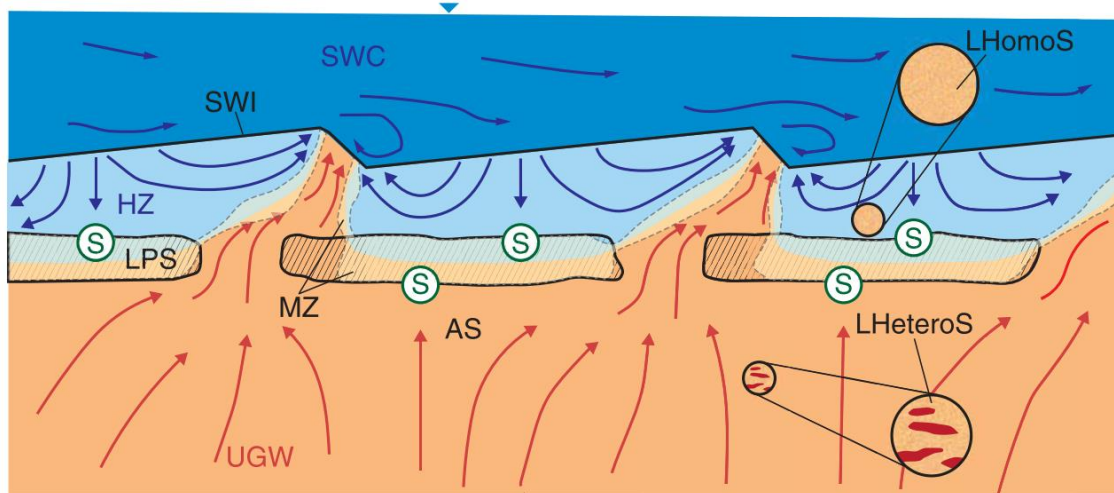


Figure 11: Conceptual representation of hyporheic flow. SWI = sediment-water interface, LPS = low-permeability sediments, S = stagnation zones, AS = ambient sediment, SWC = stream water column, UGW = upwelling groundwater, HZ = hyporheic zone, MZ = mixing zone, LHomoS = locally homogeneous sediment, LHeteroS = locally heterogeneous sediment (Gomez-Velez et al., 2014).

The hyporheic zone beneath streams has received much attention due to its potential capacity to reduce or even eliminate groundwater contaminants, such as chlorinated ethenes. Understanding the dynamics of the hyporheic zone is

therefore important to determine its potential attenuation capacity. In this chapter, implications of the hyporheic zone with respect to attenuation are described. Furthermore, quantification and conceptualisation of attenuation is discussed in the perspective of risk assessment.

6.1 Attenuation processes and the hyporheic zone

Hyporheic flow is mainly driven by variations in pressure along the streambed caused by flow over streambed structures, such as dunes, ripples and pool-riffle sequences. High and low pressures develop at the up- and downstream sides of the structure, respectively, resulting in stream water infiltration into the bed sediments and subsequent exfiltration back to the stream as shown in Figure 11 (Gomez-Velez et al., 2014; Trauth et al., 2013; Winter et al., 1998). Also meander bends can cause infiltration of stream water into the adjacent banks (Boano et al., 2014). Hyporheic flow is found to be highly variable temporally and spatially (e.g. Freitas et al., 2015), as it is impacted by, for example, ambient groundwater flow (Trauth et al., 2014, 2013; Wu et al., 2018) and low-permeability formations beneath the stream (Gomez-Velez et al., 2014).

Hyporheic flow may ensure favourable conditions for various biotransformation pathways by supporting microbial communities, rejuvenating the streambed with oxygen and dissolved organic carbon (DOC), and creating steep redox gradients at the interface between the chemically distinct groundwater and surface water components (Atashgahi et al., 2013; Boano et al., 2014; Freitas et al., 2015). Hyporheic flow with a short residence time may be associated with aerobic conditions, which increases the potential for aerobic biodegradation, while hyporheic flow with a long residence time is more likely to be associated with anaerobic conditions due to the depletion of oxygen, which favours anaerobic biodegradation (Gomez-Velez et al., 2014).

Reductive dechlorination is the most important biotransformation pathway for chlorinated ethenes (Chambon et al., 2013). In this process, higher chlorinated ethenes are anaerobically biodegraded by organohalide-respiring bacteria to lower chlorinated ethenes, i.e. degradation of PCE to TCE and further to DCE (predominantly *cis*-DCE) and vinyl chloride, which may eventually degrade to the non-toxic ethene. Redox processes affect the various steps of reductive dechlorination because chlorinated ethenes compete with redox-sensitive species, such as Fe(III) and SO₄, to be a terminal electron acceptor reacting with available electron donors. The electron donor is usually molecular hydrogen produced by fermentation of dissolved organic carbon (Abe et al., 2009; Chambon et al., 2013). Favourable conditions for reductive dechlorination are

when organohalide-respiring bacteria are highly abundant, there are sufficient amounts of electron donor available, and the redox conditions are sufficiently reduced. Moreover, the residence time should be sufficiently long for reductive dechlorination to occur before the contaminants reach the surface water. Other degradation pathways are for example oxidation of cis-DCE and vinyl chloride, which on the contrary requires oxic conditions (Weatherill et al., 2018). Such pathways are favourable from a risk assessment perspective, as no stable toxic intermediates are formed (Weatherill et al., 2018).

The frequently elevated organic carbon content in the fluvial sediments beneath streams enhance sorption of contaminants. All of the chlorinated ethenes are characterized by low $\log K_{ow}$ (Petrisor and Wells, 2008) and are thus not prone to sorption compared to many other compounds. Nevertheless, substantial sorption has been reported in the literature. For example, Conant et al. (2004) estimated mean retardation factors for PCE of up to 60 for semi-confining deposits in the Pine riverbed, Ontario, Canada (based on distribution coefficient values, K_d). Diffusive transport of contaminants into formations of low permeability may cause plume longevity resulting from back diffusion, and thus prolonged risk (e.g. Matthieu et al., 2014). Sorption in streambeds can additionally lead to enhanced risk for (micro)organisms living on the sediments.

Moreover, hyporheic flow may dilute contaminated groundwater (Hamonts et al., 2009). Dilution by infiltrating surface water does not lead to decreased contaminant mass discharge, but may locally reduce the risk.

When chlorinated ethenes reach the surface water, they are diluted and transported along with the stream flow. Chlorinated ethenes are volatile and hence they are likely to escape to the atmosphere (Petrisor and Wells, 2008). The rate of mass loss through volatilisation is among other things dependent on the stream width-to-depth ratio (Aisopou et al., 2015).

6.2 Quantifying and conceptualising attenuation

A review by Weatherill et al. (2018) has made it clear that several attenuation behaviours for discharging chlorinated ethene plumes have been reported in the literature. The wide range of attenuation behaviours makes assessment of the risk posed to streams challenging, and calls for more holistic and quantitative methods to assess attenuation, as well as conceptual models (Rønde et al., II).

Table 5: Overview of methods used in studies assessing chlorinated ethene attenuation near streams. (x) indicate that a qualitative assessment was conducted.

Field site	References	Contaminant conc.	Geology	Magnitude of GW flow	Fraction of org. carbon	Redox sensitive species	DOC	Microbial community	Hyporheic flow	CSIA	Parent-daughter relationships	Reach scale mass balance analysis
Grindsted Stream, Jutland, Denmark	Rønne et al., I, II; Sonne et al., V	x	x	x	x	x	x	x	(x)	x	x	x
Pine River, Ontario, Canada	Abe et al., 2009; Conant et al., 2004	x	x	x	x	x		x		x		
Third Creek, Tennessee, US	Şimşir et al., 2017	x	x	x		x		x				
West Branch Canal Creak, Maryland, US	Lorah and Clark, 1996; Lorah and Olsen, 1999	x	x	x	x	x	x					
Zenne River, Vilvoorde, Belgium	Hamonts et al., 2014, 2012, 2009; Kuhn et al., 2009	x	x	x	x	x		x	x	x		
River Tame, Birmingham, UK	Ellis, 2002; Ellis et al., 2007; Ellis and Rivett, 2007; Freitas et al., 2015; Roche et al., 2008	x	x	x	x	x			x		x	
River Tern, Shropshire, UK	Weatherill et al., 2014; Weatherill, 2015	x	x	x	x	x	x		x		x	
Unknown river, France	Courbet et al., 2011	x	x	x			x	x		x		x
Unnamed streams, Connecticut, USA	Chapman et al., 2007	x	x	x	x		x			x	x	x
Little Bayou Creek, Kentucky, US	(Fryar et al., 2000; LaSage et al., 2008a, 2008b)	x	x	x	x	x			x	x		x

For example, Lorah and Olsen (1999) observed substantial reductive dechlorination and sorption at West Branch Canal Creek, US, characterised by high natural DOC, reduced redox conditions and organic matter-rich wetland sediments. In contrast, Rønne et al. (II) observed limited subsurface attenuation at the Grindsted Stream site, ascribed to the low fraction of organic carbon, the high groundwater velocity, and the relatively low abundance of *Dehalococcoides* and of the functional genes *vcrA* and *bvcA*, which are associated with reductive dechlorination. Dilution by stream water, mixing and volatilisation were instead the dominant attenuation processes (Section 4.3).

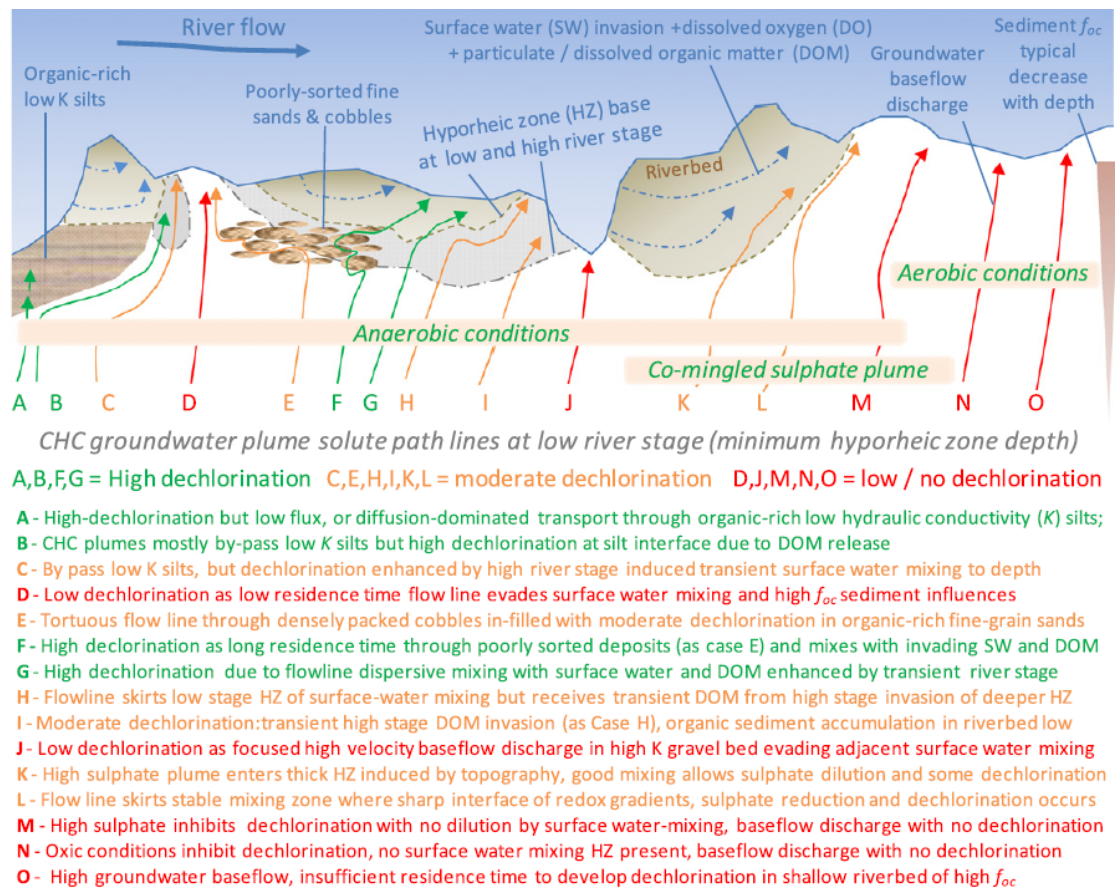


Figure 12: Conceptual model of reductive dechlorination under various locally present field conditions beneath a stream (Freitas et al., 2015).

Commonly, a multiple line of evidence approach is used to assess attenuation. This approach integrates multidisciplinary methods to gain confidence in the interpretation of the observations. Table 5 provides an overview of some of the methods (lines of evidence) most frequently encountered in field studies, as well as examples of studies that have used these methods to assess near-stream chlorinated ethene attenuation. The majority of the studies listed in Table 5

aim to assess, describe, distinguish or document the individual attenuation processes in order to advance process understanding. Such studies have for example provided valuable insight into degradation pathways (e.g. Kuhn et al., 2009). In contrast, few studies (e.g. Rønne et al., **II**) have used reach scale mass balance analyses required for the quantification of attenuation effects (Table 5). Examples of such mass balances are provided in Section 4.3.

Recent studies have additionally developed conceptual models of the attenuation of discharging chlorinated ethene plumes. For example Freitas et al. (2015) conceptualised reductive dechlorination near streams under various locally present field conditions (Figure 12).

Another example is a review by Weatherill et al. (2018), which conceptualised the degradation of chlorinated ethenes in the mixing zone between a hyporheic flow cell and upwelling groundwater (Figure 13). This conceptual model suggests that higher chlorinated ethenes are degraded to lower chlorinated ethenes through anaerobic respiration at the deeper sediments beneath the river. The lower chlorinated ethenes are then degraded in the mixing zone through aerobic metabolic and co-metabolic pathways.

A final example is a study conducted by Rønne et al. (**II**), who developed several conceptual models for stream attenuation. The models were developed based on investigations at the Grindsted Stream site, as well as a compilation of literature studies (Figure 14). In essence, these conceptual models illustrate that attenuation processes near streams – and thus the effect on the surface water quality – depend on biogeochemical and hydrogeological conditions, as well as stream characteristics. Both the hydrogeology and biogeochemistry must be favourable in order for sorption and degradation to be expected. If such conditions are only present in parts of the plume discharge zone, a patchy attenuation behaviour will be expected.

Some of the field studies were identified as endmembers or close to. One was the Grindsted Stream site, which exhibited limited attenuation (Figure 14A). In fact, this site is special in that it represents a missing piece of the palette of attenuation behaviours encountered in literature field studies. Other studies represented the opposite endmember by exhibiting extensive attenuation (Figure 14B), or they were somewhere in between the endmembers (Figure 14C,D).

The conceptual models identify some key parameters, which in addition to contaminant mass discharge can support reliable risk assessment. These parameters include: geological heterogeneity, seepage velocity, redox conditions within the plume, key microorganisms and fraction of organic carbon.

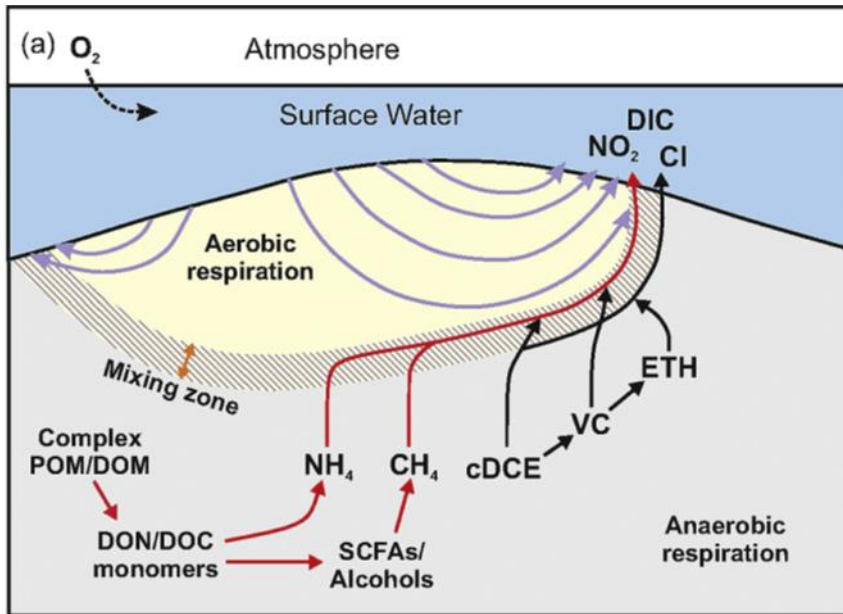


Figure 13: Conceptual model of the mixing zone between a hyporheic flow cell and surrounding upwelling groundwater supporting aerobic metabolic and co-metabolic degradation of the lower chlorinated ethenes (Weatherill et al., 2018).

The conceptual models made by Freitas et al. (2015) and Weatherill et al. (2018) advance our understanding of the implications of hyporheic processes on chlorinated ethene degradation, as well as of the various degradation pathways that chlorinated ethenes may undergo beneath streams. From this perspective, they can thus be categorised as process-based conceptual models. In contrast, the conceptual models developed by Rønde et al (II) are more holistic, as they illustrate the expectations regarding the overall attenuation behaviour for various scenarios.

In summary, from a practical risk assessment point of view, quantitative approaches, such as reach-scale contaminant mass balance analyses, can complement more process-orientated methods. Furthermore, holistic models may be more applicable in risk assessment than the more process-based conceptual models. The implication of approaches for attenuation assessment is further discussed in the following section.

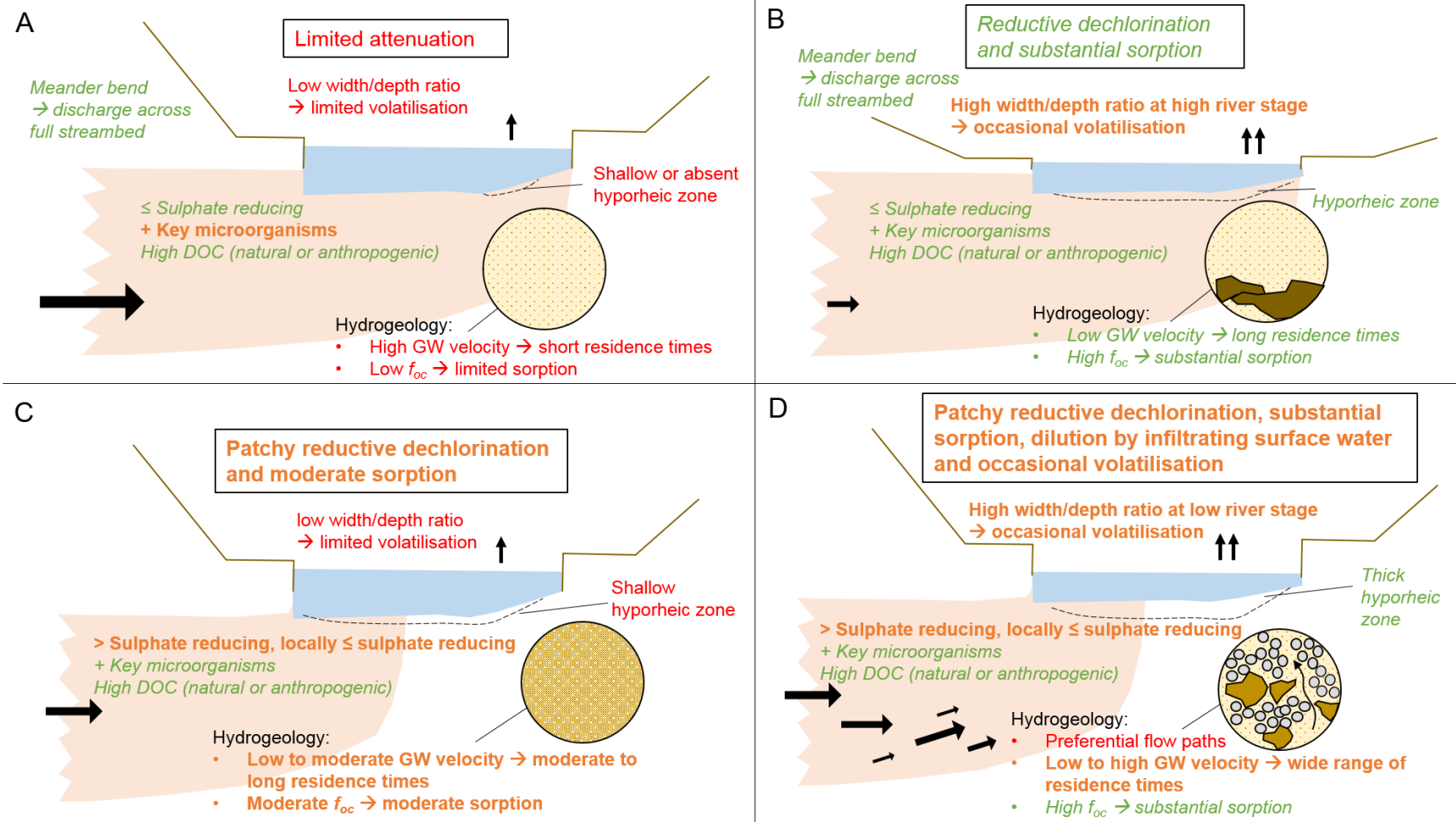


Figure 14: Conceptual models of chlorinated ethene attenuation near streams for various scenarios. Green and red fonts are used for factors that enhance and decrease the attenuation potential, respectively. Orange font is used for factors having an unclear effect on attenuation (Rønne et al., I).

6.3 Implications for risk assessment

During this PhD study, it has been observed that literature field studies tend to focus on process understanding. This is necessary in risk assessment, as for example some degradation pathways lead to the formation of vinyl chloride, while others do not (Weatherill et al., 2018). Nevertheless, documenting that a process occurs or is likely to occur does not provide information on whether this process is removing considerable mass from the system. Therefore, from a practical risk assessment perspective, it is additionally important to quantify the impact of natural attenuation on mass loss/gain of individual contaminants at the reach scale. Additionally, holistic conceptual models are required to allow for categorisation of sites into types of attenuation behaviour. Such quantitative and holistic approaches can help in prioritising sites on a regional or national level, which is required to comply with the WFD (Rønde et al., **II**).

7 Conclusions

The objectives of this thesis were to explore the advantages of applying the contaminant mass discharge near streams, evaluate field methods for contaminant mass discharge quantification, and quantify and conceptualise near-stream attenuation of chlorinated ethene plumes. By fulfilling these objectives, the aim of improving risk assessment is likewise fulfilled. The conclusions of the thesis are summarised below.

The advantages of contaminant mass discharge near streams:

The quantification of subsurface and in-stream contaminant mass discharges is a valuable approach in risk assessment of discharging contaminant plumes. This thesis exemplifies its application for prediction of stream water quality, identification and prioritisation of contaminant sources and pathways, improvement of conceptual understanding, quantification of combined and distinct attenuation processes, and evaluation of field tools.

Evaluating field methods for contaminant mass discharge quantification:

Several field methods for quantification of contaminant mass discharge exists and a selection of these were evaluated. No single method is always more advantageous than the others, but rather the most suitable method depends on the purpose, resources and specific site characteristics of the investigation. Some general conclusions are:

- Darcy's law-based methods may be less suitable near streams, due to issues related to heterogeneity, anisotropy and multi-directional flow fields.
- PVP-based methods are suitable near streams, due to the ability of PVPs to measure both the vertical and horizontal velocity components accurately.
- Passive sampling measurements may yield more representative contaminant mass discharge estimates due to their time-integrated nature.
- Support from geophysics may improve the description of the contaminant concentration distribution and thereby decrease the number of required boreholes. This method is especially suitable for large sites, where high sampling density of concentration data is infeasible.
- The in-stream contaminant mass discharge is inexpensive to quantify and the uncertainty of estimates are relatively low.

Quantifying and conceptualising near-stream attenuation processes:

Detailed mass balance analyses conducted at the Grindsted Stream site led to the following site-specific conclusions:

- No mass loss or shift in molar ratios were observed from the stream bank to the point of fully mixed conditions, where dilution by stream water and mixing were the dominant attenuation process.
- At a larger scale, volatilisation from stream water is also important, but occurs slowly.
- Stream water concentrations of vinyl chloride remained above the environmental quality criteria for several kilometers, hence Grindsted Stream is at risk.

And the following general conclusions:

- Comprehensive contaminant mass balance analyses along plume pathways can quantify the combined effect of attenuation processes.
- When combined with other methods, mass balances analyses can help in quantifying individual attenuation processes.

A set of holistic conceptual models for near-stream chlorinated ethene attenuation was developed. These models can support risk assessment by illustrating the effect of attenuation at various scenarios, and by providing guidance on which parameters to monitor besides the contaminant mass discharge.

These parameters include: geological heterogeneity, seepage velocity, redox conditions within the plume, key microorganisms and fraction of organic carbon.

8 Perspectives

Risk assessment of contaminant plumes discharging to streams is a major challenge, and hence this chapter offers several suggestions for future research to help improve risk assessment of such plumes.

Increasing the confidence in contaminant mass discharge estimates:

By evaluating various field methods for contaminant mass discharge estimation, it was found that uncertainties associated with the methods are still an issue. Improvements of field methods that would decrease this uncertainty include:

- Field testing of the effect of various environmental conditions on SBPFM and SBPVP results in order to gain confidence in measurements and to understand the impact of flow reversals and hyporheic flow.
- Handling anisotropy. Several field methods for contaminant mass discharge quantification are dependent on anisotropy estimates. Therefore, development of field methods to estimate anisotropy is of relevance.
- Expansion of the DCIP geophysical method to be applicable at highly heterogeneous sites and sites with various geological settings.

Decreasing field investigation costs for contaminant mass discharge quantification:

The evaluation of field methods additionally made it clear that expenses related to contaminant mass discharge estimation are still an issue. Possibilities to decrease costs include:

- Commercialisation of field tools. Currently, some field tools are unavailable for practitioners due to the economic resources and special expertise required for their manual construction.
- Further development of geophysical methods. Use of such methods to characterise organic contaminants are very new and needs further development to expand their applicability as mentioned in the previous section. This could considerably decrease drilling costs.

Comprehensive field studies for quantitative and holistic attenuation assessment:

Based on the conducted research, a need was identified for holistic assessment of near-stream attenuation of chlorinated ethenes. To address this need, more

field studies could be conducted in which the contaminant mass discharge approach is combined with other line of evidence in order to: 1) document the individual attenuation processes, 2) characterise the environmental conditions at which these processes occur, and 3) quantify the effect of the individual and combined attenuation processes. Some useful lines of evidence that are underrepresented in field studies on near-stream attenuation of chlorinated ethenes include:

- Detailed delineation of hyporheic flow. This could be done at the Grindsted Stream site by natural tracer tests (Freitas et al., 2015), isotope ratio monitoring (Hamonts et al., 2009), or deployment of HPFMs (Kunz et al., 2017b, 2017a).
- Quantification of degradation rates for chlorinated ethenes in aquifers and near streams. CSIA might be useful in addressing this need.
- Reach scale mass balance analysis.

Such field studies could be used to validate or build on the conceptual models for attenuation proposed by Rønne et al. (II). Furthermore, similar conceptual models for other contaminants, such as BTEX compounds or arsenic, could be developed.

Investigation of biogeochemical processes within co-mingled plumes and plumes interacting with diffuse contaminant sources:

Based on experiences from Grindsted Stream site, a need was identified to advance the understanding of the biogeochemical processes taking place within co-mingled plumes. Similarly, little is known about the interactions between plumes and diffuse contaminant sources, such as pesticides. Therefore, to conduct proper risk management, future research should provide insight into the biogeochemical processes taking place within various types of co-mingled plumes and plumes coinciding with diffuse sources of contamination.

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