

Water and contaminant fluxes at the stream-groundwater-interface

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Abstract

Streams and groundwater are inherently connected. In temperate climates, for instance, groundwater discharge to streams supplies the baseflow component of streamflow. Groundwater sustains streamflow in dry periods and is therefore critical for maintaining aquatic ecosystems and wetlands. Water fluxes between groundwater and streams also mediate the transport of contaminants between these two hydrologic compartments.

In the present work, we studied the spatial patterns of groundwater discharge to streams and the transport of organic contaminants from groundwater and streambed sediments towards the stream. First, we focused on developing a tool that can resolve the spatial pattern of groundwater discharge on a meter or even submeter scale but with an extent that covers stream reaches of up to several hundreds of metres in length. We basically used the simple technique of streambed temperature mapping. This approach takes advantage of the temperature gradient between groundwater (whose temperature remains nearly constant throughout the year) and stream water (whose temperature varies seasonally) to determine the magnitude of groundwater discharge. Shallow streambed temperatures can be temporarily sampled easily and inexpensively at hundreds of locations along a stream reach. We hypothesized that mapped streambed temperatures can be quantitatively related to the magnitudes of water flux by applying the heat-diffusion-advection equation. The key-assumption of the mapping approach is that streambed temperatures are solely influenced by the magnitude of groundwater discharge and are not disturbed by diurnal temperature variations at the surface that propagate into the streambed. We evaluated this assumption for streambed temperatures from the Pine River, Ontario, Canada. Under gaining conditions, diurnal temperature variations are insignificantly small at a depth of 0.2 m below the streambed surface. When surface water infiltrates, the temperature signal propagates deeper and the streambed temperature will no longer be completely independent from diurnal temperature variations. However, for gaining conditions a quasi steady state with respect to diurnal temperature variations applies.

To improve the robustness of the streambed temperature mapping method, we simultaneously measured the streambed temperatures at five depths using a newly constructed, multiple-depth temperature probe. In contrast to mapping streambed temperatures at a single, uniform depth, a temperature profile consisting of five measurements is obtained. Consequently, the estimated water fluxes become less sensitive to potential diurnal temperature influences and also less sensitive to random errors since the water flux estimates rely on five instead of one temperature measurement. This technique was applied to two small streams in Germany: the Schachtgraben located in the industrial area of Bitterfeld-Wolfen and the Schaugraben as part of a rural catchment in northern Germany. The length of the investigated reaches was 220 m and 750 m, respectively. At all investigated sites, the groundwater discharge was

heterogeneously distributed across the streambed area. At the Schachtgraben site, approximately 20% of the streambed area contributes 50% of the total groundwater discharge. The Schachtgraben is located in one of Germany's oldest industrial centres and is characterized by regional aquifer contamination from multiple sources. Chlorinated benzenes are the major groundwater pollutants at the studied reach. The study site is characterized by a diffuse groundwater contamination. Since the groundwater discharges to the Schachtgraben, there is a contaminant mass flux from the groundwater towards the stream.

At the Schachtgraben site, the groundwater has not been the only source of contaminants for the stream. The concentrations in the streambed are approximately one order of magnitude higher than those observed in the groundwater. The streambed is thus contributing a significant proportion of the contaminant mass fluxes. The release of untreated waste water from nearby chemical industry into the Schachtgraben until the early 1990s has severely contaminated the streambed. Since then, we assume that the concentration gradient has reversed and the contaminant fluxes are now directed from the streambed towards the stream water. Studying the role of the streambed as a contaminant source, we hypothesized that the governing transport process is the advection of water through the streambed. We calculated mass fluxes based on groundwater discharge rates and aqueous concentrations of monochlorobenzene (MCB) and dichlorobenzene (DCB) isomers in the streambed sediments. In addition, to obtain robust estimates of average contaminant concentrations, time-integrating passive samplers were installed in the streambed at zones of high and low groundwater discharge.

The streambed sediments are characterized by a considerable residual mass of MCB which remained sorbed although desorption has continued for more than ten years. Column experiments conducted at realistic flow rates that were set to be within the range of the observed magnitudes of groundwater discharge revealed that the removal of mass is inefficient. Long-term predictions of mass release indicated that the time-scales to remove 50% of the residual mass of MCB will be decades but potentially centuries.

Résumé

Les cours d’eaux et eaux souterraines sont par nature connectés. Sous des climats tempérés, par exemple, l’écoulement des eaux souterraines dans les rivières fournit le flux de base composant le débit du cours d’eau. Les eaux souterraines alimentent les rivières lors des périodes sèches et sont pour cette raison cruciales pour maintenir les écosystèmes aquatiques et les zones humides. Les échanges entre eau souterraine et rivières régulent le transport des contaminants entre ces deux compartiments hydrologiques.

Dans ce travail, nous avons étudié la répartition spatiale des apports en eau souterraine vers les rivières et le transport de contaminants organiques, des eaux souterraines et des sédiments, vers les rivières. Premièrement, nous nous sommes concentrés sur le développement d’un outil qui puisse décomposer la répartition spatiale des apports en eau souterraine, à une échelle métrique ou submétrique, mais avec une étendue qui couvre une section de rivière jusqu’à plusieurs centaines de mètres de long. Nous avons utilisé la technique de cartographie des températures du lit des rivières. Cette approche utilise le gradient existant entre les eaux souterraines (dont les températures restent pratiquement constantes durant l’année) et les cours d’eaux (dont les températures varient de façon saisonnière) pour quantifier les apports en eau souterraine. Les températures des cours d’eau peu profonds peuvent être suivies de façon temporelle, relativement facilement et à moindre coût sur une centaine d’emplacements le long d’une section de rivière. Nous avons supposé que les températures de lit cartographiées peuvent être reliées de façon quantitative aux apports en eau souterraine en appliquant l’équation chaleur-diffusion-advection. L’hypothèse clé de l’approche cartographique est que les températures du lit sont exclusivement influencées par les apports en eau souterraine et ne sont pas perturbées par les variations diurnes de température à la surface, qui se propagent dans le lit. Nous avons évalué cette hypothèse pour les températures du lit de la rivière Pine, Ontario, Canada. Dans les conditions où la rivière est alimentée par la nappe, les variations diurnes de température sont négligeables à une profondeur de 0.2 mètres en dessous la surface du lit. Quand les eaux de surface s’infiltrent, le signal de température se propage en profondeur et la température du lit ne sera plus complètement indépendante des variations diurnes de température. Cependant, dans les conditions où la rivière est alimentée par la nappe un état quasi stable s’applique, par rapport à des variations diurnes de température.

Pour améliorer la robustesse de la méthode de cartographie des températures du lit des rivières, nous avons mesuré simultanément les températures du lit à cinq profondeurs en utilisant une sonde de température multi-profondeur, récemment construite. À la différence d’une cartographie des températures à une seule profondeur uniforme, un profil de température composé de cinq mesures est obtenu. Par conséquent, le flux d’eau estimé devient moins sensible aux potentielles influences des variations diurnes de température et

aussi moins sensible à des erreurs aléatoires, puisque l'estimation s'appuie sur cinq mesures de température au lieu d'une seule. Cette technique a été appliquée à deux petits cours d'eau d'Allemagne : le Schachtgraben situé dans la zone industrielle de Bitterfeld-Wolfen et le Schaugraben dans une zone rurale du nord de l'Allemagne. Les longueurs étudiées étaient respectivement de 220 m et 750 m. Sur tous les sites étudiés, les apports d'eau souterraine étaient distribués de façon hétérogène à travers la surface du lit. Sur le site du Schachtgraben, environ 20% de la surface du lit contribue à 50% de l'apport total d'eau souterraine. Le Schachtgraben est situé dans la zone industrielle de Bitterfeld-Wolfen. Cette région est l'un des plus vieux centre industriel d'Allemagne et est caractérisée par une contamination régionale de l'aquifère provenant de sources multiples. Les chlorobenzènes sont les polluants majeurs des eaux souterraines sur le secteur étudié. Puisque le Schachtgraben est un cours d'eau alimenté par les eaux souterraines, les contaminants trouvés dans l'aquifère peuvent aussi être détectés dans le cours d'eau. Le site d'étude est caractérisé par une contamination diffuse des eaux souterraines. Les eaux souterraines s'écoulant dans le Schlachtgraben, il y a un flux de contaminants depuis les eaux souterraines vers le cours d'eau.

Sur le site du Schachtgraben, les eaux souterraines n'ont pas été les seules sources de contaminants pour le cours d'eau. Les concentrations dans les sédiments du lit sont approximativement d'un ordre de grandeur supérieures à celles observées dans les eaux souterraines. Les sédiments du lit de la rivière contribue donc au flux de contaminants dans des proportions significatives. Le déversement d'eaux usées non traitées dans le Schachtgraben provenant des industries chimiques proches, jusque dans le début des années 1990, a sévèrement contaminé le lit du cours d'eau. Depuis nous supposons que le gradient de concentration s'est inversé et les flux de contaminants sont maintenant dirigés depuis le lit vers le cours d'eau. Etudiant le rôle des sédiments du lit de la rivière comme source de contaminants, nous avons émis l'hypothèse que le processus de transport est l'advection d'eau à travers le lit. Nous avons calculé les flux de masse basés sur le taux d'écoulement d'eaux souterraines et des concentrations aqueuses des isomères de monochlorobenzene (MCB) et dichlorobenzene (DCB) dans les sédiments du lit. De plus, pour obtenir des estimations robustes des concentrations moyennes des contaminants, des capteurs passifs (intégrateurs temporels) ont été installés dans le lit de la rivière dans des zones de fort et faible apports d'eau souterraine.

Les sédiments du lit des rivières sont caractérisés par une masse résiduelle considérable de MCB qui reste piégée, bien que la désorption a continué durant plus de 10 ans. Une expérience en colonne menée à des flux réels, configurés pour être dans la gamme des grandeurs observées des apports d'eau souterraine, a montré que la désorption en masse est négligeable. Des prédictions à long terme de la réduction de la pollution ont montré que pour enlever 50 % de la masse résiduelle de MCB il faudra des décennies voire même des siècles.

Kurzfassung

Flüsse und Grundwasser stehen hydraulisch fast immer in Kontakt. In gemäßigten Klimaten bildet der räumlich verteilte Grundwasserzustrom letztlich den Basisabfluss der Flüsse. In Trockenperioden trägt der Grundwasserzustrom entscheidend zum Abfluss bei und erhält somit aquatische Ökosysteme und Feuchtgebiete entlang der Flüsse. Durch Wasserflüsse zwischen Grund- und Oberflächenwasser wird auch der Transport von Schadstoffen zwischen diesen beiden Kompartimenten gesteuert.

In dieser Arbeit haben wir die räumlichen Muster des Grundwasserzustroms in Flüsse und den Transport organischer Schadstoffe von Grundwasser in das Oberflächenwasser untersucht. Zunächst entwickelten wir eine Methode mit der die räumlichen Muster des Grundwasserzustroms auf der Skala von Metern oder wenn notwendig auch darunter für Flussabschnitte von mehreren hundert Metern Länge aufgelöst werden können. Flussbetttemperaturen können sehr einfach kartiert werden. Man nutzt den natürlichen Temperaturgradienten zwischen Grundwasser (mit fast konstanter Temperatur) und Flusswasser dessen Temperatur jahreszeitlich schwankt, um den Grundwasserzustrom zu bestimmen. Flussbetttemperaturen können einfach und kostengünstig an hunderten Punkten entlang eines Flussabschnittes gemessen werden. Mittels der Wärme-Diffusions-Advektionsgleichung können aus den kartierten Flussbetttemperaturen die Darcy-Geschwindigkeiten des Grundwasserzustroms berechnet werden. Die Grundannahme dieser Methode ist, dass die Flussbetttemperaturen ausschließlich eine Funktion der Fließgeschwindigkeiten sind und nicht durch tägliche Temperaturschwankungen im Fluss, die sich in das Flussbett fortsetzen, beeinflusst werden. Diese Grundannahme wurde am Pine River, Ontario, Kanada überprüft. Die Resultate zeigen, dass wenn Grundwasser zuströmt die täglichen Temperaturschwankungen bei 0,2 m unter der Flussbettoberfläche vernachlässigbar werden. Wenn Flusswasser infiltriert, dringen die oberflächlichen Temperaturschwankungen tiefer in das Sediment ein. Letztendlich konnten wir nachweisen, dass wenn Grundwasser zuströmt, die Flussbetttemperaturen praktisch unbeeinflusst von täglichen Temperaturschwankungen sind.

Um die Robustheit der Methode der Temperaturkartierung noch zu verbessern, wurde eine neu-entwickelte Temperatursonde eingesetzt. Mit dieser wurden die Temperaturen simultan in fünf verschiedenen Tiefen im Flussbett gemessen. Im Gegensatz zur ursprünglichen Methodik, wo die Temperaturen in der gleichen, einheitlichen Tiefe gemessen wurden, wird hier ein Temperaturprofil gemessen. In der verwendeten Konfiguration befindet sich der tiefste Messpunkt in 0,5 m Tiefe. Der Vorteil der Messung eines Temperaturprofils liegt darin, dass die berechnete Fließgeschwindigkeit weniger sensitiv gegenüber zufälligen Fehlern ist und auch weniger sensitiv gegenüber täglichen Temperaturschwankungen. Die Methodik wurde an zwei kleinen Flüssen angewandt: zum einen im Schachtgraben, der in der industriellen Region Bitterfeld-Wolfen liegt und zum anderen am Schaugraben, der in einem

landwirtschaftlichen Einzugsgebiet im Norden Sachsen-Anhalts liegt. Die Länge der untersuchten Flussabschnitte beträgt 220 m (Schachtgraben) und 750 m (Schaugraben). An allen untersuchten Flussabschnitten war der Grundwasserzustrom ungleich verteilt. Am Schachtgraben werden ca. 50% des gesamten Zustroms auf etwa 20% der Fläche realisiert. Am Schaugraben war die Ungleichverteilung etwas geringer.

Der Schachtgraben befindet sich innerhalb eines der ältesten Zentren der chemischen Industrie in Deutschland. Das Flusswasser ist durch eine Reihe von organischen Schadstoffen verunreinigt, vorwiegend aber chlorierte Benzene. Das Grundwasser im quartären Aquifer ist im Bereich des Schachtgrabens durch eine großflächige aber gering konzentrierte Kontamination mit im wesentlichen den Substanzen gekennzeichnet, die auch im Oberflächenwasser nachgewiesen wurden. Da das Grundwasser in den Schachtgraben zuströmt, besteht ein Schadstofffluss vom Grundwasser zum Oberflächenwasser.

Messungen der Schadstoffkonzentrationen im Flussbett ergaben, dass hier die Konzentrationen um etwa eine Größenordnung höher sind als im Grundwasser. Die Sedimente des Flussbetts stellen demnach eine weitere Schadstoffquelle dar und tragen signifikant zur Gesamtschadstofffracht, die in das Flusswasser gelangt, bei. Die Kontamination des Flussbetts ist wahrscheinlich auf die Einleitung ungeklärter Abwässer aus der chemischen Industrie bis zu Anfang der neunziger Jahre des 20. Jahrhunderts zurückzuführen. Wir gehen davon aus, dass sich seither die Konzentrationsgradienten umgekehrt haben und die Schadstoffflüsse heute hauptsächlich vom Flussbettsediment ins Oberflächenwasser gerichtet sind. Die Rolle des Flussbetts als Schadstoffquelle wurde eingehender untersucht. Wir haben angenommen, dass Freisetzung vom Sediment durch die Menge des Grundwasserzustroms kontrolliert wird. Die spezifischen Frachten aus dem Grundwasser und den Flussbettsedimenten wurden für Monochlorbenzen (MCB) und die Isomere des Dichlorbenzens berechnet. Zusätzlich, um zeitlich integrierte Mittelwerte der aquatischen Konzentration im Flussbett und im Grundwasser zu erhalten, wurden Passivsammler eingesetzt.

Die Flussbettsedimente sind durch eine beträchtliche residuale Kontamination mit MCB charakterisiert, dass auch nach mehr als zehn Jahre anhaltenden Desorptionsprozessen im Sediment verbleibt. Säulenversuche, die die realistischen Fließbedingungen im Flussbett nachbilden, zeigten, dass der Schadstoffaustrag aus den Sedimenten sehr ineffizient ist. Langzeitvorhersagen deuten darauf hin, dass die Zeitskala um 50% der Schadstoffmasse aus dem Sediment zu entfernen, im Bereich von Jahrzehnten, möglicherweise aber auch im Bereich von Jahrhunderten liegen könnte.

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Chapter 1

Introduction

1.1. Background

On earth, all life depends on water. Water acts as solvent and is an essential ingredient of many metabolic processes. Photosynthesis for instance, uses light, carbon dioxide and water to produce glucose and oxygen. To our current knowledge, the first life on our planet developed in liquid water.

Within the hydrologic cycle water molecules may be evaporated from the oceans, soils and plants, move as vapour with the atmospheric circulation, precipitate as rain or snow and infiltrate into the soils. The soil water moves then vertically to the water table and will form the groundwater that flows in the porous or fractured subsurface. Water flow in porous media is driven by hydraulic gradients and controlled by the hydraulic properties of the subsurface. The fundamental processes of water flow in porous media are well understood. However, predicting water fluxes at the field scale is often difficult because geological materials are practically never homogeneous or characterized by regular patterns.

Groundwater and surface waters from small streams, rivers, lakes to oceans are inherently hydraulically connected. Groundwater flows on local to regional scale flow systems from recharge areas to discharge areas. Except in semi arid and arid regions, surface waters are representations of the local water table. When the elevation of the surrounding, regional water table relative to the surface water is higher, groundwater discharges into the surface waters. The interactions between streams and groundwater have been recognized to be important for the functioning and health of streams and the maintenance of aquatic ecosystems. The interface between groundwater is typically characterized by an increased microbial diversity and activity compared to the stream or the groundwater. Associated with changes in geological materials, steep hydraulic gradients, high organic carbon content sediments and contrasts in redox conditions, the fate and transport of solutes, nutrients and contaminants can be strongly influenced or altered when water is moving through the transition zone of streams and groundwater. Needless to say, that also contaminants may migrate into surface waters with groundwater discharge and may pose a considerable risk to hyporheic and surface water habitats. Conversely, contaminants may originate from the stream water and pollute hyporheic habitats and the adjacent groundwater.

We progressively realize that an effective management and the sustainable use of water resources as well the protection of aquatic environments demands an integrated view on groundwater and surface water. The importance of the interconnections between surface water and groundwater is also increasingly reflected in water policies. The European Union Water Framework Directive (European Commission 2000) for instance requires an integrated

management of surface water and groundwater: “...*achieving good water status should be pursued for each river basin, so that measures in respect of surface water and groundwaters (...) are coordinated.*” However, knowledge on many hydrodynamic and biogeochemical processes at the groundwater-surface water-interface is still limited, in particular with regard to the spatial heterogeneity that is inherent in all geologic materials.

In this thesis we provide a tool to estimate water fluxes with high spatial resolution at the interface between ground and surface water. We further show the implications that heterogeneous groundwater discharge has on contaminant fluxes between groundwater and surface water and which role contaminated streambed sediments play for the mass fluxes and the timescales to clean up the site.

1.2. Heat transport and water flow

At first sight, subsurface temperatures and water fluxes are not very closely related. But when we look at the Darcy equation we recognize, it has the same form like Fourier's law of heat conduction. Theis (1935) presented an analytical solution to transient, radial groundwater flow to a pumping well. He adapted his solution to groundwater from the analogues problem in heat transport. Besides these mathematical analogies, early in the twentieth century it was recognized that natural temperature gradients in the subsurface can be utilized to detect groundwater fluxes (Slichter 1905).

The underlying idea of using temperature measurements to trace the water flow is based on the fact that heat transport in the subsurface is driven by a combination of advection and conduction. Heat conduction occurs along temperature gradients and is a diffusive process. In porous media heat is conducted through both the fluid and the liquid phase. When water is flowing in porous media heat is advectively transported. Ideally, the advective component of heat transport can be inferred from temperature measurements, which can be inverted to derive the flow velocity of the water.

The shallow subsurface is influenced by the seasonal temperature variations in the atmosphere. In winter, colder air temperatures result in a cooling of the shallow subsurface. Conversely, warmer summer temperatures yield to subsurface heating. With increasing depth, these annual oscillations are damped until the temperatures remain virtually constant. The penetration depths of the temperature oscillations is a function of their phase length. Long-term surface temperature oscillations will leave fingerprints in greater depths than for example diurnal oscillations which are usually not present below a depth of half a meter. On the other end of the time-scale, the surface temperature history of past decades to millennia may be reconstructed from temperature-depth profiles from deep boreholes (e.g. Majorowicz et al. 2006). A thermal oscillation of 1000 years for instance can be detected to a depth of 400m (Pollack and Huang 2000).

The movement of water in the subsurface may significantly alter the temperature fields that we would expect if heat conduction was the only transport process. In reverse, we can infer the flow velocities of water from observed temperatures. By solving the heat transport

equation as an inverse problem for groundwater flow, field measurements of temperatures can be used to estimate groundwater flow velocities. One of pioneering applications in the middle of the last century was the work of Suzuki (1960). He estimated percolation rates of water below paddy fields using temperature minima and maxima in two different known depths. The general three-dimensional, transient equation of simultaneous water flow and heat transport was presented by Stallman (1963). In 1965, Bredehoeft and Papadopolus presented an one-dimensional analytical solution with steady state boundary conditions to the general heat diffusion advection equation. Stallman (1965) extended the work to more realistic boundary conditions accounting for an sinusoidal temperature variation at the top of the domain. A very simple solution has been published by Turcotte and Schubert (1982) where the Darcy velocity can be explicitly calculated from the observed temperatures without the need for inversion.

Lapham (1989) extended the existing analytical solutions by applying a numerical model to observed and theoretical time-series of temperature-depths profiles. Today, a variety of numerical codes exist to simulate the coupled water flow and heat transport in porous media such as VS2DH (Healy and Ronan 1996) and SUTRA (Voss and Provost 2002) and the 3D Model HEATFLOW (Molson and Frind 2005).

Temperature differences between groundwater and surface water may be high in summer or winter when surface waters are relatively warm or cold, respectively. These potentially high gradients between the annually oscillating surface water temperatures and the relatively constant groundwater temperature, enable temperature measurements to be particularly an appropriate tool to determine water fluxes at the groundwater surface water interface.

In this thesis, we apply temperature measurements to study the spatial patterns and magnitudes of groundwater discharge to streams.

1.3. The stream-groundwater-interface

We are permanently surrounded by phenomena that are caused by interfaces. A rainbow, for example, forms when white sunlight is refracted into its spectral colours as it leaves water droplets across the air-water-interface.

With increasing interest researchers study the phenomena at the interface between streams and groundwater. The stream-groundwater-interface is a spatially and temporarily dynamic zone where groundwater and stream water mix. The mixing occurs on a variety of spatial scales and heterogeneous flowpaths with different flow directions. In the thesis, we focus on streambeds as interfacial zones but the dimensions can be larger and may include stream meander bends and riparian zones parallel to the stream channel. At the reach scale (hundreds of m to km), the interaction of stream and groundwater can be basically conceptualized in two ways: in gaining streams, which is the common case in temperate climates, where the water flow in the streambed is from the groundwater towards the stream and in losing streams, where the stream water infiltrates into the streambed. The direction of the water exchange depends on the hydraulic gradient between the stream surface and the connected aquifer. In

gaining reaches, the groundwater table is higher than the elevation of the stream surface and vice versa in losing reaches. Besides a net exchange of water between streams and aquifers, streamwater is characteristically downwelling into the streambed and re-emerges after a certain flowpath. When streambed sediments are permeable enough, pressure gradients between the upstream and downstream end of features in streambed morphology drive the water flow through the sediments. Usually, these exchange fluxes occur simultaneously across spatial scales, depending on the size of the specific bedforms. Riffle-pool sequences occur on the scale of a few metres (Storey et al. 2003, Gooseff et al. 2006). At smaller bedforms like stream ripples or obstructions like larger boulders or wood, the exchange flows occur on the sub meter to centimeter scale. (Thibodeaux and Boyle 1987, Elliot and Brooks 1997a, 1997b, Mutz et al. 2007). Superimposed on the bedform driven exchange flows, groundwater discharge that is driven by the reach-scale, ambient hydraulic gradients can significantly influence the shape of flowpaths in the streambed. (Storey et al. 2003, Cardenas and Wilson 2007). The flow patterns resulting from bedforms and reach-scale groundwater discharge are complex. In addition, spatial heterogeneities of streambed sediments and the underlying aquifer cause highly variable patterns of exchange fluxes and groundwater discharge.

The exchange of water between the stream and the streambed forms an ecotone – the hyporheic zone – that combines features of both groundwater and surface water environments. The flowing water supplies oxygen, organic matter and nutrients to the hyporheic zone and biofilm-forming microorganisms preferentially grow on streambed sediment surfaces. Hence, the hyporheic metabolism mediates most of the fluxes and transformations of heat, organic matter, nutrients and anthropogenic substances in stream ecosystems (Brunke and Gonser 1997, Boulton 1998). The functioning of the stream groundwater interface as buffer, filter and reactive zone is therefore critically important for the water quality, the ecological health and the resilience of streams and riparian ecosystems.

Groundwater discharge to streams accumulates to the baseflow component of streamflow. Groundwater sustains streamflow in dry periods and therefore maintains aquatic ecosystems and wetlands. As groundwater discharges to streams, contaminant plumes from industrial sites (Conant Jr. et al. 2004, Chapman et al. 2007) or larger-scale, diffuse contamination from urban and industrial areas (Ellis and Rivett 2007, Kalbus et al. 2007) may be transported to streams. On the passage through the streambed, the contaminant plumes may be essentially modified in shape, concentration patterns and composition. The stream groundwater interface may potentially play a significant role in natural attenuation of discharging groundwater contaminants because of an increased biodegradation compared to the aquifer (Conant Jr. et al. 2004). The streambed may act as primary sink for contaminants either originating from the stream water the groundwater. However, if the primary source has been cleaned up, the streambed itself may become a long-term secondary source of contamination for downstream areas.

The phenomena associated with interaction of stream and groundwater occur on a variety of spatial scales – from the bedform, the reach scale to the catchment scale and have significant implications for sustaining the water quality and aquatic ecosystems. Our understanding of hydrodynamic and biogeochemical processes at the stream groundwater interface is still limited. Although the process-understanding is improving rapidly, readily available monitoring tools and models for stream groundwater systems for field-scale applications are still scarce.

1.4. Motivation and objectives

Characterizing the flow conditions in the streambed can be challenging because of the complex flow patterns driven by bedforms and groundwater discharge. But it is an essential task since most biogeochemical processes at the stream groundwater interface are governed by the advection of water. Spatial patterns of flow and groundwater discharge in streambeds have been shown to vary on the scale of metres to centimetres (e.g. Brunke and Gonser 1997, Storey et al. 2003, Conant Jr. 2004). When we started to work on contaminant transport at the stream-groundwater-interface, we recognized that the conventional instrumentation such as seepage meters and mini-piezometers is not capable to resolve groundwater discharge pattern adequately. Hence, before we could approach to characterize patterns of groundwater discharge, the objective is to develop a tool that can quickly and accurately capture the spatial variability of groundwater discharge on a sub-reach to reach scale.

Our methodology is based on the methodology of Conant Jr. (2004). He used heat as a natural tracer and mapped streambed temperatures in a uniform depth. By relating the observed streambed temperatures empirically to water fluxes obtained from hydraulic testing of streambed mini-piezometers, he successfully determined discharge patterns. We extend his method and developed an approach where water fluxes are directly inferred from mapped streambed temperatures without the need for the installation of streambed mini-piezometers. One key objective of this thesis is to show in field applications that the new method provides reliable estimates of the magnitude of water fluxes and the spatial heterogeneities of groundwater discharge to streams.

We further attempted to estimate the mass fluxes of monochlorobenzene and dichlorobenzene from the aquifer to a stream and also assessed the contribution of a residual contamination of the streambed to the total mass fluxes. One objective of the study was to estimate the time-scales required to remove the contaminants from the streambed. This fact has important implications on the long-term mass fluxes of contaminants towards a stream, since a slow removal yields to a significant tailing of mass fluxes.

1.5. Outline

Within the thesis, the succeeding chapters are written as individual manuscripts for scientific journal publication. Hence, each chapter comprises of a separate introduction, methods, results and discussion section.

Chapter 2 presents the application of a steady-state analytical solution of the heat-advection-diffusion equation to derive magnitudes of groundwater discharge to surface waters. The underlying temperature data sets comprising mapped streambed temperatures observed in a single, uniform depth. The Chapter is taken from an article *Evaluation and field-scale application of an analytical method to quantify groundwater discharge using mapped streambed temperatures* by Schmidt et al. (2007) published in Journal of Hydrology. We explain how the methodology can be applied and illustrate it with two case studies in Ontario, Canada. We further compare the temperature based fluxes with independent flux data from seepage meter measurements and hydraulic testing of streambed piezometers. We evaluate the benefits and limitations of the temperature method. We discuss and demonstrate that a simple steady-state approach is sufficient to obtain robust estimates of groundwater discharge.

In Chapter 3 the ideas of Chapter 2 are enhanced by measuring the streambed temperatures simultaneously in five depths. We estimated the water fluxes based on the entire temperature profile. The temperature profiles have been measured along a stream reach of 220 m in length in the industrial area of Bitterfeld-Wolfen, Germany. Chapter 3 is taken from an article *Characterization of spatial heterogeneity of groundwater-stream water interactions using multiple depth streambed temperature measurements at the reach scale* by Schmidt et al. (2006) published in Hydrology and Earth System Sciences.

In Chapter 4 the mass fluxes of organic contaminants from polluted streambed sediments associated with discharging groundwater are estimated. Magnitudes and spatial distribution of groundwater discharge were taken from the previous chapter. Chapter 4 is a translated, supplemented extract from a manuscript entitled *Contaminant mass flow rates between groundwater, streambed sediments and surface water at the regionally contaminated site Bitterfeld (Schadstoffmassenströme zwischen Grundwasser, Flussbettsedimenten und Oberflächenwasser am regional kontaminierten Standort Bitterfeld)* by Schmidt et al. (2008) published in Grundwasser.

In Chapter 5 we attempt to estimate the time-scales required for the removal of monochlorobenzene from streambed sediments. Data from column experiments were modelled with a multiple rate mass transfer model to predict the mass release from the columns and hence from the streambed sediments. Our results also indicated the limited applicability of standard single-rate first-order mass transfer models. Chapter 5 is in preparation to be submitted to the Journal of Contaminant Hydrology.

In Chapter 6 we summarize and synthesize our results and present an outlook on future streambed research and the perspectives of temperature data to trace water flow.

Chapter 2

Evaluation and field-scale application of an analytical method to quantify groundwater discharge using mapped streambed temperatures

This chapter has been published as: Schmidt, C., Conant Jr., B., Bayer-Raich, M., and Schirmer, M., 2007. Evaluation and field-scale application of an analytical method to quantify groundwater discharge using mapped streambed temperatures. *Journal of Hydrology* 347 (3-4), 292-307.

2.1. Abstract

A method for calculating groundwater discharge through a streambed on a sub-reach to a reach scale has been developed using data from plan-view mapping of streambed temperatures at a uniform depth along a reach of a river or stream. An analytical solution of the one-dimensional steady-state heat-diffusion-advection equation was used to determine fluxes from observed temperature data. The method was applied to point measurements of streambed temperatures used to map a 60 m long reach of a river by Conant Jr. (2004) and relies on the underlying assumption that streambed temperatures are in a quasi-steady-state during the period of mapping. The analytical method was able to match the values and pattern of flux previously obtained using an empirical relationship that related streambed temperatures to fluxes obtained from piezometers and using Darcy's law. A second independent test of the analytical method using temperature mapping and seepage meter fluxes along a first-order stream confirmed the validity of the approach. The USGS numerical heat transport model VS2DH was also used to evaluate the thermal response of the streambed sediments to transient variations in surface water temperatures and showed that quasi-steady-state conditions occurred for most, but not all, conditions. During mapping events in the winter, quasi-steady-state conditions were typically observed for both high and low groundwater discharge conditions, but during summer mapping events quasi-steady-state conditions were typically not achieved at low flux areas or where measurements were made at shallow depths. Major advantages of using this analytical method include: it can be implemented using a spreadsheet; it does not require the installation or testing of piezometers or seepage meters (although they would help to confirm the results); and it needs only a minimal amount of input data related to water temperatures and the thermal properties of water and the sediments. The field results showed the analytical solution tends to underestimate high fluxes. However, a sensitivity analysis of possible model inputs shows the solution is relatively robust and not particularly sensitive to small uncertainties in input data and can produce reasonable flux estimates without the need for calibration.

2.2. Introduction

The exchange of water between surface water and groundwater has become an important subject in hydrogeological and river ecological research in the last two decades (Brunke and Gonser 1997, Winter et al. 1998, USEPA 2000). The interface between groundwater and surface water is often characterized by changes in geological materials, steep hydraulic gradients, high organic carbon content sediments, contrasts in redox conditions, and increased biological and microbial diversity and activity. These factors can strongly influence or alter the transport and fate of solutes, nutrients, and contaminants in water moving through a streambed or riverbed (Hedin et al. 1998, Conant Jr. et al. 2004, Laursen and Seitzinger 2005). To understand these transport and biogeochemical processes at the groundwater-surface water interface, it is necessary to accurately characterize and assess the flow conditions in the streambed (Conant Jr. 2001). Accurately characterizing this exchange is a challenge, especially since spatial patterns of flow and discharge in a streambed have been shown to vary on a scale of metres to centimetres (Brunke and Gonser 1997, Woessner 2000, Brunke et al. 2003, Storey et al. 2003, Conant Jr. 2004, Kalbus et al. 2007). Although discharge patterns in streambeds can be characterised using conventional instrumentation such as seepage meters and mini-piezometers (Lee and Cherry 1978) or other standard methods (Kalbus et al. 2006), there is a need for methods that can quickly, accurately, and unobtrusively characterize spatial variability in discharge in a streambed on a sub-reach to a reach scale. Higher resolution measurements are needed to: 1) detect small-area high-flux groundwater discharge zones that can dominate overall discharge of water and solutes along a reach (Conant Jr. 2001, Schmidt et al. 2006); 2) characterize the pattern and magnitude of discharge in order to infer the geochemical conditions or biodegradation in the streambed (Conant Jr. 2001, Kalbus et al. 2007); 3) better characterize the distribution of groundwater dependent benthic and hyporheic aquatic life (Malcolm et al. 2003, Brown et al. 2007). Moreover, recent changes in river management regulations increase the need for a better understanding of groundwater-surface water interactions. For example, the European Union Water Framework Directive requires an integrated management of groundwater and surface water bodies (European Commission, 2000) to reach a “good status” for both groundwater and surface water bodies.

Conant Jr. (2004) showed that by using heat as a natural tracer and mapping streambed temperatures in plan-view at a uniform depth, meter-scale spatial variations in flow in a streambed could be resolved along river reaches. The method can be used to quantify groundwater discharge in a way that is cost-effective, relatively quick, accurate, and robust. The concept of using subsurface temperatures to estimate the movement of water is well established and is summarized by Stonestrom and Constantz (2003) and Anderson (2005). Temperature based methods generally rely on temperature contrasts and the fact that the horizontal and vertical temperature distribution in a streambed is a result of heat transport by the flowing water (advective heat flow) and by heat conduction through the solid and fluid phase of the sediments (conductive heat flow). While subsurface temperatures in groundwater

discharge zones at depths greater than five to ten metres tend to remain relatively constant (i.e., vary less than 1.5°C) during the year (Lapham 1989), surface water temperatures undergo larger changes between summer and winter. For example, in northern climates in summer when the surface water is warmer than the groundwater, streambed sediments in zones of high groundwater discharge will be colder than in the low discharge zones (Figure 2.1). The Conant Jr. (2004) method of determining discharge flux patterns in a streambed was accomplished by mapping streambed temperatures and developing an empirical relationship that related measured temperatures to fluxes obtained using Darcy's law and hydraulic data from mini-piezometers.

The success of the Conant Jr. (2004) method relied on the streambed temperatures being measured at a sufficient depth (0.2 m) that was below the zone of diurnal temperature oscillations (Figure 2.1) and remained essentially constant at all locations during the time required to map the reach of stream. The observation that streambed temperatures at depths of 0.2 m or more are insignificantly altered by diurnal oscillations of surface water temperatures is consistent with the results of others (Keery et al. 2007). The mapping method provides observations at a uniform depth at many locations to determine fluxes but no time series of measurements at those locations, which is unlike previous applications of the heat-diffusion-advection equation that typically require that temperature be measured at multiple depths and (or) over time at a location (Carslaw and Jaeger 1959, Bredehoeft and Papadopolus 1965, Stallman 1965, Suzuki 1960, Turcotte and Schubert 1982, Silliman et al. 1995, Taniguchi et al. 1999, Hatch et al. 2006, Schmidt et al. 2006). Because of the significant effort and cost of instrumenting multiple depths and collecting time series of temperatures, the approaches that rely on vertical temperature profiles tend to be limited to a few sampling locations and are not suited for mapping meter-scale spatial variations in flux over wide areas or long reaches of rivers. Recent advances using fibre optic temperature sensing equipment (Selker et al. 2006a and 2006b, Westhoff et al. 2007) allow characterization along lengthy cables over time with a meter-scale spatial resolution, but typically measure temperatures at the surface water/sediment interface and so can be more directly affected by surface water temperatures which can reduce the sensitivity to detect lower magnitudes of groundwater discharge.

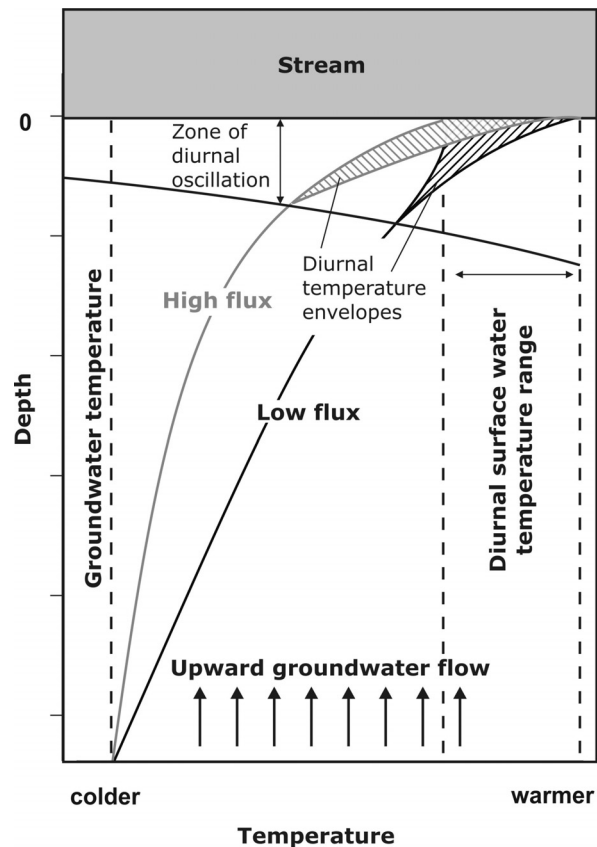


Figure 2.1. Conceptual diagram of the quasi-steady-state conditions for streambed temperatures versus depth for high and low flux and diurnal temperature changes. The diagram represents a summer case where the surface water temperatures are higher than the groundwater temperatures. The penetration depth of diurnal oscillations in the surface water increases as flux decreases. The temperature profiles will also change as long-term temperatures change (adapted Conant Jr. 2004).

It was hypothesized that if the success of the Conant Jr. (2004) method was because quasi-steady-state conditions occurred in the streambed then it would be possible to directly and accurately calculate discharge using a steady-state thermal-flux model and thereby negate the need and expense of installing and testing piezometers to obtain fluxes. This investigation evaluates the appropriateness of the steady-state assumption and demonstrates the effectiveness of using a one-dimensional steady-state analytical solution of the heat-diffusion-advection equation for calculating flux from plan-view streambed temperature measurements obtained from a river and also from a small first order stream.

2.3. Methodology

The general approach for this investigation was to select an appropriate analytical solution for use that would be easy to apply to streambed temperature mapping data. The method was then applied to streambed temperature mapping data obtained by Conant Jr. (2004), and the calculated discharge fluxes were then compared to the fluxes previously obtained using an empirical approach. The applicability of the model and the validity of the quasi-steady-state assumption were examined using the previous study's data and by performing sensitivity analyses using both the steady-state analytical model and a numerical transient heat flow

model. To test the transferability of the analytical solution approach, plan-view streambed temperature mapping data and seepage meter fluxes were collected from a second site and then simulated using the new analytical approach.

2.3.1. Model Selection

2.3.1.1. Steady-State Model

The Turcotte and Schubert (1982) analytical solution to the one-dimensional steady-state heat-diffusion-advection equation was used for this study because it had appropriate boundary conditions for the data sets being simulated and its overall simplicity. Assuming that water flow in the streambed is vertical, the governing equation for conductive and advective heat transport in the saturated porous media is:

$$\frac{K_{fs}}{\rho c} \nabla^2 T(z) - \frac{\rho c_f}{\rho c} \nabla \cdot (T(z) q_z) = \frac{\partial T(z)}{\partial t} \quad [2.1]$$

where:

$T(z)$ = is the streambed temperature at depth z (°C)

$\rho c = n \rho c_f + (1 - n) \rho_s c_s$ = volumetric heat capacity of the solid-fluid system ($\text{J m}^{-3} \text{K}^{-1}$)

$\rho_f c_f$ = volumetric heat capacity of the fluid ($\text{J m}^{-3} \text{K}^{-1}$)

$\rho_s c_s$ = volumetric heat capacity of the solids ($\text{J m}^{-3} \text{K}^{-1}$)

n = porosity of the porous media (dimensionless)

K_{fs} = thermal conductivity of the solid - fluid system ($\text{J s}^{-1} \text{m}^{-1} \text{K}^{-1}$)

q_z = specific discharge or Darcy flux (ms^{-1}) in the vertical (z) direction

Assuming vertical upward groundwater flow in the sediments and giving the boundary conditions $T = T_0$ (°C) for $z = 0$, and fixed temperature T_L (°C) at the aquifer bottom as $z \rightarrow \infty$ with $\frac{\partial T}{\partial z} = 0$ the analytical solution of Equation [2.1] is given as (Turcotte and Schubert 1982):

$$\frac{T(z) - T_L}{T_0 - T_L} = \exp\left(-q_z \frac{\rho c_f}{K_{fs}} z\right) \quad [2.2]$$

Figure 2.2 shows the geometry and boundary conditions of this analytical solution. Equation [2.2] can be rearranged to obtain a simple explicit expression for the Darcy flux q_z as:

$$q_z = -\frac{K_{fs}}{\rho c_f z} \ln \frac{T(z) - T_L}{T_0 - T_L} \quad [2.3]$$

By direct application of Equation [2.3], it is possible to estimate Darcy flow q_z through a single observation of the temperature $T(z)$ at a single depth. Equation [2.3] is based on two main assumptions (1) flow is quasi-steady-state at depth z and (2) Darcy's flux is vertical $q = (q_x, q_y, q_z)$ with $q_x = q_y = 0$ and the magnitude of flux $q_z(x, y)$ depends only on the (x, y) location of the observed temperature $T(x, y, z)$. Such models can be referred to as

“multi-one-dimensional”. Equation [2.3] can be easily incorporated into a spreadsheet programme to convert data from plan-view mapping of streambed temperatures into groundwater discharge fluxes.

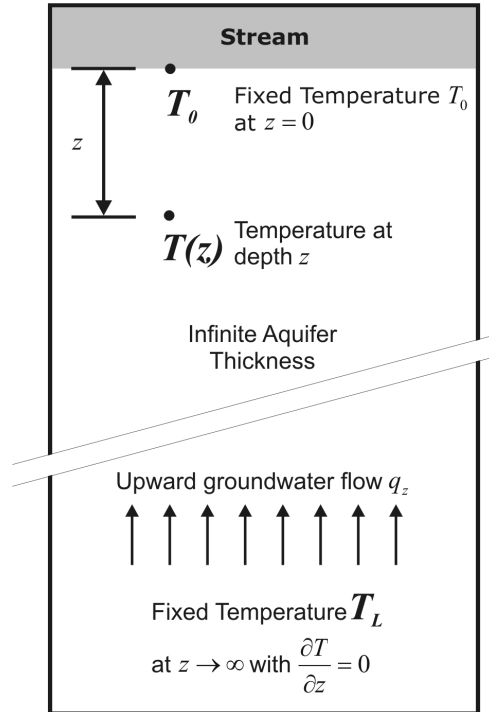


Figure 2.2. Schematic diagram of boundary conditions and inputs for the analytical solution of Turcotte and Schubert (1982).

Since the volumetric heat capacity $\rho_f c_f$ of water is $4.19 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$, the only unknown variables in Equation [2.3] are T_0 , T_L , and K_{fs} . The T_0 used to simulate field data in this study were obtained by taking the average value of observed surface water temperatures prior to and/or during streambed temperature mapping. During several day-long mapping events (especially during the summer) surface water temperatures tend to oscillate around an average value and so it is necessary and possible to transform this varying condition into a single quasi-steady-state value. The appropriate time period for averaging the surface water temperatures was examined as part of this study. Values of T_L were obtained by measuring the groundwater temperature in a relatively deep well in (or adjacent to) the stream or river and averaging them over a similar time period as T_0 . To obtain T_L , the measurement location must be sufficiently deep (e.g., 5 to 10 m) to provide constant temperature values with time.

Values of K_{fs} for saturated sediments generally fall into a relatively narrow range (0.8 to $2.5 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$, see Lapham 1989, Hopmanns et al. 2002, Ren et al. 2000, Stonestrom and Constantz 2003). The thermal conductivity of saturated sediment is essentially controlled by the proportions of the volumetric fluid and solid contents [i.e., the porosity (n)]. If thermal conductivities can not be measured, they can be derived from literature values or estimated using the volumetric proportions of the constituents of the material and equation found in

Table 2.1. In this study the thermal conductivity was obtained by making direct measurements on sediment samples.

Table 2.1. Estimation method for determining saturated thermal conductivities

Equation	Name of Method
$K_{fs} = K_s^{(1-n)} + K_f^n$	Geometric mean ^A
Required Parameters	Value
[<i>n</i>] Porosity [-]	Varies with material
[<i>K_f</i>] Thermal conductivity of fluid (Water) [J s ⁻¹ m ⁻¹ K ⁻¹]	0.6
[<i>K_s</i>] Thermal conductivity of the solids (Quartz) [J s ⁻¹ m ⁻¹ K ⁻¹]	7.7 ^B - 8.4 ^C

^A = From Clauser and Huenges (1995)

^B = From Horai and Simmons (1969)

^C = From Bristow, Kluitenberg and Horton (1994)

The Turcotte and Schubert (1982) analytical solution is only valid for ascending water flow and it was selected for use because this study was primarily interested in groundwater discharge. Other one-dimensional solutions were considered for this study (Carslaw and Jaeger 1959, Stallman 1965, Bredehoeft and Papadopolus 1965) and, although these solutions can be used to calculate upward and downward flow, they were not selected for use. For downward flow conditions, streambed temperatures typically will not be at steady state (because transient surface temperatures will propagate deeper into the streambed) and streambed temperatures will be virtually equal to surface water temperatures and will not be a function of the magnitude of the water flux (i.e., the temperature versus flux relationship will be non-unique). Solutions that include downward flow (e.g., Bredehoeft and Papadopolus 1965, Stallman 1965) would be prone to errors if it only used single depth temperature mapping data. The widely used Stallman (1965) solution was not selected for this study because its data input requirements were incompatible with the streambed mapping data. The Stallman (1965) method requires observations of streambed temperatures at each location over time and uses a time variant (sinusoidal) upper boundary condition. The Turcotte and Schubert (1982) solution appeared to be the most appropriate method for use with the streambed temperature mapping data because it simulated only upward flow, has a constant temperature upper boundary condition, and has a semi-infinite lower boundary condition that allows a time invariant groundwater temperature at depth to be used as the lower boundary condition.

2.3.1.2. *Transient Model*

The United States Geologic Survey (USGS) variably saturated two-dimensional heat flow programme (VS2DH) (Healy and Ronan 1996) was used to evaluate the transient effect of daily temperature oscillations and to examine the applicability of the steady-state analytical solution. This finite difference model is based on a variably saturated groundwater flow and transport programme (VS2DT) (Healy 1990) that was modified to simulate advective and conductive heat transport (Healy and Ronan 1996). Heat transport and groundwater flow can be simulated in one or two dimensions via the advection-dispersion equation using the graphical software package and interface VS2DHI (Hsieh et al. 2000). The numerical model code accounts for the dependency of the hydraulic conductivity on temperature because of changes in fluid viscosity but assumes a constant-density fluid.

VS2DH simulations were performed to determine to what depth diurnal changes in surface water temperatures would penetrate into the streambed and to investigate the validity of the quasi-steady-state assumption for different magnitudes of groundwater discharge flux. The first set of VS2DH simulations were compared to results from the analytical solution of Turcotte and Schubert (1982) for a test example with a realistic parameter set, similar to Conant Jr. (2004) (see parameters in Figure 2.3a and Figure 2.3b). A fixed temperature was assigned to the bottom of the domain (10 °C) and sinusoidal temperature oscillations assigned at the top of the domain that had an average temperature of 18.5 °C, a semi-amplitude of 2.5 °C and a period-length of 24 hours. Simulations were performed to show the transient evolution of the streambed temperature for time increments of two hours during a single day. A second set of VS2DH simulations were undertaken using the values in Table 2.2 but using actual observed field data for the upper and lower temperature boundaries. Streambed temperatures were simulated for depths of 0.1, 0.2, and 0.3 m in the streambed for low discharge ($\sim 0.41 \text{ L m}^{-2} \text{ d}^{-1}$) and high discharge ($\sim 446 \text{ L m}^{-2} \text{ d}^{-1}$) conditions during the 20 day period prior to and including the summer and winter streambed temperature mapping events of Conant Jr. (2004).

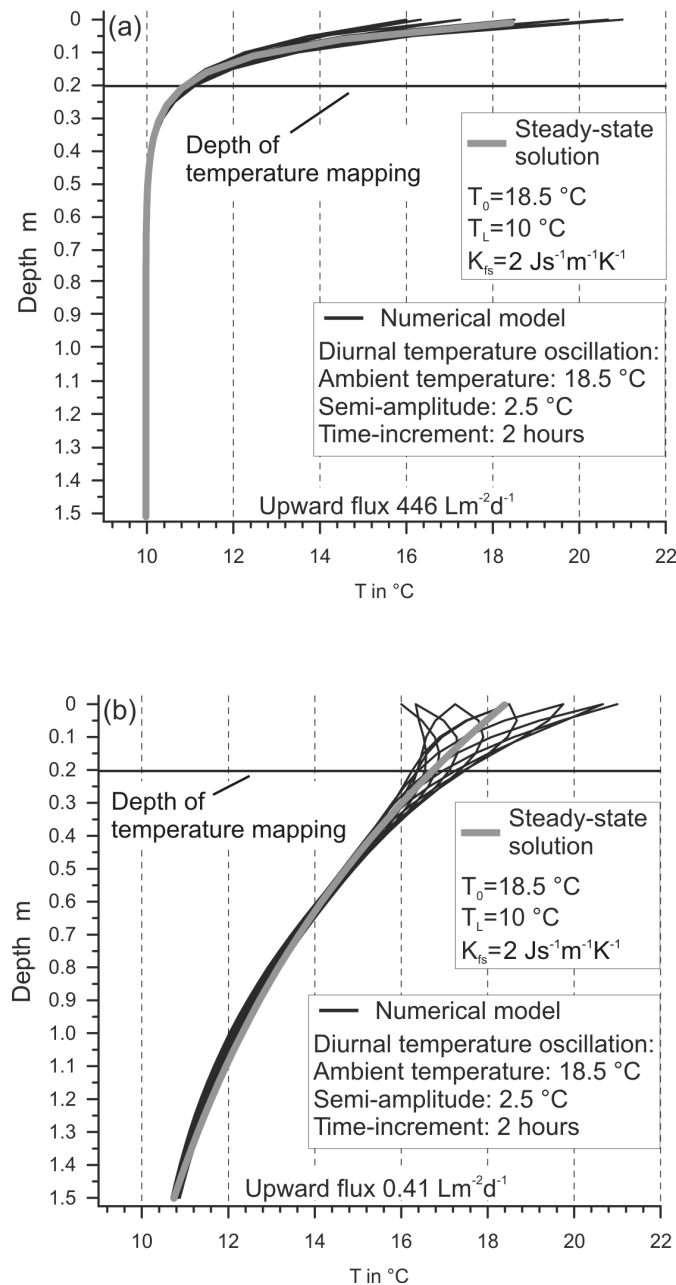


Figure 2.3. Comparison of the Turcotte and Schubert (1982) analytical solution and VS2DH numerical model simulations of streambed temperature versus depth profiles for a hypothetical case with diurnal temperature oscillations with an amplitude of 5 °C for (a) high flux and (b) low flux case.

2.3.2. Field data

2.3.2.1. Streambed Temperature Mapping in Pine River

Streambed temperatures were mapped along a 60 m reach of the Pine River in Angus, Ontario, Canada by Conant Jr. (2004). The river is about 11 to 14 m wide and in the summer has an average depth of 0.5 m and maximum depth of 1.1 m with flows of between 1.4 and 2.0 m³s⁻¹. The river has a natural channel morphology and the stream flow regime is unregulated. The shallow streambed deposits consist primarily of loose (i.e., no armouring), fluvially deposited, fine sands having an average hydraulic conductivity of $1.68 \times 10^{-4}\text{ m s}^{-1}$ and an average fraction of organic carbon content of 0.15%. Some areas of sand with gravel

and/or cobbles are found along a riffle on the northern third of the study reach. At many locations beneath the sandy fluvial deposits are silt, clay, and peat deposits of a semi-confining layer that has hydraulic conductivities between 4.4×10^{-8} and $9.3 \times 10^{-6} \text{ m s}^{-1}$. A detailed map of the surficial geology of the streambed and geology at depth is given in Conant Jr. et al. (2004).

Table 2.2. Input parameters used for VS2DH simulations

Flow parameters ^A	Value	Thermal and other parameters (constant and uniform for both cases)	Value
High discharge (~446 L m⁻² d⁻¹)		Thermal Parameters	
Hydraulic conductivity, K [m/s] at 20 °C (sand)	2.14x10 ⁻⁴	Thermal conductivity of saturated sediments, K_{fs} [J s ⁻¹ m ⁻¹ K ⁻¹]	2.0
Porosity, n [m ³ /m ³]	0.445	Thermal conductivity of dry sediments, K_{fd} [J s ⁻¹ m ⁻¹ K ⁻¹]	NA ^C
Vertical hydraulic gradient, i [m/m]	0.031	Volumetric heat capacity of the solids, $p_s c_s$ [J m ⁻³ K ⁻¹]	2.0x10 ⁶
Ratio of horizontal to vertical hydraulic conductivity [-]	1.0 ^B	Volumetric heat capacity of the water, $p_w c_w$ [J m ⁻³ K ⁻¹]	4.19x10 ⁶
Low discharge (~0.41 L m⁻² d⁻¹)		Longitudinal thermal dispersivity, α_L [m]	0.0 ^D
Hydraulic conductivity, K [m/s] for 20 °C (silt and clay)	5.8x10 ⁻⁸	Boundary Conditions and Domain	
Porosity, n [m ³ /m ³]	0.559	Thickness of domain [m]	7.0
Vertical hydraulic gradient, i [m/m]	0.108	Groundwater temperature (summer) °C	9.8 or 10.0 ^E
Ratio of horizontal to vertical hydraulic conductivity	1.0 ^B	Groundwater temperature (winter) °C	10.7
		Surface water temperature °C	varies with simulation

^A = Parameters from Conant Jr. (2004) for sand materials at piezometer SP7 and silt and clay materials at SP30

^B = Model requires an input value but it is not used in the 1-D simulations

^C = Model requires an input value but it is not used in saturated flow simulations, so was arbitrarily set to 0.1

^D = Thermal dispersion was set to 0.0 because it is negligible compared to heat conduction (Hopmans et al. 2002)

^E = The groundwater temperature was 10 °C for the hypothetical case and 9.8 °C for simulating the Pine River case.

Streambed temperature mapping of the Pine River was done in the summer (July 1998) and again in winter (February 1999) when the temperature gradients between groundwater and surface water were the highest. To obtain the spatial distribution of streambed temperatures, measurements were made on a 1 m spacing along transects spaced every 2 m perpendicular to the river flow. A total of 383 summer and 514 winter streambed temperature measurements were made over a two and a three day period, respectively. A detailed description of the methodology can be found in Conant Jr. (2004). Streambed temperature measurements were made by temporarily inserting a temperature probe to a depth of 0.2 m at each location. All groundwater and surface water temperature measurements had an accuracy of 0.1 to 0.2 °C.

The Pine River dataset was of particular interest because it included Darcy's law flux calculations performed at 34 streambed piezometer locations (SP4 through SP37) that were

then empirically related to the streambed temperatures (see Table 1 in Conant Jr. 2004 for more details on the flux calculations). Not only could the streambed temperature mapping data be used to calculate fluxes using the Turcotte and Schubert (1982) solution (Equation [2.3]), but then the results could also be directly compared to the Darcy flux calculations and the results of the empirical relation proposed by Conant Jr. (2004).

K_{fs} values for saturated sediments were obtained in this study by making direct measurements on core samples with a model KD2 Portable Thermal Properties Analyser (Decagon Instruments Inc., Pullman Washington). The KD2 analyser calculates thermal conductivity in $\text{W m}^{-1} \text{ } ^\circ\text{C}^{-1}$ (which is equivalent to $\text{J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$) by monitoring the dissipation of heat from a line heat source and it is accurate to within 5%. Measurements of K_{fs} values were made on six samples of sandy deposits from previously collected (Conant Jr. 2004) streambed cores RC2, RC4, RC7, and RC12 and two samples of clayey semi-confining deposits from cores RC2 and RC12. The KD2 measurements were repeated at least 3 times on each sample to improve accuracy. K_{fs} was also calculated indirectly using the geometric mean empirical equation (Clauser and Huenges 1995) shown in Table 2.1. Calculations of K_{fs} were made with streambed porosities previously measured using time domain reflectometry (Conant Jr. 2004) and assuming a solid phase thermal conductivity (K_s) of $7.7 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$ (Bristow et al. 1994).

2.3.2.2. Streambed Temperature Mapping at Teeterville

As an additional check on the applicability of the Turcotte and Schubert (1982) solution, streambed temperatures, surface and groundwater temperatures, hydraulic gradients, and seepage meter data was collected along a 180 m reach of an unnamed first-order stream in Teeterville, Ontario, Canada in February and March 2006. The stream is about 1.5 to 2 m wide and in the winter had an average depth of 0.14 m and a maximum of depth of 0.3 m and flowed at about $0.025 \text{ m}^3 \text{ s}^{-1}$. The stream passes through an agricultural field and, in the past, the channel has been excavated and made more linear with steep banks and has no significant pools or riffles. The streambed sediments are rather uniform and consist of fine to very fine sands with occasional silty areas. Streambed temperatures were measured every 0.5 m across the stream along transects spaced 4 m apart. A Digi-Sense Model 93210-50 ThermoLogR Thermister Thermometer was used and attached to a YSI Model 418 probe. The probe was temporarily inserted to a depth of 0.2 m at 251 different locations during a 6.5 hour long mapping event on March 1, 2006. On March 5, plastic seepage meters (0.27 m in diameter) were deployed at 22 locations (SM11 to SM32) using a technique similar to Lee and Cherry (1978). Locations for seepage meters were chosen to cover the full range of streambed temperatures observed during the temperature mapping. Three streambed sediment cores were collected and falling head permeameter tests were conducted on nine subsamples to obtain hydraulic conductivity (K) and porosity using the equipment and technique described by Sudicky (1986). The K_{fs} of deposits at the site was determined using a KD2 Thermal

Properties Analyser on six sediment samples of fine sand streambed deposits from the three sediment cores.

Model DS1922L-F5 Thermochron iButton Temperature loggers (Maxim-Dallas Semiconductor, Dallas, Texas) having an accuracy of $\pm 0.5^\circ\text{C}$ were used to measure fluctuations in surface water, groundwater and air temperatures prior to and during the streambed mapping. The logger measuring groundwater temperatures was located at a depth of 2.58 m below the streambed in well P3D which was one of four 0.025 m ID, schedule 40 PVC wells installed in the streambed at the site. Groundwater levels and surface water levels at P3D were measured to within ± 0.011 m on a 15 minute interval using In-Situ Level TROLL[®] Model 700 unvented pressure transducers and corrected using barometric measurements from a BaroTROLL[®] logger. Information regarding the site and additional instrumentation and measurements can be found in Waldick (2006).

2.4. Results

2.4.1. Evaluation of Steady-State Versus Transient Conditions

Figure 2.3a and Figure 2.3b compare the streambed temperature versus depth profiles predicted by the VS2DH model and the Turcotte and Schubert (1982) analytical solution for a hypothetical case (Table 2.2) that was similar to the summer conditions observed by Conant Jr. (2004). Temperatures within sediment at the very top of the streambed are transient as a result of the hypothetical diurnal oscillations of the surface water temperature. Simulations with the Turcotte and Schubert (1982) solution used the average value of the oscillating surface water temperatures for the top boundary condition and that value provided a good approximation of the temperature versus depth profiles for both high and low discharge.

The amplitude of transient temperature oscillations at a given depth z within the sediment depends primarily on the magnitude of the water discharge flux and the thermal properties of the sediment. The quasi-steady-state assumption was evaluated for different time periods for the temperature data collected by Conant Jr. (2004). The VS2DH model and input data in Table 2.2 were used to simulate the effect that surface water temperatures had on the streambed temperatures during both the summer and winter streambed mapping periods and the 20 days prior to mapping. Figure 2.4a and b show the observed surface water and groundwater temperatures for the winter and summer periods as well as the simulated streambed temperatures at depths of 0.1, 0.2, and 0.3 m for both high flux ($\sim 446 \text{ L m}^{-2} \text{ d}^{-1}$) and low flux ($\sim 0.41 \text{ L m}^{-2} \text{ d}^{-1}$) conditions. The simulations showed that quasi-steady-state conditions were achieved for much of the winter data set but were not achieved for certain depths and time intervals for the summer data set.

During the winter mapping period, variations in the simulated streambed temperatures decreased with increasing depth and were generally smaller for the high flux case (Figure 2.4a). Overall the streambed temperatures appeared to be at or very near a quasi-steady-state condition.

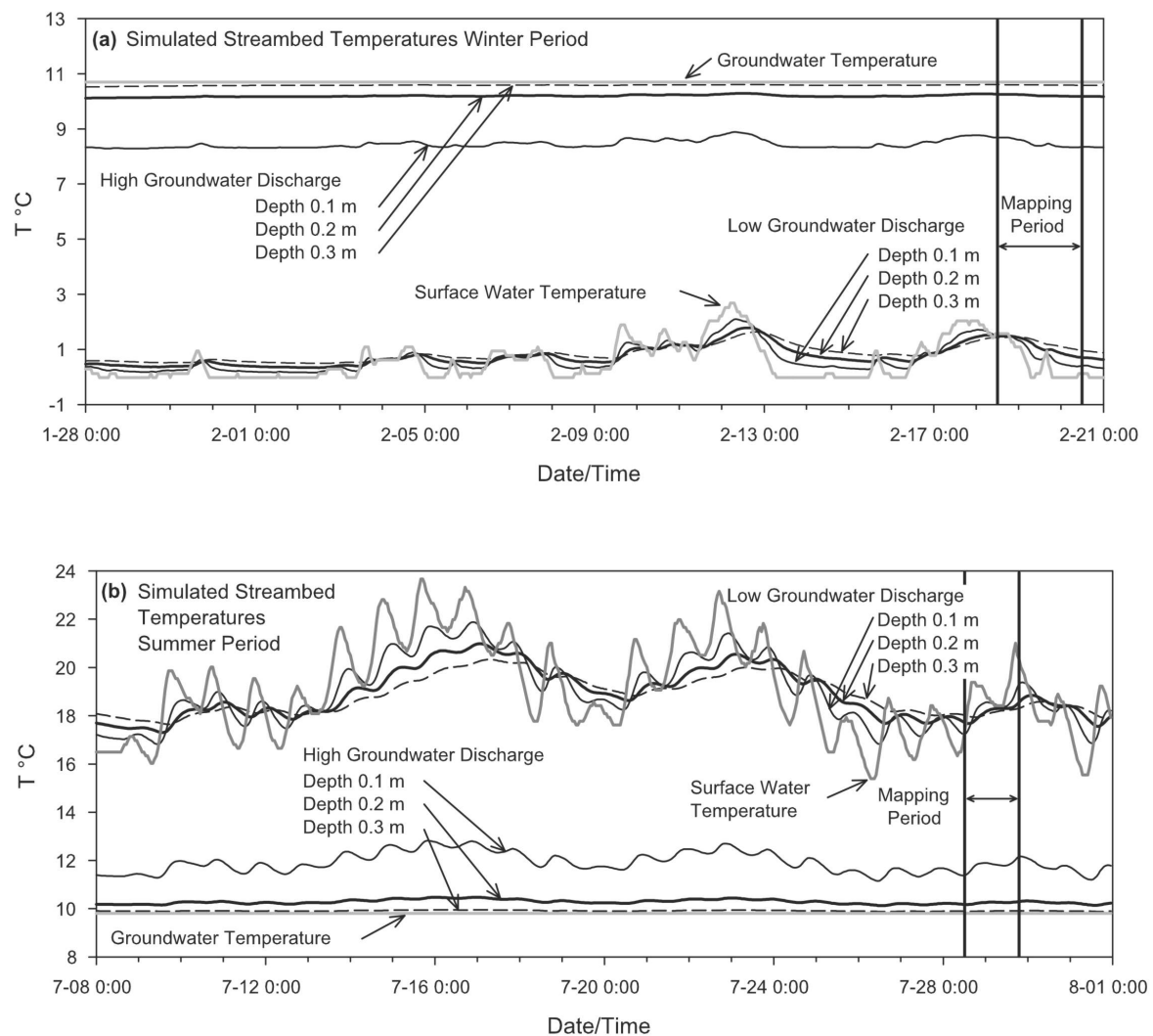


Figure 2.4. Measured surface water temperatures and VS2DH simulated streambed temperatures at 0.1, 0.2, and 0.3 m depths for the Pine River for (a) winter and (b) summer for high flux ($446 \text{ L m}^{-2} \text{ d}^{-1}$) and low flux ($0.41 \text{ L m}^{-2} \text{ d}^{-1}$) cases during the 20 day periods prior to steamed temperature mapping events.

This stability was partly a result of the relatively constant surface water temperatures (Conant Jr. 2004) that were between 0.0 and 2.0 °C during the mapping and between 0.0 to 2.7 °C during the 20 day period prior to that. For the high flux case the simulated range of temperatures at a depth of 0.2 m was 10.2 to 10.3 °C for the mapping period and slightly higher for the previous 20 day period (10.1 to 10.3 °C). Those variations are considered to be quite small and almost within the measurement accuracy of 0.1 °C for the temperature probe. For the high flux case, the quasi-steady-state condition is valid during the entire time shown in Figure 2.4a. For the low flux case, simulations resulted in higher streambed temperature variations and the quasi-steady-state condition may not be valid for the entire time shown. For example, at a depth of 0.2 m the streambed temperature range was between 0.6 and 1.5 °C for the three day mapping period and 0.3 and 1.8 °C for the 20 day period. However, for low

fluxes the streambed temperatures did go through several periods where quasi-steady-state conditions occurred with the longest being between January 28 and February 9, 1999.

Table 2.3. Input parameters for the Turcotte and Schubert (1982) analytical model

Parameter	Pine River (Winter)	Teeterville (Winter)
T_0 [°C]	0.71 [3 day average] ^A 0.65 [20 day average]	7.3[Mean during mapping] ^A 7.0 [7 day mean value]
T_L [°C]	10.7 ^B	11.3 ^C
K_{fs} [J s ⁻¹ m ⁻¹ K ⁻¹]	1.45 [Measured with KD2] ^D 1.24-2.63 [Geometric mean]	1.50 [Measured with KD2] ^D 2.63-3.10 [Geometric mean]
Depth [m]	0.2	0.2
Volumetric heat capacity of the fluid [J m ⁻³ K ⁻¹]	4.19x10 ⁶	4.19x10 ⁶

^A = The average surface water temperature was obtained for the actual day(s) that mapping was performed.

^B = Groundwater temperatures did not vary during the time intervals indicated for surface water averaging

^C = Groundwater value obtained from spring, groundwater temperatures at P3D were 10.4 to 10.6 °C

^D = Median values for sandy materials made with KD2 probe

During the summer mapping period, the quasi-steady-state assumption was valid at depths of 0.2 and 0.3 m for the high flux discharge, but was not valid for low flux conditions at a 0.1 m depth and was only valid for the 0.2 m and 0.3 m depths for relatively short periods of time. The surface water temperatures varied over a greater range during the summer period, hence making that a less desirable time than winter for characterizing the spatial temperature distribution (Conant Jr. 2004). For the mapping period, the lowest surface water temperature measured was 16.3 °C and the highest was 21.0 °C. During the prior 20 day period, the observed surface water temperatures varied between 15.4 and 23.7 °C. The higher variations in simulated streambed temperatures corresponded to the higher variations in surface water temperature. At a depth of 0.2 m the temperatures in the mapping period range from 10.1 to 10.3 °C for the high flux case and from 17.6 to 18.8 °C for the low flux case. It is apparent that in summer there is a restricted validity of the quasi-steady-state conditions for very low discharge where diurnal oscillations cause streambed temperature variations to exceed 0.5 °C at a depth of 0.2 m. This relationship is consistent with observations made by others (Lapham 1989, Stonestrom and Constantz 2003, Conant Jr. 2004) where streambed temperatures in low discharge locations are more greatly influenced by surface water temperature changes than locations at high discharge locations. Overall these temporally induced variations remain small when compared to the overall range of spatially mapped temperatures, which were between 10 °C and 18.3 °C in summer and 0.4 and 9.3 °C in winter. It is important to note that if one is calculating total fluxes through a section of the streambed, then errors in characterizing the low discharge locations likely will not result in substantial errors in the calculation of the total discharge. Therefore, the concept of a quasi-steady-state for streambed temperatures mapped at a uniform depth of 0.2 m is acceptable, but if low discharge areas are relatively large, then measuring streambed temperatures at a greater depth (e.g., 0.3 or 0.5 m) would be more appropriate.

2.4.2. Simulation of Pine River Data using the analytical Solution

Table 2.3 shows the input parameters used in the Turcotte and Schubert (1982) solution for simulating the winter Pine River streambed mapping event. Because the summer data set did not satisfy the quasi-steady-state condition as well as the winter data, only the winter data is evaluated in this section. The winter calculated fluxes versus streambed temperatures are shown in Figure 2.5. The Darcy's law calculated flux values from Conant Jr. (2004) are plotted along with the analytical flux curves obtained using the KD2 measured K_{fs} value, for a "best fit" K_{fs} value and a range of estimated K_{fs} values. Measurements using the KD2 meter ranged between 1.25 and 1.58 $\text{J s}^{-1} \text{m}^{-1} \text{K}^{-1}$ for the sandy materials and the median value of 1.45 $\text{J s}^{-1} \text{m}^{-1} \text{K}^{-1}$ was used to simulate the "measured K_{fs} " curve. Both flux curves used a T_0 of 0.71 °C, which was the three day average of surface water temperatures during the mapping.

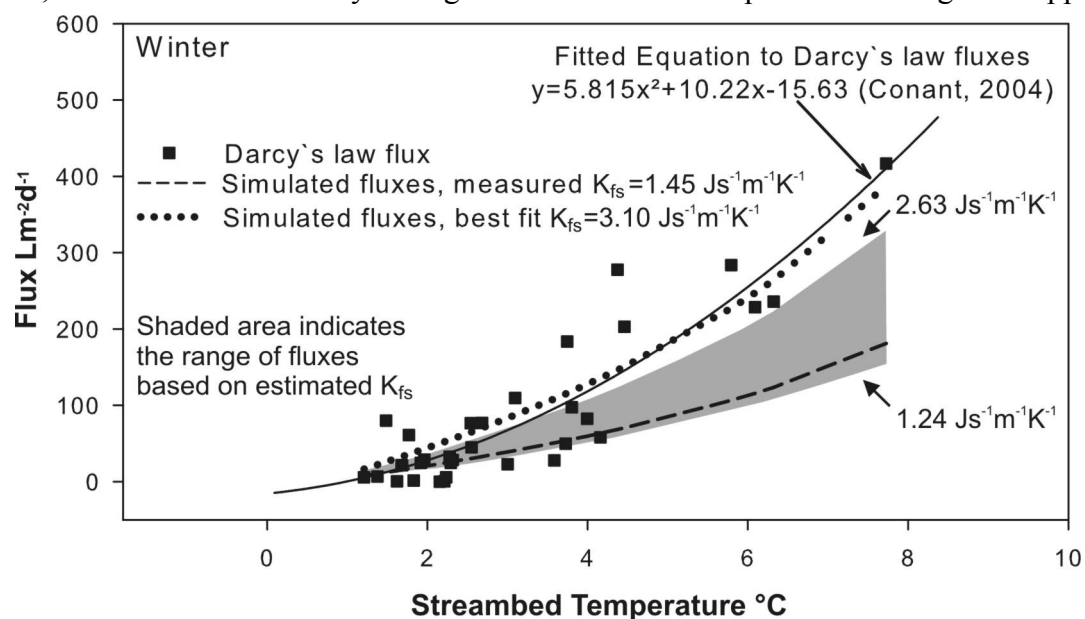


Figure 2.5. Turcotte and Schubert (1982) analytical solution simulations of flux versus streambed temperatures for the Pine River in winter compared to measured Darcy's law flux values and the empirically fitted curve from Conant Jr. (2004).

Calculated values of flux in Figure 2.5 using the measured K_{fs} were lower than the Darcy's law flux values obtained by Conant Jr. (2004), particularly at higher temperatures and fluxes. The average discharge in winter at the piezometer locations obtained using Darcy's law was 85.4 $\text{L m}^{-2} \text{d}^{-1}$ whereas the calculated average winter fluxes using the analytical expression and measured K_{fs} were 44.7 $\text{L m}^{-2} \text{d}^{-1}$. These lower values of flux are also apparent when the measured K_{fs} value was used with the Turcotte and Schubert (1982) solution to convert all the winter mapped streambed temperature data (Figure 2.6a) into fluxes (Figure 2.6b) and then compared to the fluxes obtained using Darcy's law and the empirical relationship by Conant Jr. (2004) (Figure 2.6c). The general pattern of flux in Figure 2.6b and 6c are similar but the flux values in Figure 2.6b are consistently lower. The only apparent exception to this trend is that the recharge area in the northern part of the reach is smaller in Figure 2.6b than it is in Figure 2.6c. The difference in the size of the recharge areas is an artefact of where the temperature versus flux curves (Figure 2.5) cross the x-axis (i.e., where flux is zero). The

Turcotte and Schubert (1982) solution yields upward fluxes (discharge) for streambed temperatures higher than the selected upper boundary temperatures ($T_0 = 0.71^\circ\text{C}$). For streambed temperatures $< 1^\circ\text{C}$ the empirical relation indicates recharge conditions. Therefore, the area of recharge is different because streambed temperatures between 0.71 and 1°C are interpreted as discharge in the analytical solution and as recharge in the empirical relation.

A much better visual fit to the Darcy flux values in Figure 2.5 was achieved with the analytical solution when K_{fs} was set to $3.1 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$, but this value seemed unreasonably high compared to literature values for sandy materials (Lapham 1989, Stonestrom and Constantz 2003). Even the K_{fs} values calculated using the geometric mean equation in Table 2.1, did not overlap the $3.1 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$ value (Figure 2.5).

If the KD2 measured values are believed to be correct, then there must be some other reason the simulated curve does not closely match the Darcy flux values. However, other parameters used in the analytical solution are unlikely to be in error. The most uncertain of the inputs is T_0 (because of the need to average surface water values), but the calculated flux is relatively less sensitive to T_0 than the other parameters. Also it does not seem likely that depth measurements (z) could be incorrectly measured by the 50% error necessary to obtain a better fit to the Darcy flux data. Long-term or annual temperature variations that propagate down to greater depths might influence T_L and the calculated fluxes. However, the temperature in the deep well at the Pine River only varied by about 1.2°C annually (which is $\sim 12\%$) and so T_L is unlikely to be responsible for this larger deviation in flux values.

Since the inputs to the analytical model seem correct and the assumption about a quasi-steady-state profile seems valid, it appears there might be some error associated with the Darcy flux versus temperature data obtained from Conant Jr. (2004). A review of the data indicated that although the Darcy flux data was collected when hydraulic conditions were similar to those during the streambed temperature mapping, they were measured at a different time than the mapping, and so may have introduced errors because the hydraulic heads and fluxes were not identical to those made during the earlier measurements. Moreover, several of the streambed temperatures were not measured at the exact piezometer locations but instead were interpolated from adjacent temperatures measurements. It appears that a systematic shift in flux versus temperature values has been introduced to the data. To try and resolve some of these unanswered questions regarding the appropriateness of the analytical method, a second data set was examined for a stream in Teeterville.

2.4.3. Simulation of the Teeterville Data using the analytical Solution

The results of the field investigations at Teeterville showed that the 180 m long reach of stream was gaining water at every location investigated. Discharge from the 22 seepage meters ranged from 10 to $1503 \text{ L m}^{-2} \text{ d}^{-1}$ and upward vertical gradients were observed in all four piezometers and 10 mini-piezometers in the streambed. Figure 2.7 shows the relationship between the seepage meter fluxes measured on March 5, 2006 and the streambed temperatures measured at those exact same locations during the mapping on March 1. The

hydraulic gradients and flow conditions did not change during this time period because the water levels measured by pressure transducers in the stream and in piezometer P3D remained constant. The groundwater temperature at a depth of 2.58 m below the streambed at P3D changed by 0.3 °C during the week prior to mapping. The minimum and maximum temperatures observed at a depth of 0.2 m in the streambed during the mapping were 6.0 °C and 11.3 °C, respectively. Even colder temperatures (as low as 3.4 °C) were observed at a depth of 0.2 m at the waterline at the very edge of the stream, but they were likely affected by the frozen soils at the waterline and adjacent to the stream. Porosity values (n) measured on sediment samples from the cores were between 0.39 and 0.42. Table 2.3 contains a summary of all the parameters used for the analytical model. The KD2 probe measurement of K_{fs} values ranged between $1.38 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$ and $1.90 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$, with the median value of $1.50 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$ used as input for the analytical solution.

The overall analytical model fit to the seepage meter flux data (Figure 2.7) is much better than the one obtained for the Pine River data (Figure 2.5), most likely because: (1) the mapping and flux measurements were made much more closely together in time; (2) the seepage meters are a more direct measurement of flux than using data from piezometers; and (3) temperatures were measured exactly at the same location that the seepage meters were installed. The analytical solution still tends to underestimate the seepage meter measurements at higher fluxes.

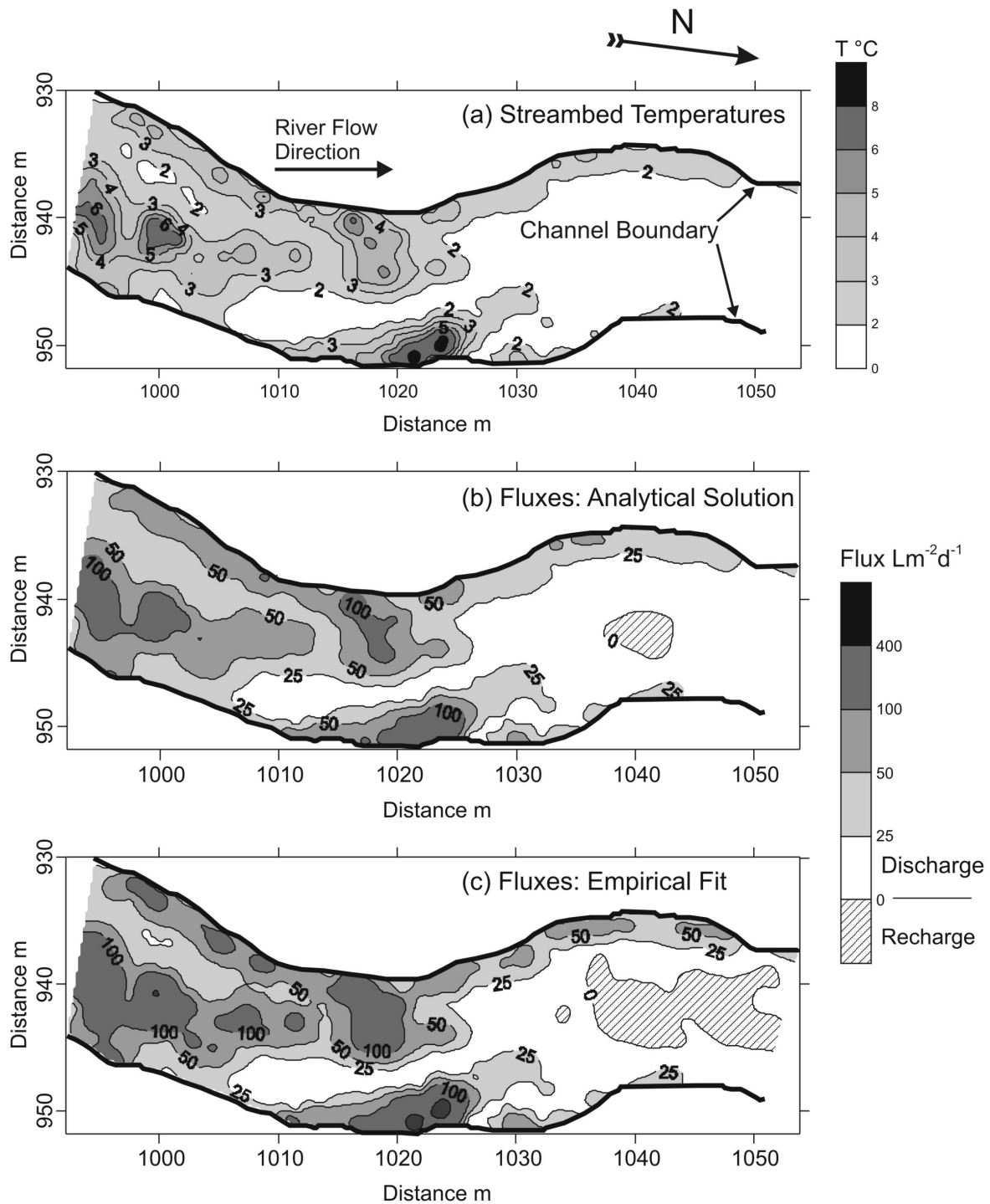


Figure 2.6. Plan-view contour maps of the Pine River in winter for (a) mapped streambed temperatures, (b) vertical fluxes calculated with the Turcotte and Schubert (1982) analytical solution ($K_{fs} = 1.45 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$), and (c) vertical fluxes using the empirical relationship from Conant Jr. (2004).

The Teeterville data set showed a potential problem in the application of the Turcotte and Schubert (1982) solution. When observed streambed temperatures are higher than the assigned T_L or lower than the assigned T_0 , the analytical solution does not provide meaningful results. In this study, the initial value of T_L chosen for simulations was the temperature observed in piezometer P3D during the mapping (10.4°C), but it was lower than the

streambed temperatures observed near springs in the streambed, so the analytical solution was unable to provide flux estimates for those data points. The maximum streambed temperature of 11.3 °C (observed 0.2 m below the streambed surface at spring) was thought to be more representative of the actual groundwater temperature than data from the shallow piezometer P3D. This stream is in the middle of an agricultural field and not near any anthropogenic sources of heat or water and so the spring temperature could have only represented deeper groundwater. Using a T_L of 11.3 °C and the measured K_{fs} value, the median simulated flux for the 22 seepage meters was 95.0 L m⁻² d⁻¹ which closely matches the 115.6 L m⁻² d⁻¹ value obtained directly from the seepage meters. Overall, the simulated average flux at the 22 seepage meters was 165.5 L m⁻² d⁻¹ which underestimated the average fluxes of the seepage meters (280.5 L m⁻² d⁻¹) by 41%, but the difference in average values is skewed by high seepage meter fluxes occurring near the non-unique portion of the curve (Figure 2.7).

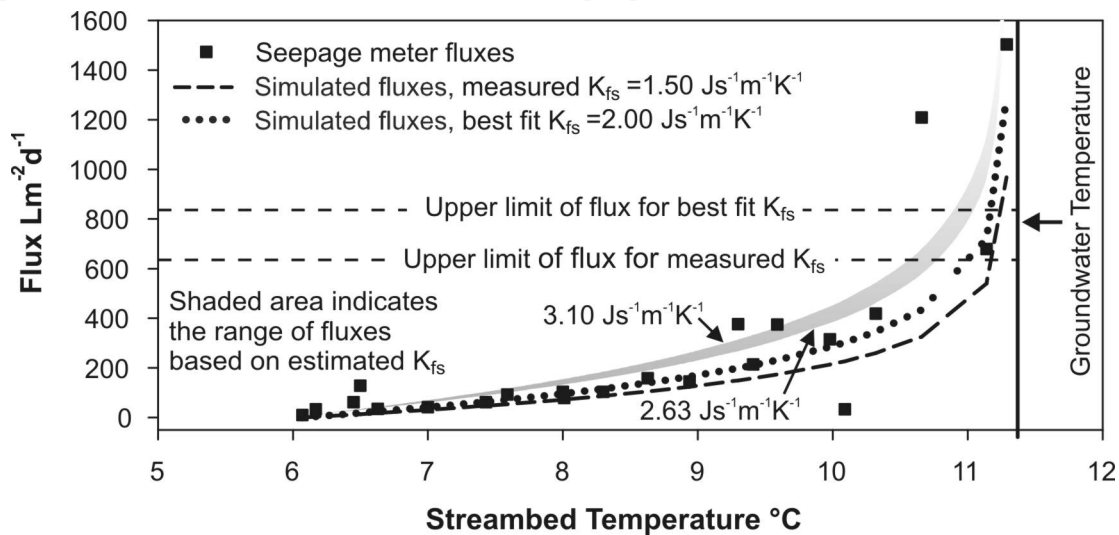


Figure 2.7. Turcotte and Schubert (1982) analytical solution simulations of flux versus streambed temperatures for the Teeterville stream in winter compared to measured fluxes from seepage meters.

The best fit curve (Figure 2.7) was achieved by reducing T_0 from 7.0 to 6.1 °C and increasing K_{fs} from 1.5 J s⁻¹ m⁻¹ K⁻¹ to 2.0 J s⁻¹ m⁻¹ K⁻¹, and keeping all other parameters the same. The reduction of T_0 is reasonable and appropriate, considering that iButtons temperature logger have been known to provide temperatures that are 0.5 to 1.0 °C higher than the true temperature (Johnson et al. 2005). The best fit curve ($K_{fs}=2.0$ J s⁻¹ m⁻¹ K⁻¹, $T_L=11.3$ °C and $T_0=6.1$ °C) gave a median simulated flux for the 22 seepage meters that was 126.62 L m⁻² d⁻¹ which closely matches the 115.6 L m⁻² d⁻¹ median value obtained directly from the seepage meters. Overall, the simulated average flux was 220.7 L m⁻² d⁻¹ which underestimated the average fluxes of the seepage meters (280.5 L m⁻² d⁻¹) by 21.3%. The results of the Teeterville data set show that the Turcotte and Schubert (1982) solution can be successfully applied to obtain reasonable fits to observed fluxes without having to deviate very far (< 33%) from the independently derived input data values.

2.4.4. Sensitivity Analyses

The analytical solution used in this paper does not require internal model calibration (e.g., least squares fitting) so all the uncertainties in the model's results originate from uncertainties in the input parameters. The relative changes of the simulated fluxes $\Delta q_z/q_z$ were evaluated with regard to relative changes of the input parameters $\Delta p/p$, where p denotes the input parameters ($T(z)$, T_0 , T_L , K_{fs} , or z). The ratio of relative changes in model output with regard to relative changes in model input can be approximated by the partial derivative with respect to p :

$$\frac{\Delta q_z/q_z}{\Delta p/p} = \frac{p}{q_z} \frac{\partial q_z}{\partial p} \quad [2.4]$$

The term on the right hand side of Equation 2.4 is called the relative sensitivity coefficient (RSC). The dimensionless RSC allows the direct comparison of the relative sensitivity of the model output with respect to different model input parameters. The RSCs of K_{fs} and z are 1 and -1 respectively and indicate that the error in q_z is proportional to the error in K_{fs} and inversely proportional to the error in z . The RSCs of the temperatures $T(z)$, T_0 , and T_L are not linear and depend on the magnitude of q_z . Figure 2.8 shows the RSCs of the model parameters as a function of the dimensionless normalized streambed temperature (τ). Values of τ near 1 indicate low fluxes whereas τ values close to 0 represent high fluxes. For $T(z)$, T_0 , and T_L the RSCs increase with increasing τ (decreasing q_z). Low fluxes are associated with a relatively high sensitivity towards deviations in the input parameters $T(z)$, T_0 , and T_L . Uncertainties in $T(z)$ and T_L will have the highest relative impact on q_z for low and medium fluxes but have lower relative impacts than K_{fs} and z for high q_z . T_0 has the lowest relative impact of all parameters for medium and high fluxes and only increases significantly for very low fluxes with $\tau > 0.9$. However, the absolute influence of uncertainties in the parameters $T(z)$, T_0 and T_L can be particularly significant for low fluxes (large τ). For instance, a deviation of -0.2°C (which is near the accuracy of the temperature measurements) in observed streambed temperatures of 2°C in winter (equivalent to $\tau = 0.85$ for the Pine River winter mapping) will cause q_z to change from $20 \text{ L m}^{-2} \text{ d}^{-1}$ to about $40 \text{ L m}^{-2} \text{ d}^{-1}$.

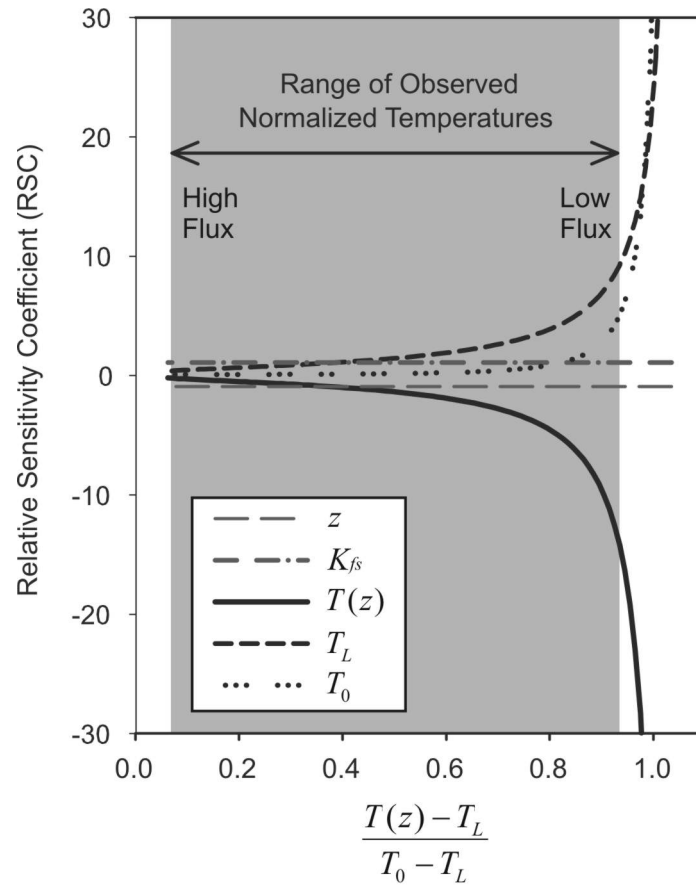


Figure 2.8. Relative Sensitivity Coefficients (RSC) for the parameters $T(z)$, T_0 , T_L , K_{fs} , z as a function of the dimensionless normalized streambed temperature (τ).

2.5. Discussion

The main advantage of this analytical method for converting streambed temperature mapping data to estimates of groundwater discharge is that it can be done with only a very minimal amount of additional field data and computational effort. K_{fs} is the only additional piece of field data needed because the proper interpretation and delineation of discharge areas by streambed temperature mapping already requires collection of surface and groundwater temperature data over time. Subsequent calculations can be easily done using a spreadsheet programme, which is considerably less effort than more data intensive numerical models like VS2DH. The analytical solution is also fairly robust and it even gave a reasonable estimate of flux for the Teeterville site data without having to resort to any kind of calibration when using the KD2 measured value of K_{fs} . Even using literature values for K_{fs} in the analytical model would have yielded a reasonable approximation to the observed fluxes.

The analytical solution even can be applied without the benefit of additional site specific flux data from seepage meters or mini-piezometers, however, the interpretation of the flow through the streambed would certainly benefit from such data. If such additional data is collected (like it was at the Pine River and Teeterville sites), the analytical solution still provides a more physically based and better temperature versus flux relationship (i.e., curve shape) than the empirical polynomial curve fitting approach of Conant Jr. (2004). If the “best fit” curve is difficult to achieve or does not match all the measured fluxes when reasonable

input data is used, it is likely either the assumption regarding quasi-steady-state or vertical flow has been violated or geological heterogeneities are affecting the measured fluxes.

When the analytical model calculations using independently measured K_{fs} and temperature data were compared to flux measurements from piezometers at the Pine River, the model provided fluxes that were lower than the observed data at the medium to high flux end of the curve. The same pattern of underestimating fluxes was also observed for the Teeterville data (but to a much lesser extent) and suggests some kind of systematic error. For the Pine River the lack of a match was likely because the piezometer data was obtained at a different time than the streambed temperature data, but it also might be a systematic problem with calculating fluxes indirectly using Darcy's law and having to assume homogeneous streambed conditions at each location. Variations in hydraulic conductivities and anisotropic ratios with depth can lead to uncertainty and systematic errors when using slug testing results (Landon et al., 2001). The Teeterville observed flux data was collected in a way that avoided this temporal problem and directly measured fluxes using seepage meters, and so the deviation from observed data for Teeterville was much less than for the Pine River data.

The 33% difference between the observed K_{fs} curve (i.e., unfitted curve) and the "best fit" for the Teeterville data is relatively small (Figure 2.7) in comparison to the size of potential errors that can be associated with Darcy's law calculations involving the hydraulic conductivity (K), since measured K values varied by a factor of 43 at this site. Nonetheless, it is appropriate to investigate the reason for the difference between the observed K_{fs} curve and the seepage meter data. The seepage meter data was properly collected in accordance with recommendations in Lee and Cherry (1978). If hydraulic heads required to inflate the collection bag of seepage meters are constant and are so small that their effect on the flux is negligible, the seepage meters should accurately determine the magnitudes of groundwater discharges. The bag resistance typically causes an underestimation of the actual fluxes (Murdoch et al. 2003). Conversely, water flow over the bag causes an increased measured flux. At the Teeterville site, shields were used to prevent bags from being buffeted about by the current. Figure 2.7 shows some seepage meter data appear to be outliers and do not fall along the simulated line (e.g., the seepage meter flux of $1209 \text{ L m}^{-2} \text{ d}^{-1}$ at 10.66°C at SM20 and $33.3 \text{ L m}^{-2} \text{ d}^{-1}$ at 10.09°C for SM29). These variations may be a result of spatial heterogeneity in flow as a result of local geological conditions in the streambed but these spatial effects would typically cause random errors and not produce systematic deviations in measured seepage meter fluxes. It seems that fluxes calculated using streambed temperatures systematically underestimate the fluxes derived from seepage meters. The fluxes calculated from temperatures should be treated as lower bound of the actual fluxes across the streambed.

Other potential problems that can affect the analytical solution's fit to the Teeterville seepage meter data include: 1) violations of model assumptions; 2) errors in temperature data collection; and 3) spatial variations in subsurface conditions. The quasi-steady-state assumption was determined to be reasonable for the time of mapping, but it is difficult to measure and confirm the assumption of perfectly vertical flow in a streambed. If groundwater

is flowing from both sides towards a river it is likely that in the center of the channel groundwater flow lines are essentially vertical. Close to the riverbanks groundwater flow would likely show a stronger deviation from vertical. In reaches with strong hyporheic zone exchange the flow direction in the streambed is not vertical either. Assuming vertical flow in the streambed is appealing because it can easily be implemented in one-dimensional models. It is also a common assumption in both older and more recent applications (e.g. Suzuki 1960, Land and Paull 2001, Hatch et al. 2006, Keery et al. 2007). A deviation from vertical water flow in streambed would likely lead to an underestimation of true fluxes since the streambed temperature profile is only sensitive to vertical advection of colder (summer) or warmer (winter) water. In general, the horizontal component of water flow is difficult to detect using streambed temperatures.

Spatial heterogeneity in the streambed is expected and is a fundamental reason for undertaking temperature mapping to obtain fluxes in the first place but assuming that K_{fs} is uniform over an entire reach may contribute to the systematic underestimation of the high fluxes in Figure 2.7. Textural changes in sediments can dramatically affect K values (which range over many orders of magnitude) but saturated K_{fs} values for unconsolidated geologic materials typically range between 1.4 and 2.2 J s⁻¹ m⁻¹ K⁻¹ (Stonestrom and Constantz 2003) and are usually assumed to be spatially constant in comparison. However, Lapham (1989) shows that coarse-grained deposits may have 5% to 30% higher K_{fs} values than fine-grained materials (for the same value of bulk density). If the high fluxes observed at seepage meters are a result of coarse-grained materials, then in actuality higher K_{fs} values should have been used to simulate those particular locations and that would have resulted in higher simulated values and a better fit to the observed fluxes. For the Teeterville site, the K_{fs} of 2.0 J s⁻¹ m⁻¹ K⁻¹ for the best fit curve is 33% higher than the average of all K_{fs} measured values and almost equal to highest measured value of 1.90 J s⁻¹ m⁻¹ K⁻¹. K values from the nine permeameter tests on streambed core samples ranged from 4.1x10⁻⁶ to 1.8x10⁻⁴ m s⁻¹ and coarser grained materials were found at the high flux locations. However, plots of K_{fs} versus K values (not shown) did not show a clear trend of increasing K_{fs} with increasing K most likely because the lab analyses were done on repacked and disturbed samples. In situ field measurements or analysis on undisturbed samples would likely be needed to confirm or refute the hypothesis of high K_{fs} values at high flux locations at the site.

At some locations in a streambed, spatial heterogeneity in groundwater discharge may also affect the ability of the analytical model to accurately estimate flux values because three-dimensional heat flow in the streambed is simulated as one-dimensional. When streambed temperatures vary by 5 to 10 °C laterally (e.g., near a spring), steep temperature gradients will occur resulting in lateral thermal diffusion. This so called halo-effect (Conant Jr. 2004) at high discharge zones may mean treating the areas immediately adjacent to those high flow locations as one-dimensional may not be appropriate. For example, in winter the heat is conducted from the relatively warm high discharge areas to the surrounding area. This leads to increased streambed temperatures in the area adjacent to the spring compared to what

would occur for solely vertical heat flow. The analytical solution would over predict water fluxes based on these “altered” observed temperatures.

2.6. Recommendation for Applying the Analytical Method

2.6.1. Basic conditions for application

To successfully apply the analytical method for calculating flux some basic conditions have to be fulfilled:

1) There must be a contrast between ambient groundwater and surface water temperatures (which is usually the case in summer or winter).

2) Surface water temperatures do not vary spatially and any temporal variations during mapping should be minimized. Best conditions are in winter because diurnal oscillations and long-term trends in surface water temperature are smallest. The quasi-steady-state approach may not be valid if long-term temperature changes are occurring during the mapping campaign..

3) T_0 and T_L values should bracket the entire range of observed streambed temperatures.

4) Groundwater flow is upward through the streambed (discharge) and not downward (recharge).

5) The flow conditions (e.g., hydraulic gradients across the streambed) do not change during the time of mapping.

2.6.2. Parameter estimation

Application of the quasi-steady-state approach means some assumptions have to be made in order to estimate the proper boundary conditions and input parameters.

1) *Surface water temperature T_0* : T_0 can be estimated by averaging time series surface water temperature data measured during the mapping campaign and sometimes can include a time period prior to the mapping. If streambed temperature mapping events do not exceed a five day period, a then diurnal sinusoidal oscillation will likely be the main component of the surface water temperature variation and averaging the surface water temperatures for the time of the mapping yields should provide a valid estimate for the quasi steady-state T_0 conditions (Figure 2.3). Especially for short mapping campaigns of one day, the prior surface water temperatures should be considered. Surface water temperatures should be monitored for at least 24 to 48 hours (or preferably for a week) prior to mapping to check if there are major steps or non- diurnal trends in the ambient surface water temperature. Optimal quasi steady-state conditions can be assumed when the 24 hour moving average of the surface water temperatures is virtually constant. Long-term trends may mean it is not appropriate to make the quasi-steady-state assumption and it will make it difficult to select a representative T_0 .

2) *Groundwater temperature T_L* : Although variations in deeper groundwater temperatures tend to be small, time series measurements of groundwater temperature would help to estimate T_L and assess steady-state conditions. In some cases, if the well used to obtain

groundwater temperatures is not deep enough (as appeared to be the case at Teeterville), it is reasonable to use the highest (in winter) or lowest (in summer) temperature observed in the streambed or at a spring for T_L . The assumption is that the highest temperature in the streambed in winter (or lowest temperature in summer) would be the result of a high discharge zone or spring where the groundwater comes up rapidly and the temperature does not have sufficient time to be altered by temperature conditions at the surface.

3) Thermal conductivity K_{fs} : Direct measurements of K_{fs} on site sediments are preferred, but, as a second choice, literature values will provide a good approximation. The thermal conductivity can also be estimated using the geometric mean method (Table 2.1), but empirical methods usually are valid for only a particular range of porosities and can potentially result in completely unreasonable results (Clauser and Huenges 1995), which was the case for the volume ratio, upper and lower limit equations (not shown). In most studies the average value of measurements from a few samples collected at different locations are assumed to be representative and adequate for the entire stream segment. At Teeterville the difference between a good fit and a best fit K_{fs} was only 33%, so spatial variability in K_{fs} values could have accounted for the deviations between simulated and observed flux.

4) Streambed temperature $T(z)$: Streambed temperatures typically should be measured at depths of between 0.2 m and 0.5 m. Measurements need to be below the zone of diurnal temperature oscillations but if taken too deep they might be taken where fluxes are non-unique because temperatures are essentially equal to groundwater temperatures (Figure 2.1). Deeper measurements also have the disadvantage that they are difficult to achieve everywhere especially if obstructions like gravel or cobbles are present. The analytical solution is sensitive to this parameter so ideally the probe should always be placed in exactly the same depth at each location. If a measurement has to be made at a shallower depth, a flux can still be calculated using the different z value.

2.6.3. Quasi-steady-state streambed temperature confirmation

To confirm that streambed temperatures are in quasi-steady-state condition it is recommended that streambed temperature measurements be repeated over time at several locations to show temperatures are staying constant (Conant Jr. 2004). Selected locations for temporal monitoring should cover the full range of fluxes at the site, but, at a minimum, should include low discharge locations since they are the most sensitive to surface water temperature fluctuations. Measurements of temperature versus depth profiles within the streambed over time at low flux locations (and other locations) are also a good way of directly demonstrating quasi-steady state conditions before and during mapping events. Transient temperature modeling using surface water temperatures can also be used to evaluate quasi-steady-state conditions. The VS2DH modelling in this study was helpful because it showed not only the diurnal changes in temperature at depth but also revealed long-phase temperature changes lasting a few days during the 20 day period prior to mapping (Figure 2.3b).

Simulations also showed quasi-steady-state conditions were not achieved for certain depths for low flux and even high flux conditions (e.g., at a depth of 0.1 m).

2.6.4. Limits of Applicability

Relating mapped streambed temperatures to vertical water fluxes is subject to several limitations previously described by Conant Jr. (2004). One fundamental limitation of the analytical approach is that it is limited to vertical upward flow and only quantifies groundwater discharge (not recharge) to a stream. The solution is not applicable to downward fluxes ($q_z < 0$) but it is possible to input temperatures into the analytical equation that are less than T_0 , which then result in the calculation of a negative flux. These negative fluxes are erroneous and should be rejected as invalid results and not mistakenly interpreted as true recharge (although negative values can still be used to indicate possible recharge conditions as shown in Figure 2.6). In general, mapping streambed temperatures at a single depth is not the appropriate method to reliably quantify downward fluxes. The method is also not applicable to horizontal hyporheic flow because that flow is not vertical. Another fundamental limitation occurs when streambed temperatures essentially equal groundwater temperatures and the relationship between water flux and temperature becomes asymptotic and non-unique. Based on Equation 2.3, the upper limit of flux ($q_z^{\max}$) can be easily calculated using Equation 2.5:

$$q_z^{\max} = -\frac{K_{fs}}{\rho c z} \ln \frac{(-1)^a T_{AC}}{T_0 - T_L} \quad [2.5]$$

where $a=1$ for $T_0 < T_L$ (winter) and $a=2$ for $T_0 > T_L$ (summer). T_{AC} is the accuracy of the temperature measurement equipment. This value represents the smallest temperature difference between T_L and $T(z)$ that can be detected. In other words, when $T(z)$ is within T_{AC} of the groundwater temperatures (T_L), $T(z)$ is essentially no longer a function of q_z . For the Teeterville dataset the upper limit of flux is $611 \text{ L m}^{-2} \text{ d}^{-1}$ for measurements taken at a 0.2 m depth, $T_{AC} = 0.1 \text{ }^\circ\text{C}$, and $K_{fs} = 1.5 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$. K_{fs} and $q_z^{\max}$ are proportional, therefore, the upper limit increases to $815 \text{ L m}^{-2} \text{ d}^{-1}$ when using the best-fit K_{fs} value of $2.0 \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$. It is possible to increase $q_z^{\max}$ and quantify even higher fluxes in high flux areas if the measurement depth is reduced since $q_z^{\max}$ and z are inversely proportional, but in low flux areas a reduction in measurement depth might result in questionable data if diurnal variations reach that depth.

2.7. Conclusions

The Turcotte and Schubert (1982) analytical solution to the one-dimensional steady-state heat advection-diffusion equation was successfully applied to two sets of mapped streambed temperatures to estimate groundwater discharge. Conant Jr. (2004) previously demonstrated that streambed temperature mapping could be used to delineate groundwater discharge zones

and, using Darcy's law fluxes obtained from mini-piezometers, developed an empirical relationship to convert streambed temperatures to fluxes. The analytical solution has significant advantages over the empirical approach because it can be applied without installing and testing mini-piezometers and it is a physically based model. The analytical solution is very simple, has minimal data requirements, and can be easily applied using a spreadsheet programme. The analytical method is simpler and less data intensive than the transient VS2DH numerical model and can provide reasonable results without calibration (i.e., directly inputting independently derived parameters such as K_{fs} from KD2 measurements). A key requirement for applying the Turcotte and Schubert (1982) solution is to assure streambed temperatures are quasi-steady-state during mapping. Transient VS2DH simulations of the Pine River data prior to and during streambed temperature mapping events showed that quasi-steady-state conditions did occur, but not under all circumstances. If streambed temperature measurements are too shallow or groundwater discharge fluxes are too low, diurnal variations or long-term trends in surface water temperatures may mean quasi-steady-state conditions are not achieved and the method will not provide reliable flux estimates. Continuous monitoring of surface water and/or streambed temperatures prior to and during mapping events is important way of assessing the quasi-steady-state condition without the need for transient modelling.

The streambed temperature versus flux curves produced by the analytical solution tended to underestimate higher fluxes for both the Pine River and Teeterville sites. For the Pine River site this mismatch was attributed to the Darcy's law flux data not being collected at the exact same time as the mapping data so deviations were caused by temporal changes in streambed conditions. The Teeterville mapping and seepage meter flux data set was superior to the Pine River site data and the analytical model's match to the data was good, but still somewhat underestimated the high fluxes. Differences were attributed to minor changes ($< 33\%$) in K_{fs} values caused by spatial heterogeneities in geological materials. High flux locations have high hydraulic conductivity deposits that are usually coarser grained materials that tend to have higher K_{fs} values. Increases in K_{fs} values at these locations would account for the differences and improve the model fit to the data. Although sensitive to K_{fs} , the degree of sensitivity is a function of the magnitude of the flux, but overall the solution is linearly related to K_{fs} and is more sensitive to T_L than T_0 (so monitoring of deeper groundwater temperatures is important). The analytical solution has some limitations (e.g., flow of water should be vertical and the solution becomes non-unique at very high fluxes) but the range of its applicability is easily defined. Overall the method is quite simple, inexpensive to implement, and relatively robust and can be a valuable and appropriate tool for estimating groundwater discharge along stream or river reaches.

Chapter 3

Characterization of spatial heterogeneity of groundwater-stream water interactions using multiple depth streambed temperature measurements at the reach scale

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3.1. Abstract

Streambed temperatures can be easily, accurately and inexpensively measured at many locations. To characterize patterns of groundwater-stream water interaction with a high spatial resolution, we measured 140 vertical streambed temperature profiles along a 220 m section of a small man-made stream. Groundwater temperature at a sufficient depth remains nearly constant while stream water temperatures vary seasonally and diurnally. In summer, streambed temperatures of groundwater discharge zones are relatively colder than downwelling zones of stream water. Assuming vertical flow in the streambed, the observed temperatures are correlated to the magnitude of water fluxes. The water fluxes are then estimated by applying a simple analytical solution of the heat conduction-advection equation to the observed vertical temperature profiles. The calculated water fluxes through the streambed ranged between $455.0 \text{ L m}^{-2} \text{ d}^{-1}$ of groundwater discharging to the stream and approximately $10.0 \text{ L m}^{-2} \text{ d}^{-1}$ of stream water entering the streambed. The investigated reach was dominated by groundwater discharge with two distinct high discharge locations accounting for 50% of the total flux on 20% of the reach length.

3.2. Introduction

Understanding and quantifying physical processes and ecological implications of groundwater surface water interaction is becoming an important subject in hydrogeological and river ecological studies. Stream water and groundwater can interact on a wide variety of scales down to heterogeneities within metres to centimetres (Brunke and Gonser 1997, Woessner 2000). Investigation of groundwater-stream water interactions (water fluxes through the streambed, hyporheic flowpaths, subsurface flow velocities and travel times) can be classified according to “where-you-stand” as viewing interactions from the stream or the subsurface (Packman and Bencala 2000). In studies where the point of view is from the stream, the hyporheic exchange is often the focus. Hyporheic exchange is the downwelling of stream water into shallow sediments and the return to the stream after a certain distance.

These flow systems transport oxygenated stream water, nutrients and dissolved organic carbon into the hyporheic zone. This leads to increased microbial activity and significantly influences the nutrient and carbon cycling in stream systems. Nonetheless, the continuous hyporheic exchange also affects the downstream transport and fate of contaminants.

Various studies incorporating different methods have analyzed hyporheic exchange. Deterministic approaches have shown that stream morphologic features can induce advective flow from the surface to the subsurface. Theory, laboratory experiments and field studies have investigated the influence of scale (cm to tens of m) and shape of bedforms and stream morphology on flowpaths, pore flow velocities and residence times of surface water in the hyporheic zone (Thibodeaux and Boyle 1987, Elliott and Brooks 1997 a, b, Cardenas et al. 2004, Storey et al. 2003, Salehin et al. 2004, Saenger et al. 2005, Anderson et al., 2005, Gooseff 2005). In general, an increased bed form wavelength and amplitude leads to increased depths and lengths of hyporheic flow paths for vertical features like pool and riffle sequences. The presence of meanders, secondary streams and streamsplits induce lateral near stream flow paths (Harvey and Bencala 1993, Wroblicky et al. 1998, Kasahara and Wondzell 2003). In this study, the interactions are viewed from the subsurface. As Storey et al. (2003) suggested, groundwater discharge can have a significant impact on the extent of the hyporheic zone and can affect the distribution of benthic and hyporheic fauna (Brunke and Gonser 1997). In a modelling study Cardenas et al. (2006) underlined the importance of groundwater discharge for the flow systems and the biogeochemistry at the stream-groundwater interface. Temporal changes of hydraulic gradients between an aquifer and a stream can alter the near stream groundwater flow field and the magnitude of both downwelling streamwater and upwelling groundwater (Wroblicky et al. 1998). Furthermore, it becomes essential to consider the spatial patterns and magnitude of groundwater discharge when the transport and the fate of contaminants from the aquifer to the stream has to be assessed (Conant Jr. et al. 2004, Conant Jr. 2004). Independently from the point of view of the investigation, whether from the stream or the subsurface, it is crucial to consider the spatial distribution and the magnitude of groundwater discharge to a stream. In general, a variety of factors from the catchment scale to single bedforms are controlling the interactions of groundwater and stream water. As a result of different mechanisms, flow patterns within the streambed can vary on small spatial scales. Investigations at the stream reach scale which consider small-scale patterns of flow require a high density monitoring network. Due to instrumentation and measurement effort, such studies are often limited to a relatively small spatial extent (Baxter and Hauer 2000). Thus there is a need for an inexpensive, quantitative method that has the capability to characterize the spatial heterogeneity of groundwater-stream water interactions. The characterization of spatial patterns of flow at the groundwater surface water interface requires a measurement concept that allows many measurements with high spatial resolution during a relatively short period of time. The horizontal and vertical temperature distribution in the streambed is a result of heat transport by the flowing water (advective heat flow) and by heat conduction through the sediment grains and the pore water (conductive heat flow) of the saturated

sediments. While groundwater temperature remains nearly constant at the mean annual air temperature at a sufficient depth, stream water temperatures vary seasonally and diurnally. For example, in summer, streambed temperatures in groundwater discharge zones should be relatively colder than in stream water downwelling zones. The streambed temperature measurements coupled with an appropriate model can be used as a surrogate for head and hydraulic conductivity measurements (Anderson 2005). Analytical solutions to solve the heat transport equation for water flux were developed in the 1960s (Suzuki 1960, Stallman, 1965, Bredehoeft and Papadopolus 1965). In recent years there have been several applications of temperature profiles for estimating magnitude and direction of water flow at the groundwater surface water interface (e.g., Bartolino and Niswonger 1999, Constantz et al. 2003, Lapham 1989, Silliman et al. 1995, Stonestrom and Constantz 2003). Conant Jr. (2004) was the first who showed that streambed temperatures measured in a short period of time at many locations can be related to spatial variations of groundwater discharge. In contrast to the work of Conant Jr. (2004) who correlated mapped streambed temperatures with water fluxes estimated from 34 streambed piezometers and Darcy's law calculations, we used temperature measurements for direct estimation of water fluxes across the streambed.

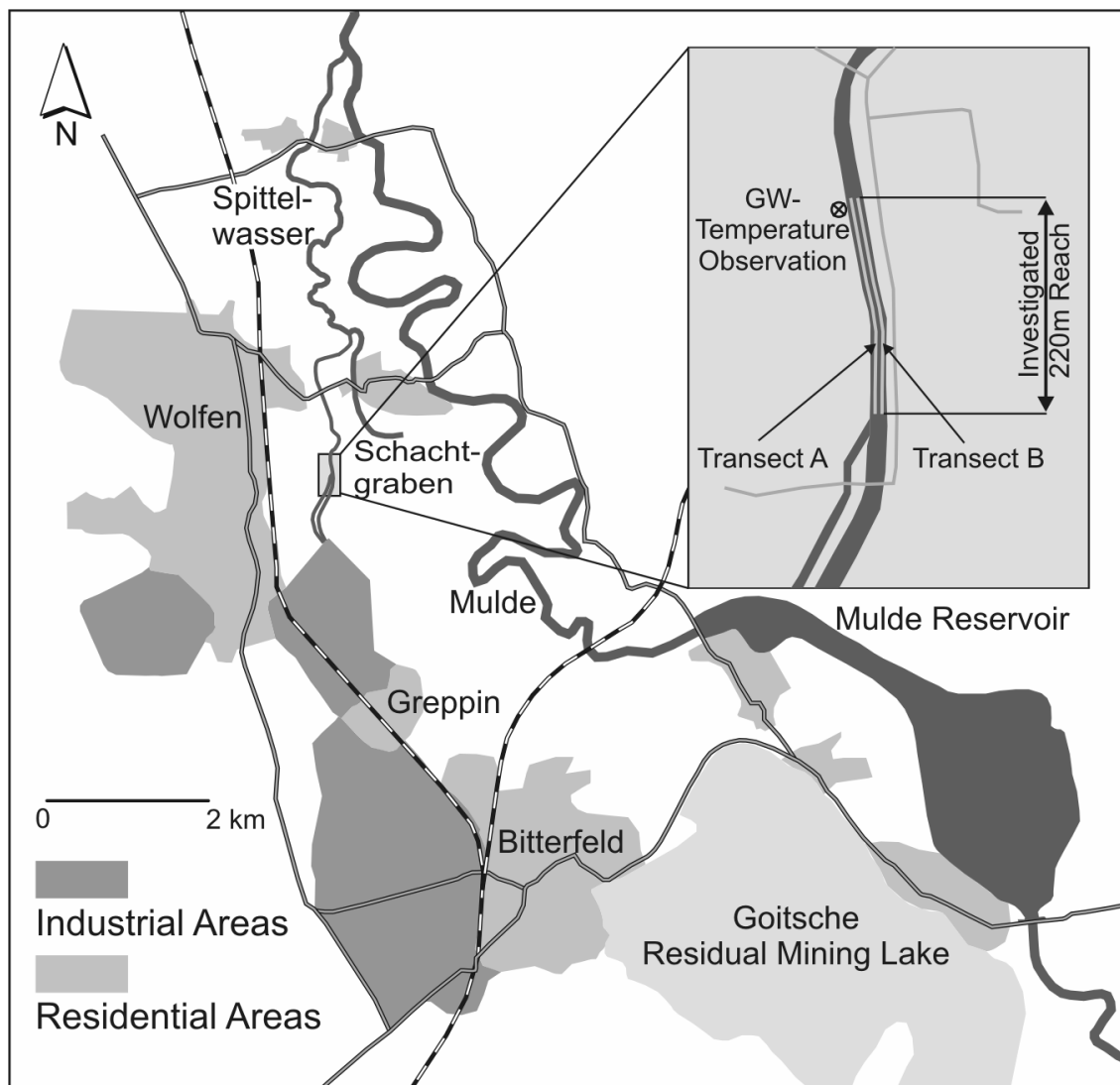


Figure 3.1. Overview of the Bitterfeld-Wolfen region, showing the location of the Schachtgraben and illustrating the position of the investigated transects.

In this study, we show that streambed temperatures can be used to delineate patterns of groundwater discharge to a stream in fine detail on the scale of stream reaches with lengths of hundreds of metres. On the basis of the observed streambed temperature profiles, the vertical water fluxes through the streambed were quantified by applying a simple one dimensional analytical model of the heat advection-conduction equation.

3.3. Study site

The temperature measurements were carried out along a 220 m long reach of the Schachtgraben near the town of Wolfen (Figure 3.1). The Schachtgraben is a man-made channel with a regular width between 2.5 and 3m. The mean annual stream discharge is 0.2 m³/s and the gradient is 0.0008 m/m. For the past one hundred years, Wolfen has been a major chemical industry site in Germany. In the second half of the 20th century the spectrum of products was extended to 5000 substances, including chlorinated solvents, pesticides and plastics (Walkow 1996, Chemie AG Bitterfeld-Wolfen 1993). The deposition of contaminated waste products in abandoned lignite pit mines nearby the production sites as well as inappropriate handling and transport of chemicals and war damages led to a large scale contamination (25 km²) of groundwater, soils, surface water and floodplain sediments (Heidrich et al. 2004). For decades, untreated process waste waters were discharged via the Schachtgraben and the Spittelwasser into the Mulde River which is a tributary of the Elbe River. The Schachtgraben channel is located in the Mulde River floodplain system. The channel cuts the floodplain sediments and is located in the sediments of the shallow Quaternary aquifer. The channel bed itself is constructed of a homogeneous coarse gravel layer of 0.4 m thickness. Groundwater levels in the adjacent unconfined aquifer are generally 0.1 to 0.2 m higher than the water level in the stream. The shallow aquifer is composed of Weichselian glacio-fluvial sandy gravels. Today streambed sediments and the groundwater in the adjacent aquifer and in the streambed sediments are contaminated with a wide range of substances but mainly with chlorinated benzenes and hexachlorocyclohexanes. Further downstream in the Spittelwasser floodplain, sediments were found to be contaminated with polychlorinated naphthalenes and dioxins (Brack et al. 2003, Bunge et al. 2003, Walkow 2000). The investigated reach of the Schachtgraben and the Mulde River floodplain are the subject of additional studies concerning water flow as well as transport and fate of heavy metals and organic contaminants at the interface between groundwater and surface water.

3.4. Field methods

3.4.1. Temperature measurements

The streambed temperatures were measured along two longitudinal transects in a four day measuring programme from August 30 until September 2, 2005. The longitudinal transects were located at one third and two thirds of the total river width. The programme consisted of

140 measurements with 70 for each transect. Streambed temperatures were measured using a multilevel stainless steel temperature probe with attached data logger (TP 62, Umwelt Elektronik GmbH; Geislingen, Germany). The probe was temporarily inserted into the streambed to a depth of 0.5 m. Along the probe five temperature sensors are placed in a way that the temperatures are simultaneously measured at 0.1 m, 0.15 m, 0.2 m, 0.3 m and 0.5 m below the streambed surface when the end of the probe is positioned in the depth of 0.5 m (Figure 3.2). The measurements were generally taken with 3 m spacing but were refined between locations with high temperature differences. During the study, stream temperatures were measured hourly using a self containing Stowaway TidbiT -5 to 37 °C range temperature logger (Onset Computer Corporation, Pocasset, Massachusetts). Groundwater temperature was observed hourly with temperature and pressure transducers placed directly into the aquifer with a vertical spacing of 1 m between depths below ground surface of 1 m to 5 m (Figure 3.3). It was assumed that groundwater and surface water temperatures were spatially uniform and representative for the entire reach. Air temperature data was provided from a meteorological station in Bitterfeld (Figure 3.3).

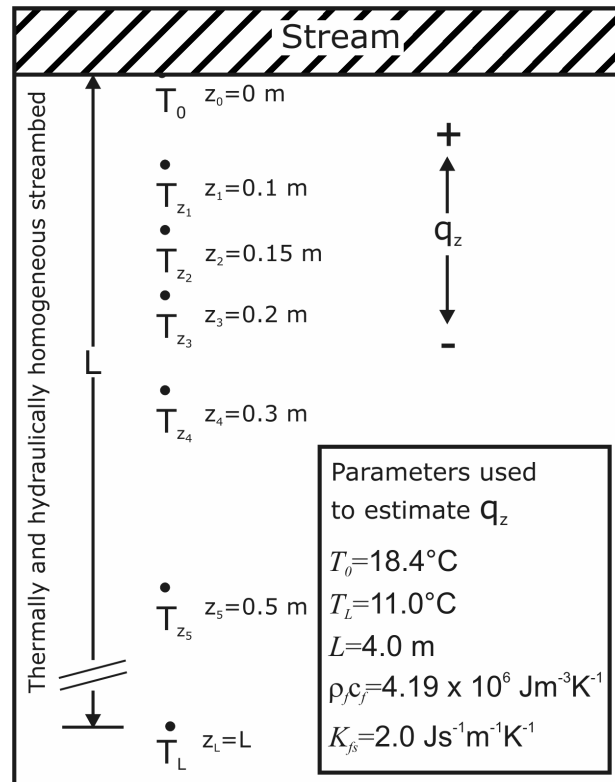


Figure 3.2. Concept of vertical temperature profiles, boundary conditions and parameters used for the analytical model

3.4.2. Piezometer installation and slug testing

To confirm the fluxes obtained from the streambed temperature profiles with an independent method, streambed piezometers were installed to gain information on hydraulic gradients and hydraulic conductivity. Locations were chosen according to high and low groundwater discharge zones indicated by the observed temperatures (high discharge locations: P2, P4, P5 P7; low discharge locations: P1, P3, P6). One pair of piezometers (P4,

P5) was installed at a distinct groundwater discharge location at Transect A with 1 m spacing to obtain the small scale heterogeneities of streambed hydraulic properties and fluxes.

The piezometers consist of 1.6 m long HDPE (high density polyethylene) pipes with 0.04 m outside diameter. The 0.2m screened section of each piezometer was installed between 0.3 and 0.5 m below the streambed surface. The hydraulic head differences between the stream surface and the piezometers were estimated following the method of Baxter et al. (2003). To obtain the hydraulic head differences, an additional open pipe was attached outside the piezometer (“stilling well”) to minimize the influence of turbulence on stream water elevation. The hydraulic head difference was measured using parallel chalked wires connected at the top. The chalked wires were inserted into a piezometer and the attached stilling well and after removal the distance between the water marks was measured.

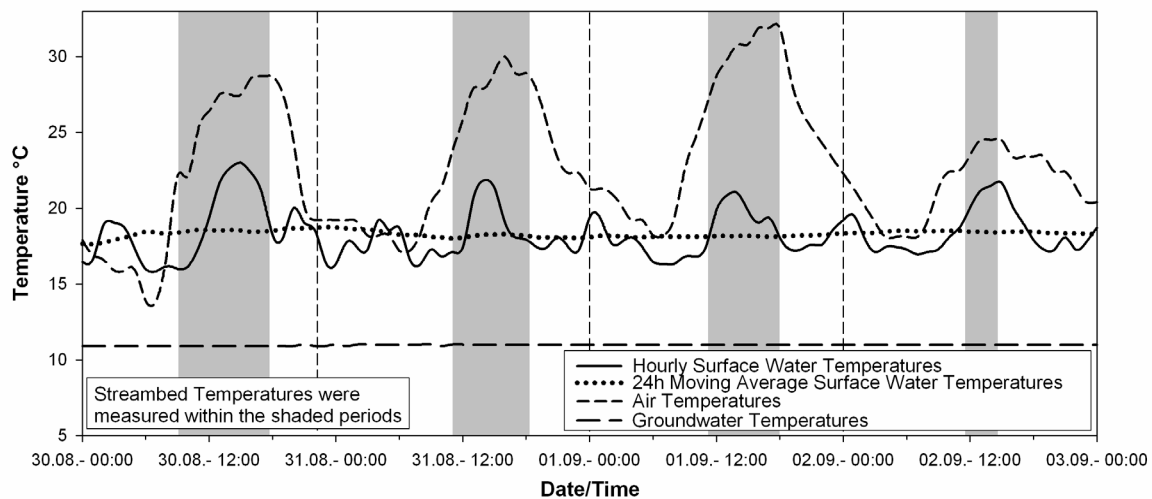


Figure 3.3. Surface water, air and groundwater temperatures during the four day measurement programme in August/September 2005

Each piezometer was tested twice with a falling and rising head slug test. Rising head slug tests were performed by removing the water from the piezometer using an Eijkelkamp 12V peristaltic pump (Eijkelkamp, Giesbeek, The Netherlands). Falling head slug tests were carried out by releasing water from an attached reservoir at the top of the piezometers. The rise and fall of the water level in the piezometers was observed with an “HT 575 Kompakt” pressure transducer (Hydrotechnik GmbH, Obergünzburg, Germany).

3.4.3. Analytic procedure

Streambed temperatures have a highly transient character due to seasonal and diurnal changes of stream water temperatures. It is essential for the concept of streambed temperature mapping that differences of temperature can be attributed to spatial differences of water fluxes and are not a result of temporal variations. Streambed temperatures measured at a sufficient depth below the influence of diurnal variations represent the quasi - steady - state conditions of streambed temperatures for the finite time of the mapping programme.

With the assumption that water flow in the streambed is essentially vertical, the governing equation for one-dimensional conductive and advective heat transport is:

$$\frac{K_{fs}}{\rho c} \nabla^2 T_z - \frac{\rho c_f}{\rho c} \nabla \cdot (-q_z T_z) = \frac{\partial T}{\partial t} \quad [3.1]$$

where T_z [$^{\circ}\text{C}$] is the streambed temperature at depth z (positive downward); t is time [s]; q_z is the vertical Darcy velocity [m s^{-1}] (positive upward); ρc is the volumetric heat capacity of the solid - fluid system which can be written as $\rho c = n\rho c_f + (1-n)\rho_s c_s$ where $\rho_f c_f$ is the volumetric heat capacity of the fluid, $\rho_s c_s$ is the volumetric heat capacity of the solids [$\text{J m}^{-3} ^{\circ}\text{C}^{-1}$] and n is the porosity [-]. K_{fs} is the thermal conductivity of the saturated sediment [$\text{J s}^{-1} \text{m}^{-1} \text{K}^{-1}$].

With boundary conditions $T = T_0$ for $z = 0$, and a fixed temperature T_L for $z = L$, where L [m] is the vertical extent of the domain, the solution of Equation 3.1 can be obtained as (Bredehoeft and Papadopolus 1965):

$$\frac{T(z) - T_0}{T_L - T_0} = \frac{\exp\left(\frac{-q_z \rho_f c_f}{K_{fs}} z\right) - 1}{\exp\left(\frac{-q_z \rho_f c_f}{K_{fs}} L\right) - 1} \quad [3.2]$$

Equation. 3.2 can be solved for q_z for a given L . It is assumed that the vertical temperature distribution at different locations is only a function of q_z , i.e. other parameters on the right- hand side of Equation 3.2 are considered to be homogeneous for all observed temperature profiles. The objective function for obtaining q_z is given with:

$$Error_k(L) = \sum_{j=1}^5 \left[T_{jk} - \frac{\exp\left(\frac{-q_{z_k} \rho_f c_f}{K_{fs}} z_j\right) - 1}{\exp\left(\frac{-q_{z_k} \rho_f c_f}{K_{fs}} L\right) - 1} (T_L - T_0) + T_0 \right]^2 \quad [3.3]$$

where q_{z_k} is the value of q_z that minimizes $Error_k(L)$ for a given L at each temperature profile consisting of $j=5$ temperature observations.

It was tested if a change of L has an influence on the estimated q_z and the quality of the fit. The objective function to find one optimal L for all observed temperature profiles implies the optimization of $Error_k(L)$. We computed an optimal q_{z_k} at each profile k for the overall L ranging between 0.6 and 10 m. For $k=140$ observed temperature profiles, the objective function is given with:

$$f(L) = \sum_{k=1}^{140} [Error_k(L)] \quad [3.4]$$

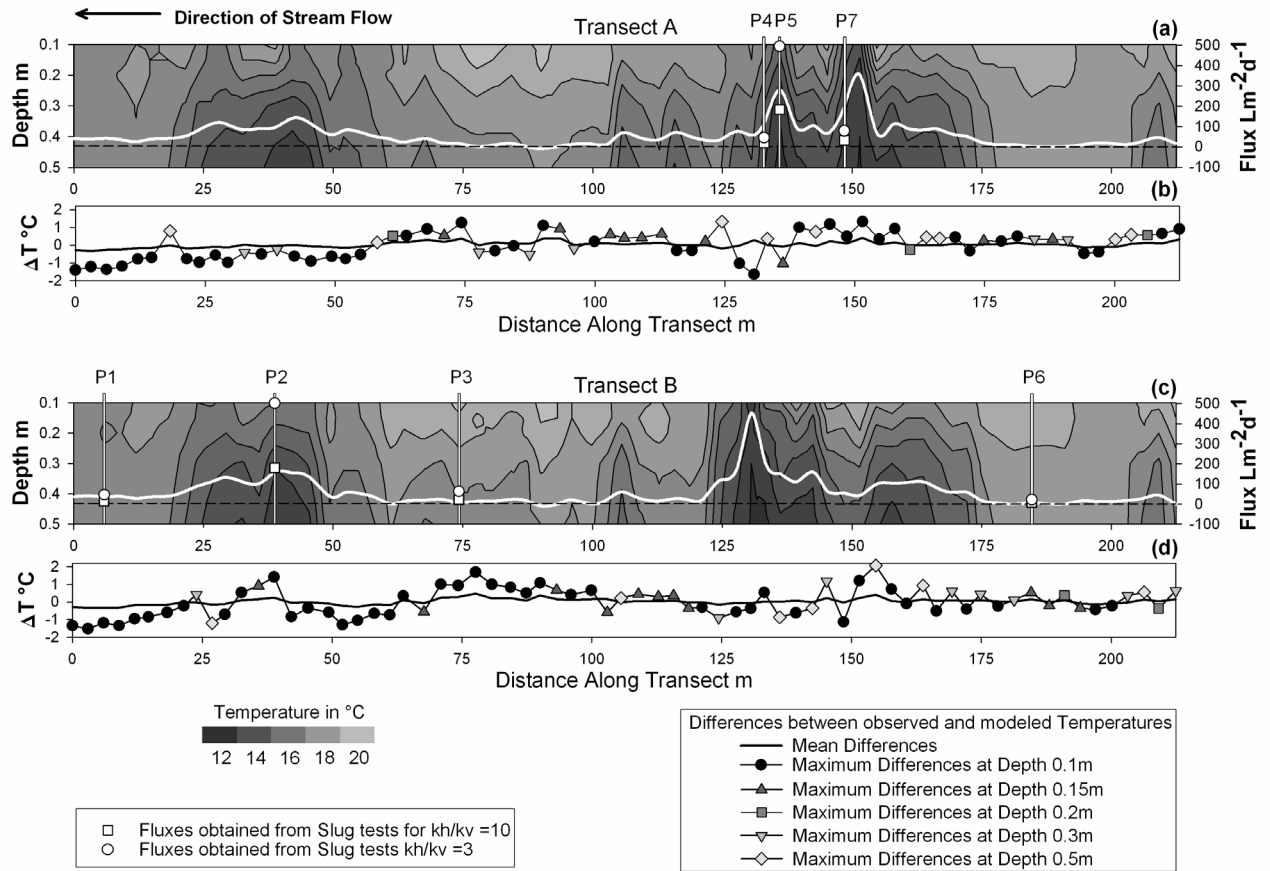


Figure 3.4. Temperature distribution, temperature based fluxes, the locations of streambed piezometers, and the fluxes from Darcy's law calculations at each piezometer for different anisotropy ratios along Transects A (a) and B (c), Note the vertical exaggeration of the longitudinal profile by factor 50. Mean and maximum differences between observed and simulated temperatures for each temperature profile for Transects A (b) and B (d) The maximum difference is given with the respective depth.

Once the optimal q_z for a chosen L is obtained from Equation 3.3, q_z can be substituted into Equation 3.2 to obtain a simulated streambed temperature distribution. To test the quality of fit between observed and simulated temperatures, the difference of temperatures ΔT [°C] can be obtained from Equation 3.5:

$$\Delta T = T(z) - \frac{\exp\left(\frac{-q_z \rho_f c_f}{K_{fs}} z\right) - 1}{\exp\left(\frac{-q_z \rho_f c_f}{K_{fs}} L\right) - 1} (T_L - T_0) + T_0 \quad [3.5]$$

3.5. Results and discussion

3.5.1. Stream water, groundwater and air temperatures

During the field programme, the stream water temperatures showed variations with a low of 15.8 and a high of 23.0 °C (Figure 3.3). The dotted line in Figure 3.3 illustrates the 24 h

moving average of stream water temperatures. It varies only between 17.6 °C and 18.6 °C around the overall average of 18.4 °C during the field campaign. This indicates that the temperature oscillations are of diurnal character. The temperature regime is characterized by anthropogenic influences which become apparent in temperature peaks in the early morning (Figure 3.3)

Groundwater temperatures were observed in hourly intervals at depths between 1 and 5 m below the streambed surface, adjacent to the stream (Figure 3.1). At depths of 4 and 5 m the groundwater temperatures are 11 °C. Temperatures increase to 15 °C at a depth of 1 m below the streambed surface. The groundwater temperatures were measured at a location close to a zone of relatively high streambed temperatures. Thus the shallow groundwater temperatures correspond well with the streambed temperatures of 16.8 °C at a depth of 0.5 m. The coldest streambed temperatures are nearly identical to groundwater temperatures observed at a depth of 4 m.

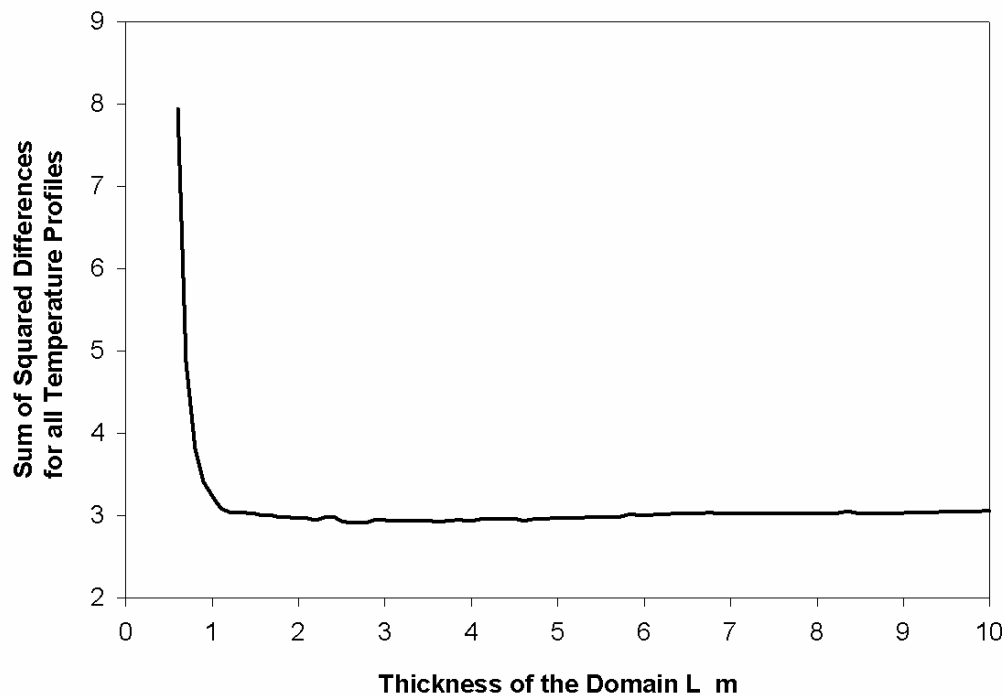


Figure 3.5. Sum of squared errors of all temperature profiles vs. the thickness of the domain L . The results show that for the given parameter set, the quality of fit and the derived vertical fluxes are essentially constant for $L > 1.0$ m.

The air temperatures were observed in a meteorological station in Bitterfeld 6.5 km south of the study site. During the field programme the air temperatures varied between 13.9 and 31.9 °C with an average of 22.7 °C (Figure 3.3).

3.5.2. Streambed temperatures

The observed streambed temperatures varied spatially between 11.5 and 17.5 °C at a depth of 0.5 m in the streambed. At the shallow depth of 0.1 m, the temperatures showed a wider

range and a higher minimum and maximum of 12.2 and 19.9 °C. In summer, groundwater discharge is indicated by relatively low streambed temperatures. Along the observed 220 m reach, two major groundwater discharge zones were identified. The first discharge zone is located between 20 and 50 m and the second between 125 and 170 m (Figure 3.4).

The discharge zones are characterized by streambed temperatures at 0.5 m being less than 15 °C. Within the second discharge zone, there are distinct locations showing temperatures less than 13 °C at 0.5 m depth and even at 0.1 m depth, temperatures are less than 15 °C (Figure 3.4). These distinct locations of very low temperatures are restricted to a length of 3 to 5 m. Both major discharge zones have a very similar spatial extent.

Along both longitudinal transects, very similar patterns of streambed temperature are visible. Variations of streambed temperatures occur primarily and along each reach while the differences between the eastern and western bank are of minor significance.

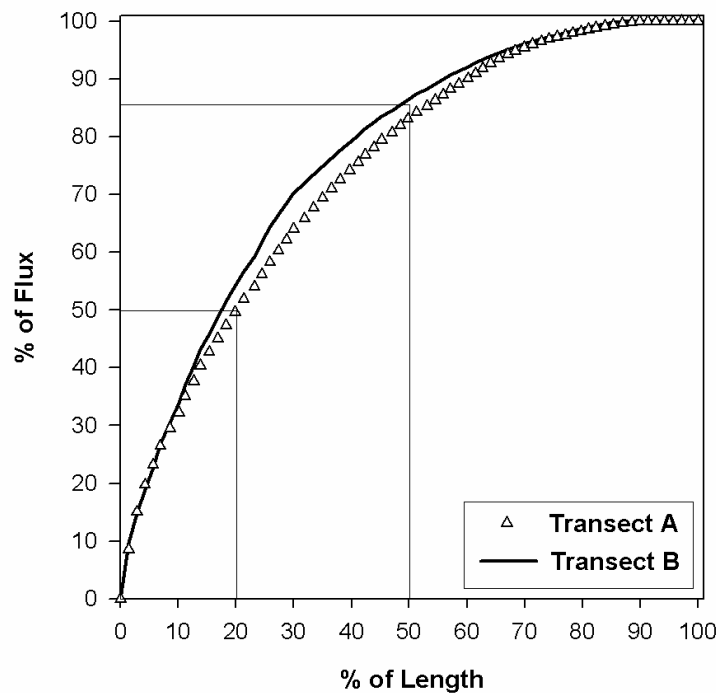


Figure 3.6. Percentage of flux vs. percentage of length of the Transects A and B. Approximately 50% of the total flux occur on 20% of the total length.

3.5.3. Fluxes obtained from temperature profiles

As temperature can be easily measured at hundreds of locations, the water fluxes in the streambed can be estimated with a high spatial resolution. The water fluxes were obtained at each location from Equation 3.2 by minimizing the differences between observed and modelled temperature profiles (Equation 3.3). At each temperature profile, q_z was estimated for L ranging from 0.6 to 10 m. It was found that q_z for L larger than 1.0 was essentially independent from L (Figure 3.5). The resulting fluxes are not influenced by the depth at

which T_L is obtained as long as T_L remains constant with the increasing depth. This is basically the case when upward flow from groundwater to surface water is present. The observed groundwater temperature at a depth of 4 m below the streambed surface was 11.0 °C and was constant during the measuring campaign. Hence, the lower boundary condition T_L was set to 11.0 °C. The upper boundary condition T_0 was set to 18.4 °C which is the average stream water temperature of the four-day mapping period. Equation 3.2 requires the thermal conductivity K_{fs} as an input parameter which was not measured within this study. However, the range of thermal conductivities of water saturated sediments is small thus K_{fs} can be reliably estimated and was set to 2.0 J s⁻¹ m⁻¹ K⁻¹ (Stonestrom and Blasch 2003). The parameter set used for estimating q_z from the observed temperature profiles is summarized in Figure 3.2.

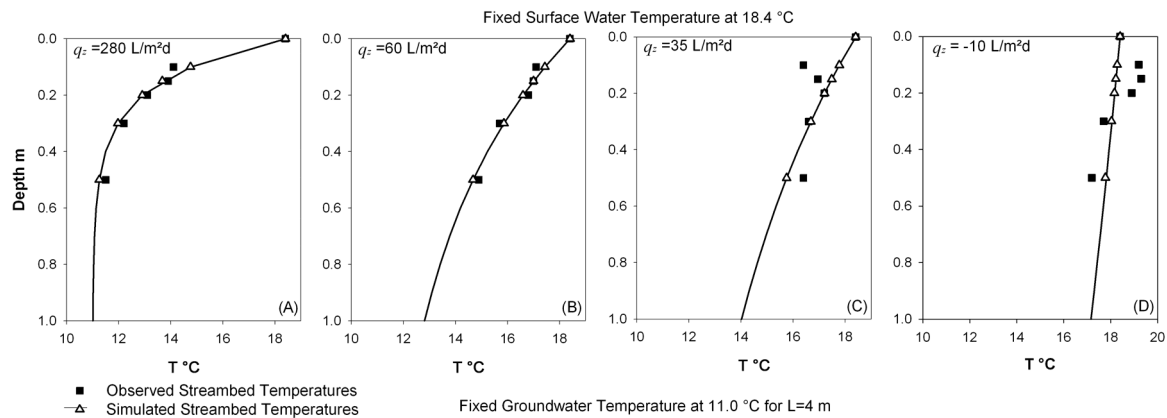


Figure 3.7. Comparison of observed and simulated streambed temperatures for three example profiles. The illustrated profiles represent high (A), medium (B) and low (C) groundwater discharges and are located proximal to the positions of streambed piezometers P5 (A), P4 (B) and P1(C).

The resulting water fluxes ranged between -10.0 and 455.0 L m⁻² d⁻¹ (Figure 3.4a and Figure 3.4c). The average groundwater discharge is 58.2 L m⁻² d⁻¹ and the average recharge is 2.3 L m⁻² d⁻¹. Figure 3.4a and Figure 3.4c illustrate the spatial distribution of fluxes in relation to the length of the observed reach. Analogous to the temperatures, the flux distribution is very similar in the two longitudinal transects. Recharge occurs only along less than 1 % of the reach. The zones with discharges higher than 100 L m⁻² d⁻¹ are present on 16% of the total length of Transect A and on 19% of Transect B. Approximately 20% of the total length contributes 50% of the total discharge (Figure 3.6). Around 85% of the total discharge occurred at 50% of the total length (Figure 3.7) Only four profiles were observed to have discharges higher than 200 L m⁻² d⁻¹ which contribute about 10 % to the total discharge (Figure 3.4a and Figure 3.4c). These relations as well as the order of magnitude of fluxes are comparable to those observed by Conant Jr. (2004). Spatially distinct high discharge zones were also observed in other studies but with higher maximum discharges (Baxter and Hauer 2000, Conant Jr. 2004). Yet the maximum discharges are more than 4 times higher than the average discharge. The reduced spread of fluxes compared to natural rivers can be explained

with a reduced streambed heterogeneity in terms of morphologic features and hydraulic properties. According to the maximum fluxes, the homogeneous streambed might lead to less significant preferential flowpaths and thus to lower maximum fluxes. The observed heterogeneities are likely to be also controlled by zones of preferential flow in the underlying aquifer. Highest discharges will occur at locations where permeable zones of the streambed are connected to high hydraulic conductivity zones in the aquifer (Conant Jr. 2004). There are studies addressing the significant role of aquifer heterogeneity for the magnitude and spatial distribution of flow from the stream to the subsurface in losing stream reaches (Fleckenstein et al. 2007, Bruen and Osman 2004). As the work of Conant Jr. (2004) and Conant Jr. et al. (2004) indicates aquifer heterogeneity will have an analogous effect in gaining streams but it has not been examined in a theoretical study to date.

Recharge occurs only at few locations and at low flow rates (up to $10 \text{ L m}^{-2} \text{ d}^{-1}$). Admittedly, in these cases the fit of the analytical solution to the observed streambed temperatures is rather poor (Figure 3.7d). Thus the estimated recharges are associated with high uncertainty, in particular with regard to the observed vertical hydraulic gradients in the streambed piezometers and the water table elevation adjacent to the Schachtgraben channel which indicate a gaining reach. Moreover, Storey et al. (2003) reported that a streambed hydraulic conductivity below 10^{-4} m s^{-1} will result in a restricted topographically induced downwelling of water. Downward flow can occur at pool and riffle structures and at smaller spatial scales at streambed ripples (Thibodeaux and Boyle 1987) and obstructions (Hutchinson and Webster 1998). Because of the artificial origin of the homogeneous gravel streambed, natural pool and riffle sequences are assumed not to be present at the Schachtgraben. Consequently, the combination of a streambed with no apparent geomorphological heterogeneity and low streambed hydraulic conductivities leads to the observed low recharge fluxes. It is likely that if downwelling of stream water occurs it will be mainly due to streambed roughness induced by the single gravel grains. Since hyporheic flowpaths are related to the vertical extent of the streambed morphologic features, hyporheic flow in the Schachtgraben can only occur in the upper few centimetres of the streambed.

In conclusion, the interactions of stream and groundwater at this site are dominated by groundwater discharge at distinct locations. Morphological features like pool and riffle structures or obstructions were not apparent at the investigated reach. Because of the artificial origin the streambed appeared to be relatively homogeneous in its hydraulic properties. Therefore, it is likely that the observed spatial heterogeneities of groundwater discharge are not solely controlled by the streambed. High permeable zones of the underlying aquifer connected to the streambed are expected to significantly influence the observed discharge patterns.

The mean difference between all observed and simulated temperatures is 0.023°C at Transect A and 0.028°C at Transect B. The highest calculated difference at Transect A was 2.1°C , located at a depth of 0.1m and at was -1.6°C Transect B also at a depth of 0.1m (Figure 3.4b and Figure 3.4d).

Table 3.1. Hydraulic conductivities, hydraulic gradients and vertical fluxes obtained from slug-tests using streambed piezometers

Name	Horizontal Hydraulic Conductivity K_h ms ⁻¹	Vertical Hydraulic Gradient	Vertical Hydraulic Conductivity K_v ms ⁻¹ for $K_h / K_v = 3$	Vertical Flux q_z L m ⁻² d ⁻¹ for $K_h / K_v = 3$	Vertical Hydraulic Conductivity K_v ms ⁻¹ for $K_h / K_v = 10$	Vertical Flux q_z L m ⁻² d ⁻¹ for $K_h / K_v = 10$
P1	2.38E-05	0.070	7.92E-06	47.9	2.88E-06	17.4
P2	5.82E-05	0.295	1.94E-05	494.6	7.04E-06	179.5
P3	1.99E-05	0.113	6.63E-06	64.4	2.41E-06	23.4
P4	1.20E-05	0.113	4.01E-06	39.0	1.46E-06	14.1
P5	6.87E-05	0.245	2.29E-05	484.6	8.31E-06	175.9
P6	1.36E-05	0.063	4.52E-06	24.4	1.64E-06	8.9
P7	5.82E-05	0.043	1.94E-05	71.9	7.04E-06	26.1

3.5.4. Differences between observed and simulated temperatures

At both transects, although the observed patterns of temperatures were very similar, the highest differences between simulated and observed temperatures occurred at different locations. The differences are clearly related to certain depths but seemed to be randomly distributed along the transects (Figure 3.4). At 82 out of 140 temperature profiles (58.6%), the maximum difference between observed and simulated temperatures occurs at 0.1m depth. At the other depths of 0.15 m, 0.2 m, 0.3 m and 0.5 m the maximum differences are similarly distributed, respectively 13.6%, 5.9%, 11.4% and 11.4%. This distribution of differences indicates that there is an influence of diurnal stream water temperature oscillations at the shallow depth of 0.1m, disturbing the quasi-steady-state profile. As well it is possible that shallow, non-vertical hyporheic flow paths could have influenced the upper 0.1m of the streambed. Figure 3.7 illustrates examples of simulated temperature profiles after q_z was obtained from observed temperatures using Equation 3.3 and the related observed temperatures at $T(z)$. A recalculation of fluxes excluding the temperature measurements at a depth of 0.1 m showed that there is no significant influence for low and medium fluxes. At high flux locations the resulting fluxes decrease when the shallowest measurement is excluded. For example the calculated maximum flux is reduced from 455 to 325 L m⁻² d⁻¹ without the temperature at 0.1 m depth. Although there are indications that temperatures within 0.1 m are influenced by diurnal temperature oscillations in the surface water, there is no evidence for an increased uncertainty in the resulting fluxes. In particular for groundwater discharge, where streambed temperatures change from groundwater temperature to stream water temperature in the upper few centimetres of the streambed, it is essential to have an observation point at a shallow depth.

3.5.5. Verification of flux calculations with piezometer data

A total of 7 streambed piezometers was installed and tested to confirm the magnitude of water fluxes obtained from the temperature profiles (Figure 3.4a and Figure 3.4c). The

observed head differences Δh between the streambed and the aquifer indicated an upward flow direction at all streambed piezometers. The maximum Δh occurred at piezometer P2 with 0.118 m, the minimum Δh at piezometer P7 with 0.017 m. The vertical hydraulic gradient was obtained by dividing Δh with Δl which is the length between the centre of the piezometer screen and the top of the streambed. All piezometers were installed at the same depth in the streambed and thus Δl is 0.4 m at all piezometer locations. The resulting vertical hydraulic gradients are between 0.043 and 0.295.

Streambed hydraulic conductivities were estimated from rising and falling head slug tests using the Hvorslev (1951) case G, basic time lag equation. Horizontal hydraulic conductivities K_h varied within a relatively small range of one order of magnitude between $1.39 \cdot 10^{-4}$ and $1.26 \cdot 10^{-5} \text{ ms}^{-1}$. As the cobbly streambed makes it impossible to install permeameters to obtain the vertical hydraulic conductivity K_v in the field, the anisotropy ratio has to be estimated. Freeze and Cherry (1979) gave an anisotropy ratio of core samples K_h / K_v between 3 and 10. The resulting hydraulic conductivities are within the range given by Calver (2001) and lower than the vertical hydraulic conductivities observed by Chen (2004)

Employing both an anisotropy ratio of 3 and 10, the resulting fluxes based on the piezometer data are within one order of magnitude of the fluxes obtained from the temperature data (Table 3.1 and Figure 3.4). In general, the fluxes obtained from Equation 3.2 correspond reasonably well with the fluxes obtained from Darcy's law calculations. At piezometer locations P3 and P5, fluxes calculated with an anisotropy ratio of 3 overestimate the temperature based fluxes while fluxes based on an anisotropy ratio of 10 underestimate them.

3.5.6. Applicability and limitations

Using streambed temperatures to quantify groundwater-stream water interactions is limited to locations and time periods where groundwater and stream water have sufficient temperature differences which is normally the case in summer or winter. The best conditions to perform the temperature measurements are given if during the measurements the surface water temperatures vary solely diurnal (no ambient trend), the surface water temperature maximum (winter) or minimum (summer) does not reach groundwater temperature.

In this approach the conceptualization of water fluxes in the streambed is based on the assumption of vertical flow. In streams with intense non-vertical hyporheic flow in the streambed, the presented approach may not be valid. At locations with a very high groundwater discharge, streambed temperatures can be nearly equal to groundwater temperature. If the flux is doubled or tripled, the temperature will remain the same (Conant Jr. 2004). Lapham (1989) states if upward fluxes exceed $305 \text{ L m}^{-2} \text{ d}^{-1}$ (1 ft d^{-1}) the temperature in the streambed would be equal the groundwater temperature and remain unaffected by fluctuations in stream temperature. We observed higher magnitudes of fluxes (up to $455 \text{ L m}^{-2} \text{ d}^{-1}$). The constraints depend strongly on the

depths in which the measurements were taken. We observed in depths of 0.3 and 0.5 m below the streambed surface that streambed temperatures can be nearly equal to groundwater temperatures. This never occurred in depth of 0.15 or 0.1m. With a decreased measurement depth the magnitude of fluxes that can be accurately quantified can be increased.

A similar behaviour occurs for high downward fluxes. In these cases, the observed streambed temperatures can be essentially equal to stream water temperatures. At these particular locations the calculated fluxes would represent the minimum flux but the true fluxes could be higher. Streambed temperatures cannot be used for a reliable quantification of the water fluxes at these locations. The presented method focuses on spatial patterns of groundwater-stream water interactions. Temporal changes of flow conditions in the streambed are beyond the scope of this approach.

3.5.7. Conclusions

We measured streambed temperatures at depths of 0.1, 0.15, 0.2, 0.3 and 0.5 m along a 220 m long reach of an artificial stream. Based on the observed temperatures, the vertical water fluxes were estimated by applying a one-dimensional analytical solution of the heat-advection-conduction-equation. As temperature can be inexpensively and easily measured, hundreds of measurements can be taken to draw a high resolution picture of groundwater-stream water interactions on the scale of stream reaches. The simple concept of relating streambed temperatures to spatial differences of vertical water flux might be subject to several limitations and uncertainties but provides a reasonable agreement between simulated and observed temperatures. Furthermore, the independent results of Darcy's law calculations based on streambed piezometer data confirmed the fluxes derived from the temperature profiles.

Although the artificial streambed at our study site appears to be relatively homogeneous in comparison to natural streams, a considerable spatial heterogeneity of groundwater-stream water interactions was observed. Only 20% of the total length contributes to 50% of the total groundwater discharge to the stream. A significant downwelling of streamwater was not observed.

Investigations aiming at characterization of groundwater surface water interaction can benefit from using multiple methods and techniques. The quantification of water fluxes through the streambed is of particular importance when mass fluxes of solutes and contaminants at the interface between groundwater and surface water are of interest. In cases of groundwater contamination, high groundwater discharge locations will contribute a great extent to the contaminant input into the stream. It is essential that these locations are identified precisely on river segments to 1 km length to assess, for instance, the potential impact of large scale groundwater contamination on the stream. We consider streambed temperature measurements to be a useful tool to gain insight into the spatial heterogeneity of fluxes along a stream reach. Because of its proven effectiveness, this method can be applied on a field site before other methods are used for choosing the locations of additional instrumentation.

Chapter 4

Contaminant mass fluxes between groundwater, streambed sediments and surface water at the regionally contaminated site Bitterfeld

Translated and supplemented extract of an article published in German as: Schmidt, C., Kalbus, E., Krieg, R., Bayer-Raich, M., Leschik, S., Reinstorf, F., Martienssen, M., Schirmer, M. 2008. Contaminant mass fluxes between groundwater and surface water at the regionally contaminated site Bitterfeld (Schadstoffmassenströme zwischen Grundwasser, Flussbettsedimenten und Oberflächenwasser am regional kontaminierten Standort Bitterfeld). *Grundwasser*, 13(3), 133-146.

4.1. Abstract

As a result of intensive industrial, mining, and urban development, numerous large-scale contaminated areas exist in Germany. These so-called megasites represent a challenge to risk assessment and remediation strategies. At the Bitterfeld megasite, the contaminated groundwater interacts with the local streams. Along a stream reach of 280 m in length, the mass fluxes of monochlorobenzene (MCB) and dichlorobenzene (DCB) were estimated by combining integral pumping tests (IPT), streambed temperature mapping, and analyses of contaminant concentrations in the streambed sediments. Average concentrations estimated from the IPT combined with the average groundwater discharge revealed a mass flux of $724 \mu\text{g m}^{-2} \text{d}^{-1}$ MCB and $186 \mu\text{g m}^{-2} \text{d}^{-1}$ DCB (sum of isomers) approaching the stream from the aquifer. Mass flux calculations that are based on aqueous contaminant concentrations in the streambed were significantly higher than those from the aquifer alone. The streambed itself acts as secondary contaminant source for the stream water.

4.2. Introduction

At large-scale contaminated sites like the industrial area of Bitterfeld-Wolfen, multiple contaminant sources may have resulted in a contamination of groundwater, surface water and soils. Highly contaminated zones are restricted to the industrial areas (Figure 4.1.) However, due to continuous discharge of contaminants to groundwater and surface waters, a diffuse contamination may expand to a regional scale (Heidrich et al. 2004b). When groundwater plumes are approaching local streams, the contaminants will potentially migrate into the streams and pose a risk to surface water habitats and downstream receptors. The stream system on its part may retain contaminants originating from both groundwater and direct discharges.

In this chapter we estimate the mass fluxes towards the Schachtgraben, a small man-made stream in the industrial area of Bitterfeld-Wolfen, that are associated with groundwater discharge. Mass flux estimations provide a better insight into the significance of contaminant migration between groundwater, streambed and stream water than a site assessment based solely on concentration measurements. Estimates of mass fluxes between environmental compartments can help to evaluate and prioritize management options and remediation designs (Jawitz et al. 2005, Basu et al. 2006).

At the study site, the contaminants that migrate to the stream water may only partially originate from the groundwater. Aqueous concentrations in the streambed were found to be higher than those observed in the adjacent aquifer. We hypothesized that the streambed sediments may act as a potential source of contaminants. Groundwater discharge through the streambed potentially induces contaminant fluxes from the streambed sediments towards the overlying stream water. Unfortunately, mass fluxes at the stream – streambed interface can as yet not directly be measured. Hence, our estimates rely on the measurements of water flux and aqueous concentrations. The accuracy of mass flux calculation is improved when flux-averaged aqueous concentrations are available. When the mass transfer from the sediments is rate limited, the aqueous concentrations will be different for locations with water flow and stagnant low or no flow zones. The aqueous concentration in stagnant zones will be higher than those observed in zones with higher advection. For contaminant flux calculations the flux concentrations are more relevant than the resident concentration. To obtain flux concentrations across a monitoring plane (in our case the stream-streambed interface) all flowing water or at least large sampling volumes must be captured and analysed. This approach is realistic for control planes in aquifers where large volumes can be pumped, but is not feasible for streambeds. However, mass flux estimates are also possible from locally measured resident concentrations presuming that the resident concentration represents the local flux concentration for a given water flux (Bloem et al. 2008). At the Schachtgraben, a spatially highly resolved data set of water fluxes was obtained by temperature mapping (Chapter 3). In this chapter we calculate the mass fluxes from the aquifer and the streambed to the stream. The local aqueous concentrations in the streambed were derived from snap-shot sampling and alternatively from passive sampling using time-integrating passive samplers. Further, we conducted a column experiment with material from the streambed and applied flow rates that represent the conditions in the field. With the column experiment we could derive flux-averaged concentrations and mass fluxes. To distinguish between the contribution of the groundwater and the contribution of the streambed to the total mass fluxes, the potential contaminant fluxes from the groundwater were estimated separately with data from an integral pumping test (IPT) performed adjacent to the stream (Kalbus et al. 2007).

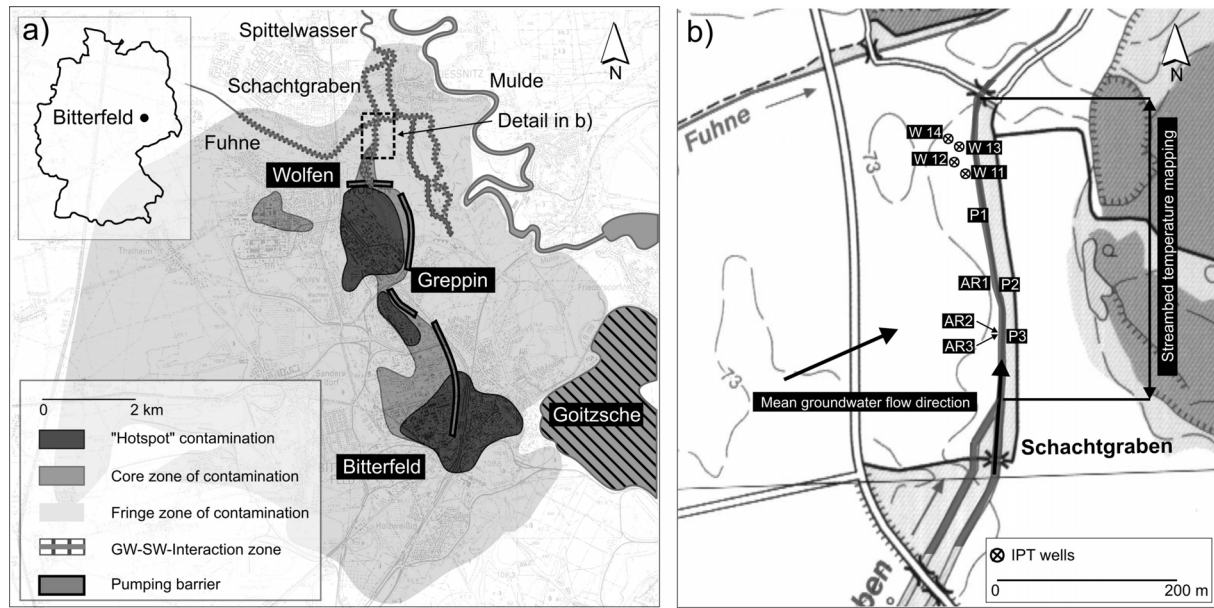


Figure 4.1. a) Overview of the extent of the groundwater contamination at the regionally contaminated site Bitterfeld-Wolfen (after HEIDRICH et al 2004b), the location of potential stream-groundwater-interaction zones and the location of the Schachtgraben site; b) Detailed map of the Schachtgraben site showing the location of the IPT wells and the streambed sediment sampling locations (P1-P3) and the location of the streambed passive sampling arrays (AR1-AR3).

4.3. Background

The investigations were conducted along a 280 m long reach of the Schachtgraben located in the industrial area of Bitterfeld-Wolfen, about 130 km south of Berlin, Germany (Figure 4.1). The stream is part of the Mulde River system which is a tributary to the Elbe River. The Schachtgraben was man-made and had originally been constructed for mine water discharge from open-cast lignite mines. Later on, it was also used for waste water discharge from the chemical industry. The streambed of the Schachtgraben consists of a 0.6 m thick layer of crushed rock. The pore space of the crushed rock layer is filled with allochthonous, sandy, fluvial material. The stream is about 3 m wide and has an average water depth of 0.6 m. It partially penetrates a Quaternary alluvial aquifer.

For approximately 30 years (starting in the 1960s and lasting until the early 1990s) high contaminant loads were discharged to the stream. Additionally, the hydraulic conditions were presumably different from those observed today. During the 1970s and 1980s the regional groundwater table was regionally lowered by extensive open cast lignite mining and the streamflow in the Schachtgraben was presumably higher than today because of the waste water inputs. We think that the combination of discharging highly contaminated water to the stream and the hydraulic conditions at that time fostered the contamination of the streambed.

The water table in the aquifer is nowadays generally higher than the water level in the stream. Hence, the Schachtgraben can be classified as a gaining stream. The mass fluxes are now from the subsurface towards the surface water.

4.4. Materials and Methods

4.4.1. Integral pumping test

An integral pumping test (IPT) (Bockelmann et al. 2001) was conducted to estimate the average contaminant concentrations of the groundwater water flow across control planes (CP) in the aquifer adjacent to the stream (Kalbus et al., 2007). Because of the large aquifer volume that is investigated by pumping, the estimates are more representative than those from conventional sampling at monitoring wells. For the implementation of IPT a number of pumping wells was arranged perpendicular to the groundwater flow direction and form the CP. Over the course of the pumping, the water is sampled and analysed for the target compounds. The resulting concentration time-series are used as input parameter to evaluate the IPT. The first analytical solution for the evaluation of IPTs was derived by Schwarz (2002), valid for the case of circular isochrones. A generalization of Schwarz's solution, which accounts for noncircular isochrones is given in Bayer-Raich et al. (2004). Effects of linear sorption and retardation of the target compounds can be considered in the evaluation (Bayer-Raich et al. 2006). A number of IPT field applications has been described in previous studies (e.g., Bockelmann et al. 2003; Bauer et al., 2004; Rügner et al., 2004; Jarsjö et al., 2005).

At the Schachtgraben site, four wells were drilled along a control plane parallel to the stream (Figure 4.1). The wells were fully screened and penetrated the shallow Quaternary aquifer to a depth of 11 m. The wells were spaced at intervals of 15 m to ensure that the CP will be fully covered by the expected capture zones for the selected pumping rate and test duration. The four wells were pumped simultaneously with a constant pumping rate of 1 L s^{-1} per well over the course of the IPT of 5 days (120 h). Water samples were taken from all wells and from the stream water every 3 hours. The samples were analysed using gaschromatography coupled to a mass spectrometer (GC-MS) for monochlorobenzene (MCB) and dichlorobenzene (DCB) with detection limits of $0.15 \mu\text{g L}^{-1}$ (MCB) and $0.2 \mu\text{g L}^{-1}$ (DCB) respectively. Details of the analysis method are provided in Kalbus et al. (2007).

For design of the IPT and simulation of flow during pumping, we set up a numerical flow model using MODFLOW-96 (McDonald and Harbaugh 1996). Mean aquifer thickness, hydraulic gradient, hydraulic conductivity and effective porosity were estimated from field data and assigned to the grid cells assuming a homogeneous aquifer (Kalbus et al. 2007). The capture zone of each well was determined using particle tracking with the code MODPATH 3.0 (Pollock 1994). The average contaminant concentrations were estimated using the solution of Bayer-Raich et al. (2006).

4.4.2. Snap-shot sampling

Pore water samples could not be taken directly from the streambed because the crushed rock layer prevented the installation of streambed piezometers. To circumvent this problem, samples of the water-saturated sediments were collected and the pore water was analysed. The

sampling locations were selected with respect to different magnitudes of groundwater discharge. Sampling point P3 represents a high-discharge location ($\sim 450 \text{ L m}^{-2} \text{ d}^{-1}$), sampling point P2 a medium-discharge location ($\sim 35 \text{ L m}^{-2} \text{ d}^{-1}$), and sampling point P1 does not show a significant groundwater discharge. For the mass flux calculations we attributed the lowest observed groundwater discharge to P1 ($\sim 10 \text{ L m}^{-2} \text{ d}^{-1}$).

The sediment samples were taken from depths between 0 and 0.5 m below the streambed surface. The crushed rock layer in the streambed inhibited depth-oriented sediment coring with the available technology. Hence, the sediment samples were taken as integral samples over the entire sediment column. The samples were fully water-saturated. Each bulk sample was stored in a glass bottle. The porewater was analysed immediately after returning to the laboratory using static head-space GC-MS (Varian GC-MS Type CP 3800 MS Quadrupole 1200, column 60m Zebron ZB1, inner diameter 0.25 mm, injection volume 1 ml).

4.4.3. Passive sampling

Since repeated direct sampling was difficult, time-integrating passive samplers were deployed in the streambed. These devices can be placed directly in the streambed sediments at well-defined depths and are presumed to be capable to capture representative aqueous concentrations. The underlying principle of time-integrating passive samplers (also called “kinetic samplers”) is that the analytes accumulate in a receiving phase in the sampler. It is assumed that the mass of analyte accumulated after a certain exposure time is linearly proportional to the ambient analyte concentration in the water outside the sampler (Martin et al. 2003).

Table 4.1. Parameters required for time-weighted average contaminant concentration determinations using the ceramic dosimeter (adapted from Bopp et al. 2005).

	Symbol	Value	Comment
Parameters defined by the membrane			
Thickness	Δx	0.15 [cm]	Flux-controlling barrier; diffusion distance
Surface area (tube length: 5 cm; tube diameter: 1 cm)	A	8.5 [cm ²]	Taking reduction of total surface area due to PTFE caps into account (from Martin et al., 2003)
Porosity	ε	0.305 [-]	from Martin et al., 2003
Archie's law exponent	m	2.0 [-]	from Martin et al., 2003
Analyte-specific parameters			
Diffusion coefficient in water	D_w	6.505 x 10 ⁻¹⁰ (MCB) [m ² s ⁻¹] 5.646 x 10 ⁻¹⁰ (DCB) [m ² s ⁻¹]	Calculated for each substance according to Worch, 1993
Accumulated mass	M	[g]	Measured during sampling; a determinant of water viscosity thus influencing diffusivity D_w
Equations			
$C = \frac{M \cdot \Delta x}{A \cdot t \cdot D_e}$	$D_e = D_w \cdot \varepsilon^m$		C = average contaminant concentration in the pore water

Possible short-term variations in aqueous concentrations are averaged by the time-integrating type of passive samplers. However, if frequent changes in the flow direction occur the averaging might be problematic for the calculation of mass fluxes (Kalbus et al. 2006). Observations of the hydraulic gradient at the Schachtgraben indicate constantly gaining conditions and thus, the derived concentrations are assumed to be representative.

The passive sampling system applied in this study (ceramic dosimeter, Bopp et al., 2005) consists of 4.5 cm long ceramic tubes filled with an adsorbent material (Dowex Optipore L493). To prevent the dosimeter from damages, a steel casing was used (see Figure 1 in Bopp et al., 2005), which increased the entire length of the passive sampling system to 5.0 cm. In order to obtain depth-orientated estimates of contaminant concentrations, we deployed the dosimeters at four different depths at each sampling location (0.10-0.15, 0.20-0.25, 0.30-0.35 and 0.40-0.45 m below the streambed surface) in the streambed sediments. The sampling locations were chosen with respect to the groundwater discharge regime as identified in Chapter 3 and by Schmidt et al. (2006). One array of dosimeters (AR1) was deployed at a low-discharge zone with a groundwater flux of $10 \text{ L m}^{-2} \text{ d}^{-1}$, arrays AR2 and AR3 were placed at a high-discharge zone with a groundwater flux of $280 \text{ L m}^{-2} \text{ d}^{-1}$. Additionally, two dosimeters were placed in groundwater monitoring wells (W11 and W12), and two were deployed in the surface water. The ceramic dosimeters remained in the streambed, surface water and groundwater for three months.

Contaminants are diffusing across the ceramic membrane and are adsorbed over the entire sampling period to the adsorbent material. The average contaminant concentration in the water can be obtained from the adsorbed contaminant mass and the duration of exposure (Martin et al. 2003, Bopp et al. 2005). The parameters required to derive the average concentration from the adsorbed mass are given in Table 4.1. For sample extraction from the adsorbent material within the ceramic dosimeters, a modification of the method described by Bopp et al. (2005) was used. Prior to extraction, the metal cage of the ceramic dosimeter was opened and the caps were removed. The adsorbent material was divided into two aliquots to obtain a duplicate sample. Each sample was extracted two times with 5 mL of acetone and 5 minutes contact time. The extracts were analysed by GC-MS (Finnigan GC-MS, GC Type 9001, MS Type GCQ TM, Column: Chrompack Zekrosil-8-CB, 30m, ID 0.25 mm, FD 0.25 μm , injection volume 1 ml splitless).

4.4.4. Column experiment

The column experiment was designed to observe time-series of the effluent contaminant mass flow rate at realistic flow velocities as observed in the streambed of the Schachtgraben. The flow rates in the six columns ranged between 15 and 204 mL d^{-1} which is equivalent to a vertical water flux (q_z) of 33 to $439 \text{ L m}^{-2} \text{ d}^{-1}$. This range is similar to the range estimated from streambed temperature profiles in the Schachtgraben (see Schmidt et al 2006 and Chapter 3). The columns (30 cm long, diameter of 2.44 cm) were packed with aliquots of a mixed sample of the fine grained fraction (the crushed rock was not included) of streambed

sediment. Although undisturbed sediment cores would have been preferable, the crushed rock component of the streambed prevented the sampling of cores as described above. The column effluents were directly collected into glass vials to minimize sorption to plastic tubes. The effluent samples were analyzed by head-space GC-MS (Varian GC-MS Type CP 3800 MS Quadrupole 1200, column 60 m Zebron ZB1, inner diameter 0.25 mm, injection volume 1 ml) and concentrations were obtained by using deuterated MCB as internal standard. Initially, the columns were sampled every 24 hours. Later, when the concentrations did not vary significantly on a daily basis the sampling interval was increased to 168 h (once in a week). The average mass flow rates used in this analysis were derived from effluent concentrations sampled at the late time of the column experiment (between 457 and 1153 hours of the course of the column experiment).

4.4.5. Contaminant mass flux estimation

The different components of water and contaminant fluxes that have been considered in this study are conceptualized in Figure 4.2. The mass fluxes were evaluated for MCB and the isomers of DCB. Average contaminant concentrations in the groundwater (C_{GW}) have been estimated with the IPT. The contaminant mass fluxes from the groundwater to the stream (J_{GW}) can be estimated from C_{GW} and the average groundwater discharge that is entering the stream $q_{z,av}$ with:

$$J_{GW} = q_{z,av} \cdot C_{GW} \quad [4.1]$$

To estimate the contaminant mass fluxes originating from the streambed sediments (J_{SED}), we used the contaminant concentrations obtained from snap-shot sampling and passive sampling of porewater in the streambed C_{SED} and the water fluxes q_z at the respective sampling location (x, y) :

$$J_{SED}(x, y) = q_z(x, y) \cdot C_{SED}(x, y) \quad [4.2]$$

The resulting mass fluxes from the streambed, however, comprise both the mass fluxes from the groundwater and the additional mass fluxes from the streambed sediments. It is not feasible to extract those originating solely from the sediments, thus: $J_{GW} \in J_{SED}$.

To derive mass fluxes (mass flow rate per m^2 of the streambed) from the column experiments (J_{COL}), the measured mass flow rates that leave the cross sectional area of one column (4.66 cm^2) were extrapolated to derive a value per m^2 .

The water fluxes were estimated using mapped streambed temperatures. The streambed temperatures were evaluated for magnitudes of groundwater discharge applying the methodology described in Chapter 3 and in Schmidt et al. (2006), respectively. The vertical groundwater flux q_z is derived for each temperature observation point (x, y) .

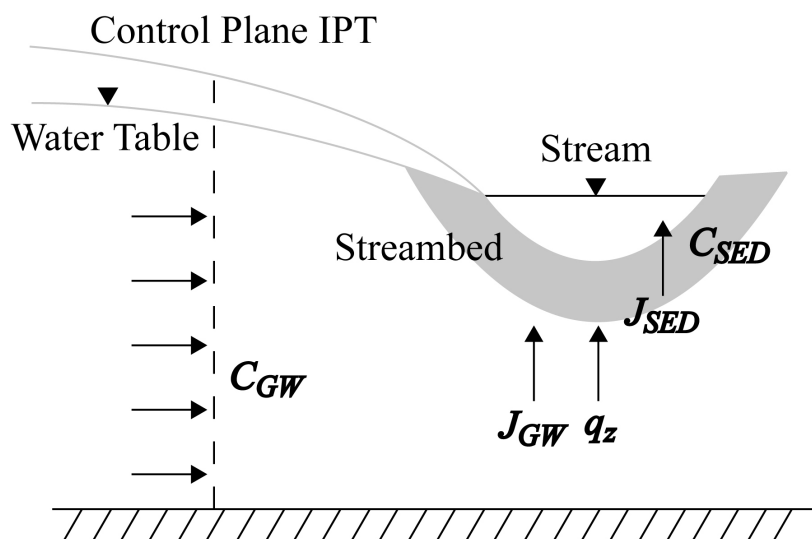


Figure 4.2. Conceptual scheme of water and advective contaminant fluxes. J_{GW} and J_{SED} are the mass fluxes from the groundwater and from the streambed sediment which were calculated from the respective concentrations C_{GW} and C_{SED} as well as q_z . J_{GW} is a component of J_{SED} .

4.5. Results

4.5.1. Integral pumping test

The observed concentration time-series remained nearly constant over the course of the pumping. This behaviour suggests that the pumping wells are located in a wide plume with a fairly homogeneous contaminant distribution (see also Bockelmann et al. 2001).

The average concentrations of MCB varied between 18.15 (W11) and 9.64 (W14) $\mu\text{g L}^{-1}$, and of DCB between 2.59 (W13) and 3.97 (W11) (sum of isomers) (Table 4.2). The contaminant concentrations in the groundwater were overall significantly lower than in the stream water (Table 4.2).

Table 4.2. Average contaminant concentrations in the pumping wells ($C_{W11} - C_{W14}$), in the groundwater (C_{GW} = average from all wells), and in the stream water during the IPT

	C_{W11} [$\mu\text{g L}^{-1}$]	C_{W12} [$\mu\text{g L}^{-1}$]	C_{W13} [$\mu\text{g L}^{-1}$]	C_{W14} [$\mu\text{g L}^{-1}$]	C_{GW} [$\mu\text{g L}^{-1}$]	stream water [$\mu\text{g L}^{-1}$]
MCB	18.15	12.41	10.22	9.64	12.61	24.73
1,2-DCB	1.66	1.17	1.04	1.45	1.33	2.62
1,3-DCB	1.71	1.24	1.15	1.42	1.38	4.10
1,4-DCB	0.60	0.36	0.40	0.61	0.49	1.65
sum DCB	3.97	2.77	2.59	3.48	3.2	8.37

4.5.2. Snapshot sampling

The contaminant concentration in the porewater of the streambed varied according to the magnitude of groundwater discharge. The total concentration (sum of all target compounds) was found to be lowest at the high-discharge zone (P3) with 76.4 $\mu\text{g L}^{-1}$. At the location with low groundwater discharge (P1), the concentration was 195.1 $\mu\text{g L}^{-1}$ and even higher at the

medium-discharge location (P2) with $224.2 \mu\text{g L}^{-1}$. (Figure 4.3). Figure 4.3 provides an overview on the detected chlorinated benzenes and HCH at the Schachtgraben site. The concentrations of MCB and 1,3-DCB and 1,4-DCB in the stream water and in the groundwater were consistently lower than those observed in the streambed. In contrast, 1,2-DCB was not detected at locations P2 and P3 in the streambed. MCB showed always the highest concentrations of all analysed compounds. Besides the concentration differences, the occurrence of compounds varied between the streambed and the water samples from groundwater and surface water. In general, fewer compounds were detected in the streambed. The most significant substances are MCB and the isomers of DCB.

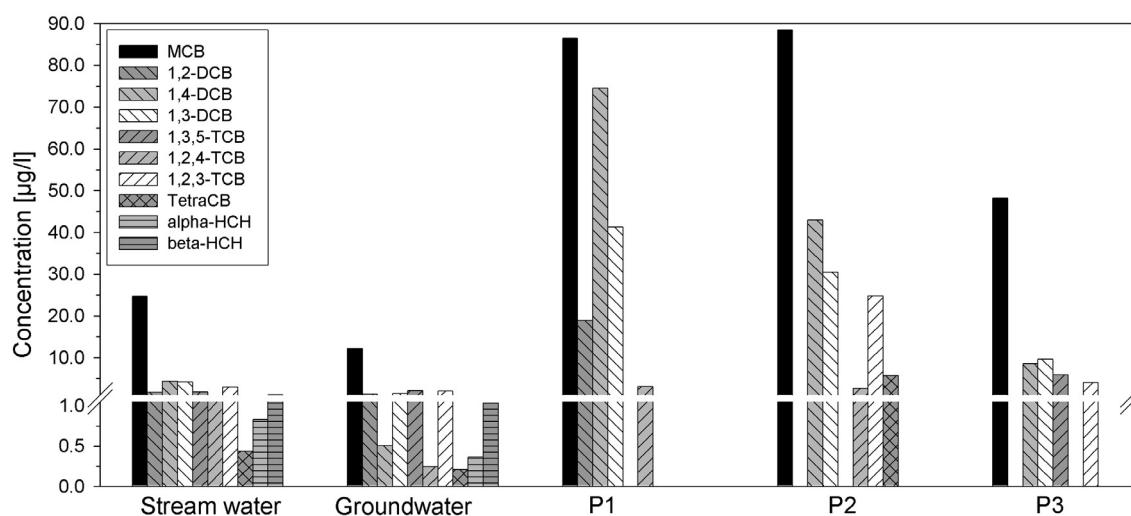


Figure 4.3. Comparison of aqueous contaminant concentration in the streambed at locations with medium (P1), low (P2) and high (P3) groundwater discharge with those measured in stream water and groundwater.

4.5.3. Passive sampling

Overall, the concentrations derived from the ceramic dosimeters seem to be reasonable in comparison to the concentrations from the snap-shot sampling and IPT. The dosimeters (no. 17 and 20) deployed in the stream upstream and downstream of the investigated reach revealed similar concentrations. At the upstream sampling location the average concentrations in the stream water were estimated to $14.1 \mu\text{g L}^{-1}$ (MCB), 0.8, 5.0, $2.6 \mu\text{g L}^{-1}$ (1,2-DCB, 1,3-DCB, 1,4-DCB) and at the downstream location $13.8 \mu\text{g L}^{-1}$ (MCB) and 0.9, 4.5, $2.8 \mu\text{g L}^{-1}$ (1,2-DCB, 1,3-DCB, 1,4-DCB). Obviously, the inputs from the streambed did not result in an increasing concentration in the surface water along the study reach of 280 m in length. The inputs originating from the streambed are not necessarily reflected in the contaminant concentrations of the surface water because dilution and volatilization might significantly reduce the concentrations (Conant Jr. et al. 2004).

The monitored concentrations (sampler no. 18 and 19) in two groundwater monitoring wells (W11 and W12) adjacent to the stream (Figure 4.1) were characteristic for the diffuse contamination present at the site with average values of $5.1 \mu\text{g L}^{-1}$ (MCB) and 0.1, 0.2, $0.3 \mu\text{g L}^{-1}$ (1,2-DCB, 1,3-DCB, 1,4-DCB). In one of the monitoring wells no DCB was observed (Figure 4.4). The five-day IPT at four groundwater monitoring wells (in two of which dosimeters were deployed) revealed average concentrations of $12.6 \mu\text{g L}^{-1}$ MCB and $3.2 \mu\text{g L}^{-1}$ DCB (sum of isomers) (Kalbus et al. 2007) and Table 4.2. Average concentrations in the single wells ranged from 12.1 (W11) to 18.2 (W11) $\mu\text{g L}^{-1}$ MCB and from 2.8 (W12) to 4.0 (W11) $\mu\text{g L}^{-1}$ DCB (sum of isomers).

In the streambed, equally to the snapshot-sampling, the aqueous concentrations differed between zones of high and low groundwater discharge as well as vertically at each passive sampler array. The highest concentrations were observed at the low-discharge zone (array 1), the lowest at one of the high-discharge zones (array 3). Average concentrations (averaged over the four individual samplers in an array) at the low-discharge zone were $65.5 \mu\text{g L}^{-1}$ MCB, $6.5 \mu\text{g L}^{-1}$ 1,2-DCB, $22.4 \mu\text{g L}^{-1}$ 1,3-DCB and $32.9 \mu\text{g L}^{-1}$ 1,4-DCB. The two high-discharge zones, although spatially separated by two metres only, differed significantly in their average concentrations. At array 2 the average concentration of MCB ($65.6 \mu\text{g L}^{-1}$) was similar to that at the low-discharge zone (array 1). Conversely, the average concentrations of the DCB isomers ($1.3 \mu\text{g L}^{-1}$ 1,2-DCB, $8.5 \mu\text{g L}^{-1}$ 1,3-DCB and $8.3 \mu\text{g L}^{-1}$ 1,4-DCB) at array 2 were within the order of magnitude of the DCB concentrations at array 3 ($0.7 \mu\text{g L}^{-1}$ 1,2-DCB, $4.4 \mu\text{g L}^{-1}$ 1,3-DCB and $4.1 \mu\text{g L}^{-1}$ 1,4-DCB). Overall, the aqueous contaminant concentrations in the streambed were lower at zones of high groundwater discharge than at zones of low groundwater discharge.

The comparison of aqueous concentrations in the groundwater and the streambed reveals that MCB and DCB concentrations in the interstitial pore water in the streambed sediments were approximately one order of magnitude higher than in the groundwater and the surface water. Significant differences occur between zones of high and low groundwater discharge. Focusing on the vertical distribution of contaminants in the streambed, Figure 4.4 illustrates that the lowest aqueous concentrations of all substances in the streambed were observed in the shallow dosimeters (no. 8, 12, 16) installed at depths of 0.10-0.15 m below the streambed surface. In the arrays 1 and 2, the highest concentrations were present at the subsequent depth of 0.20-0.25 m. Then, with increasing depth the concentrations decreased in the two arrays. Array 3 did not show this vertical pattern. Here, the concentrations of MCB increased from 33.6 to $24.6 \mu\text{g L}^{-1}$ from the top to the bottom of the streambed, while concentrations of DCB were virtually independent of the sampling depth (Figure 4.4).

The low aqueous concentrations at the top of the streambed may be caused by different processes. Advective exchange with the surface water may have resulted in the observed lower concentration. Also diffusive fluxes will be higher closer to the sediment-water interface and will therefore result in decreased concentrations compared to greater depths.

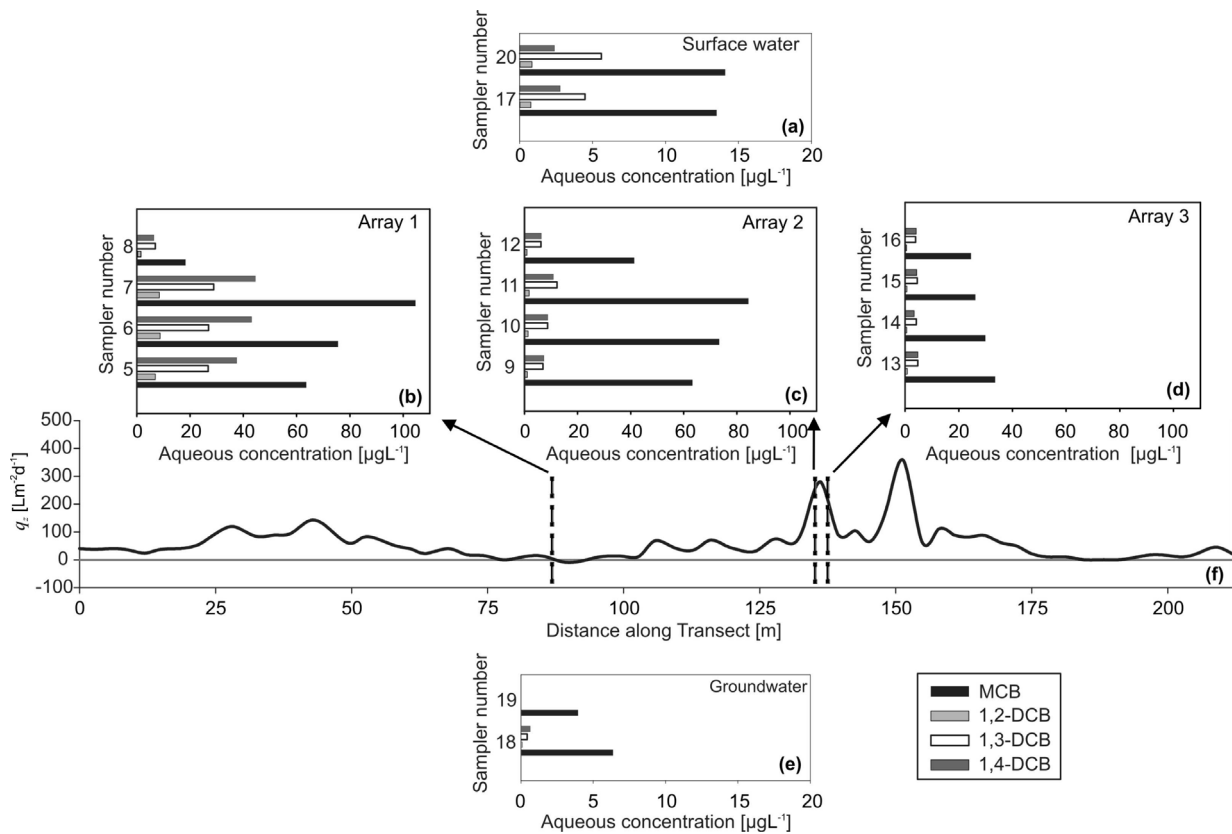


Figure 4.4. Average aqueous concentrations of MCB and DCBs derived from the ceramic dosimeters in the surface water (a) and the groundwater (e). Aqueous concentrations in the streambed are plotted for different depths at a low groundwater discharge location (b) and two high groundwater discharge locations (c,d) along the studied reach with heterogeneous groundwater discharge patterns (f).

4.5.4. Mass fluxes from the aquifer

The potential contaminant mass fluxes from the groundwater to the stream can be obtained through the average concentrations from the IPT and the groundwater discharge to the stream (Table 4.3) (Kalbus et al. 2007). Initially, the mass fluxes from the streambed are omitted from the analyses. Since the contaminant concentrations did not vary significantly between the four pumping wells, the average concentration of all wells was considered as the representative concentration in the groundwater that is approaching the stream. For the groundwater discharge the average of $58.2 \text{ L m}^{-2} \text{ d}^{-1}$ from Chapter 3 (Schmidt et al. 2006) was assumed to be representative. The resulting average mass flux for MCB was $734 \mu\text{g m}^{-2} \text{ d}^{-1}$. The results for the other compounds are summarized in Table 4.3. The mass fluxes of MCB along the control plane in the aquifer ranged between 1705 and $3138 \mu\text{g m}^{-2} \text{ d}^{-1}$, with an increasing trend from well 14 to well 11. The mass fluxes of the DCBs ranged between $63 \mu\text{g m}^{-2} \text{ d}^{-1}$ (1,4-DCB, W12) and $296 \mu\text{g m}^{-2} \text{ d}^{-1}$ (1,3-DCB, W11). Since the underlying concentrations are the same, the results show that the average water flux in the aquifer is higher than the average groundwater discharge to the stream.

Table 4.3. Average contaminant mass fluxes (J_{GW}) from the groundwater to the stream. C_{GW} is the contaminant concentration averaged over the four IPT wells, $q_{z,m}$ is the average groundwater discharge.

	C_{GW} [$\mu\text{g L}^{-1}$]	$q_{z,av}$ [$\text{L m}^{-2} \text{d}^{-1}$]	J_{GW} [$\mu\text{g m}^{-2} \text{d}^{-1}$]
MCB	12.61		733.9
1,2-DCB	1.33	58.2	77.4
1,3-DCB	1.38		80.3
1,4-DCB	0.49		28.5
sum DCB	3.20		186.2

4.5.5. Mass fluxes from the streambed-snapshot sampling

Although the concentrations are lower at locations with high groundwater discharge, the mass fluxes are significantly higher there than at locations with low and medium groundwater discharge but with higher concentrations (Table 4.4). The estimated mass mass fluxes for MCB range from $884 \mu\text{g m}^{-2} \text{d}^{-1}$ (P2; $q_z=10$) to $21678 \mu\text{g m}^{-2} \text{d}^{-1}$ (P3; $q_z=450$). For DCB the mass fluxes range from 733 to $8214 \mu\text{g m}^{-2} \text{d}^{-1}$, respectively. Obviously, the large range of mass flux is driven by the differences in water flux that are large compared to the differences in concentration. However, the presented estimates are associated with considerable uncertainty because the measured concentrations may not be representative for the local water flux. The measured resident concentrations potentially overestimate the flux concentration and therefore the resulting mass fluxes are overestimated particularly at the high groundwater discharge zone. However, even at the low-discharge zones the mass fluxes are higher than the mass fluxes from the aquifer, indicating that the streambed contributes to the total mass flux.

Table 4.4. Aqueous contaminant concentrations in the streambed for medium (C_{SEDp1}), low (C_{SEDp2}) and high (C_{SEDp3}) groundwater discharge and the respective mass fluxes (J_{SEDp1} ; J_{SEDp2} ; J_{SEDp3}).

	C_{SEDp1} [$\mu\text{g L}^{-1}$]	C_{SEDp2} [$\mu\text{g L}^{-1}$]	C_{SEDp3} [$\mu\text{g L}^{-1}$]	J_{SEDp1} [$\mu\text{g m}^{-2} \text{d}^{-1}$]	J_{SEDp2} [$\mu\text{g m}^{-2} \text{d}^{-1}$]	J_{SEDp3} [$\mu\text{g m}^{-2} \text{d}^{-1}$]	$q_{z,P1}$ [$\text{L m}^{-2} \text{d}^{-1}$]	$q_{z,P2}$ [$\text{L m}^{-2} \text{d}^{-1}$]	$q_{z,P3}$ [$\text{L m}^{-2} \text{d}^{-1}$]
MCB	86.4	88.4	48.2	3024.7	884.3	21678.0			
1,2-DCB	18.9	n.n	n.n	660.45	-	-	35	10	450
1,3-DCB	41.3	30.5	9.7	1444.8	304.6	4356.0			
1,4-DCB	74.5	42.9	8.6	2608.2	429.1	3858.0			
sum DCB	134.7	73.4	18.3	4713.45	733.7	8214			

4.5.6. Mass fluxes from the streambed-passive sampling

The mass fluxes relying on concentrations estimates from the passive samplers were calculated in two ways. Firstly, only the concentrations from the uppermost passive samplers which represent the concentrations in the shallow streambed were used. Secondly, the average

concentrations of one array were used to estimate an average potential mass flux at each array. In general the observed concentrations were lower in the uppermost samplers and consequently were the resulting mass fluxes. The passive samplers of array AR1 were placed in a low flow area with water fluxes of approximately $10 \text{ L m}^{-2} \text{ d}^{-1}$. AR2 and AR3 were spaced at a distance of 0.5 m at a high groundwater discharge location with a groundwater flux of $280 \text{ L m}^{-2} \text{ d}^{-1}$. Provided that the concentrations represent the local flux concentrations, the mass fluxes of MCB derived for the upper samplers ranged between 6860 and $11650 \text{ } \mu\text{g m}^{-2} \text{ d}^{-1}$ at the high-discharge location and $180 \text{ } \mu\text{g m}^{-2} \text{ d}^{-1}$ at the low-discharge location. The mass fluxes of DCB (sum of isomers) ranged between 2390 and $3770 \text{ } \mu\text{g m}^{-2} \text{ d}^{-1}$ at the high-discharge location and $150 \text{ } \mu\text{g m}^{-2} \text{ d}^{-1}$ at the low-discharge location (Table 4.5).

The mass fluxes of MCB calculated from average concentrations varied between 7990 and $18360 \text{ } \mu\text{g m}^{-2} \text{ d}^{-1}$ at the high-discharge location and $660 \text{ } \mu\text{g m}^{-2} \text{ d}^{-1}$ at the low-discharge location. The mass fluxes of DCB (sum of isomers) were between 620 and $5090 \text{ } \mu\text{g m}^{-2} \text{ d}^{-1}$ at the low-discharge and the high discharge location, respectively (Table 4.6).

Table 4.5. Concentration and mass flux estimates based on the uppermost passive sampler.

	$C_{\text{SED,AR1,up}}$ [$\mu\text{g L}^{-1}$]	$C_{\text{SED,AR2,up}}$ [$\mu\text{g L}^{-1}$]	$C_{\text{SED,AR3,up}}$ [$\mu\text{g L}^{-1}$]	$J_{\text{SED,AR1,up}}$ [$\mu\text{g m}^{-2} \text{ d}^{-1}$]	$J_{\text{SED,AR2,up}}$ [$\mu\text{g m}^{-2} \text{ d}^{-1}$]	$J_{\text{SED,AR3,up}}$ [$\mu\text{g m}^{-2} \text{ d}^{-1}$]
MCB	18.3	41.3	24.5	180	11650	6860
1,2-DCB	1.6	1.0	0.5	16	280	150
1,3-DCB	7.0	6.2	3.9	70	1740	1100
1,4-DCB	6.5	6.3	4.1	60	1760	1140
sum DCB	15.1	13.5	8.5	150	3770	2390

Table 4.6. Concentration and mass flux estimates based on the average of all samplers.

	$C_{\text{AR1,m}}$ [$\mu\text{g L}^{-1}$]	$C_{\text{AR2,m}}$ [$\mu\text{g L}^{-1}$]	$C_{\text{AR3,m}}$ [$\mu\text{g L}^{-1}$]	$J_{\text{AR1,m}}$ [$\mu\text{g m}^{-2} \text{ d}^{-1}$]	$J_{\text{AR2,m}}$ [$\mu\text{g m}^{-2} \text{ d}^{-1}$]	$J_{\text{AR3,m}}$ [$\mu\text{g m}^{-2} \text{ d}^{-1}$]
MCB	65.5	65.6	28.5	655.1	18360	7990
1,2-DCB	6.5	1.3	0.7	64.8	370	190
1,3-DCB	22.4	8.5	4.4	224.1	2390	1220
1,4-DCB	32.9	8.3	4.1	329.1	2330	1160
sum DCB	61.8	18.1	9.2	618.0	5090	2570

4.5.7. Mass fluxes from the streambed-column experiment

The mass flux estimates from the column experiments represent a conceptually different approach compared to those from the field samples. The mass fluxes from the field samples rely on measurements of resident concentrations, while in the column experiments the contaminant concentrations were measured directly in the effluent. The mass flow rates of MCB, 1,3-DCB and 1,4-DCB versus time are displayed in Figure 4.5. The effluents were also

sampled for 1,2-DCB but this analyte was found to be below the limit of detection (as in the snapshot samplings).

Initially, the mass flow rates from the six columns (each operated at a different flow rate) were different. High flow rates correlated with high mass flows. After the first pore volumes were flushed, the mass flow rates converged to values that became independent from the flow rate. In all columns, the concentrations declined shortly after the beginning of the experiment. The initially high mass fluxes are likely to be an effect of the equilibration between the solid and the fluid phase in the bulk sample during the time between sampling and column packing. In other words, we think that the tailing of the mass flow rates in the column experiment represents the conditions in the field rather than the first flushing and the associated high mass release. The observed decline is highest for the columns with higher flow rates. Since the mass flow rates are similar after a certain time, the concentrations are inversely proportional to the flow rate, $c \sim Q^{-1}$. This behaviour indicates non-equilibrium conditions and thus a rate-limited mass transfer from the sediments to the water phase. The results from the column experiment are contradictory to the findings in the field. The range of aqueous concentrations observed in the streambed was much smaller than the range of water fluxes. Hence, although the aqueous concentrations in the streambed were lower at high groundwater discharge, the highest mass fluxes were associated with high-discharge locations.

The average mass flow rates from all columns at the late-time period of the experiment (between 453 and 1053 hours) were $0.53 \mu\text{g d}^{-1}$ MCB (standard deviation: $0.18 \mu\text{g d}^{-1}$, 95% confidence bounds: ± 0.06), $0.22 \mu\text{g d}^{-1}$ 1,3-DCB (standard deviation: $0.22 \mu\text{g d}^{-1}$, 95% confidence bounds: ± 0.07) and $0.15 \mu\text{g d}^{-1}$ 1,4-DCB (standard deviation: $0.22 \mu\text{g d}^{-1}$, 95% confidence bounds: ± 0.07). The mass flow rates of the isomers of DCB show a higher scatter than those of MCB.

The estimated mass flux of MCB was $1136.7 \mu\text{g m}^{-2} \text{d}^{-1}$ with lower and upper 95% confidence bounds of 1007.3 and $1266.1 \mu\text{g m}^{-2} \text{d}^{-1}$, respectively. The mass fluxes of 1,3-DCB and 1,4-DCB were $462.6 \mu\text{g m}^{-2} \text{d}^{-1}$ (lower and upper 95% confidence bounds: 307.0 and $618.3 \mu\text{g m}^{-2} \text{d}^{-1}$) and $330.8 \mu\text{g m}^{-2} \text{d}^{-1}$ (lower and upper 95% confidence bounds: 176.5 and $485.2 \mu\text{g m}^{-2} \text{d}^{-1}$). The mass fluxes from the column experiment were consistently above the mass fluxes in the groundwater approaching the Schachtgraben and, therefore, indicate a contribution of the streambed to the total mass flux.

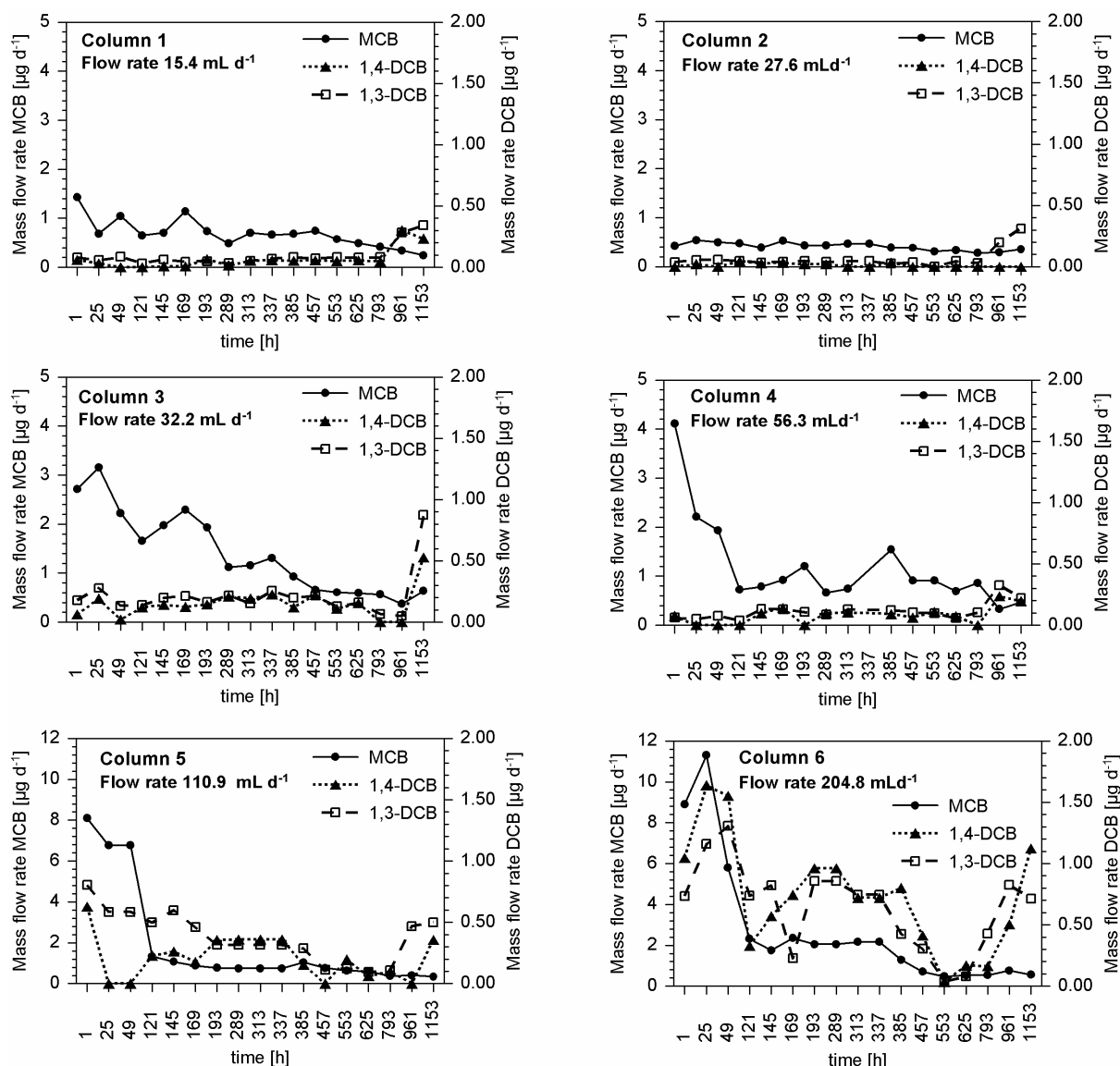


Figure 4.5. Mass flow rates of MCB, 1,3-DCB and 1,4-DCB at the column outflow. For the mass flux calculations the values between 457 and 1153 hours were used.

4.6. Discussion

Obviously, the results from the field sampling and from the column experiments are contradictory. The results from the field sampling indicate a relationship between mass fluxes and the magnitude of groundwater discharge. High groundwater discharge is associated with high mass fluxes because the variation of concentration is small compared to the variation of fluxes. In other studies, the variation of resident concentrations was much higher than in our case and thus, the apparent dependence of mass fluxes on water flow was lower. In the study of Conant Jr. et al. (2004) for instance, where the discharge of a distinct, high-concentration contaminant plume to a river was investigated, the observed aqueous concentrations in the streambed (sampled at a depth of 0.3 m below the streambed surface) varied over four orders of magnitude. They did not perform mass flux calculations but it is visible from their data that the highest mass fluxes were associated with the zones of highest concentrations. Recently, Ellis et al. (2007) presented mass flux estimates from VOC-(volatile organic compounds)

contaminated groundwater to a 7.4 km reach of a river. Their streambed piezometer based water flux (Darcy's law) and concentration measurements showed considerable variability. The streambed trichloroethene (TCE) concentration varied between <0.1 and $62 \mu\text{g L}^{-1}$ (mean $4.5 \mu\text{g L}^{-1}$) and the hydraulic conductivities between 0.08 and 23 md^{-1} (mean 3.13 md^{-1}). Ellis et al. (2007) concluded that high mass fluxes occur at locations with high concentrations. However, considering the range of hydraulic conductivities, high mass fluxes can also be expected at locations with average concentrations and high magnitudes of groundwater discharge.

The column experiment that was conducted with streambed sediments from the Schachtgraben could not fully confirm the relationship between mass flux and the magnitude of groundwater discharge. The mass fluxes derived from the column experiments are practically independent (at late times of the experiment) from the flow velocity indicating that rate-limited desorption is controlling the mass flow rates. The observed concentrations are approximately inverse-proportional to the flow velocities. Although the repacked columns do not represent the in-situ sediment structure, the desorption-controlling processes should presumably be the same as in the field. Rate-limited desorption can be conceptualized in different ways. Mass transfer from immobile zones or states can be either conceptualized by physical or chemical processes. Physically immobile zones are characterized by low hydraulic conductivities and can occur at any scale from macroscopic clay lenses to individual grains. Large differences between resident and flux-averaged concentrations indicate that distinctive immobile zones exist. When the mass transfer to the mobile zone is rate-limited, the observed flux-averaged concentrations depend on the flow velocity in the mobile zone. In our case, the observed resident concentrations in the streambed are likely to be not representative for the attributed water flux. The heterogeneity of mobile and immobile zones is beyond the resolution of the water flux measurements. This becomes apparent when the results from the passive samplers are compared. AR2 and AR3 are laterally separated by two metres. Both arrays were attributed to the same magnitude of groundwater discharge but significant concentration differences were observed. (Table 4.6 and Figure 4.4). Thus, the uncertainties of mass flux estimations increase when the heterogeneity of groundwater discharge increases. Given the long time-scale of streambed contamination on the other hand, diffusion from immobile to mobile zones should have resulted in a significant decrease of local concentration gradients. Small concentration differences between mobile and immobile zones support the hypothesis that the resident concentrations are representative means for the flux concentrations. Additional uncertainty to the mass flux estimates is introduced by the different scales of observation. The IPT samples a large aquifer volume and can be considered to be the most representative sampling method applied in this study. Snap-shot samplings are point measurements in space and time and the results from the passive samplers are point measurements in space but integral in time. Consequently, a reliable quantitative interpretation of the streambed contribution to the total mass fluxes can not be readily done. A comparison of the range of mass fluxes of MCB and DCB that have been estimated from the

different methods is shown in Figure 4.6. Despite the high variability of the results from the point-scale methods compared to the IPT, it is apparent that the mass fluxes originating from the streambed are consistently above the values originating from the aquifer (IPT).

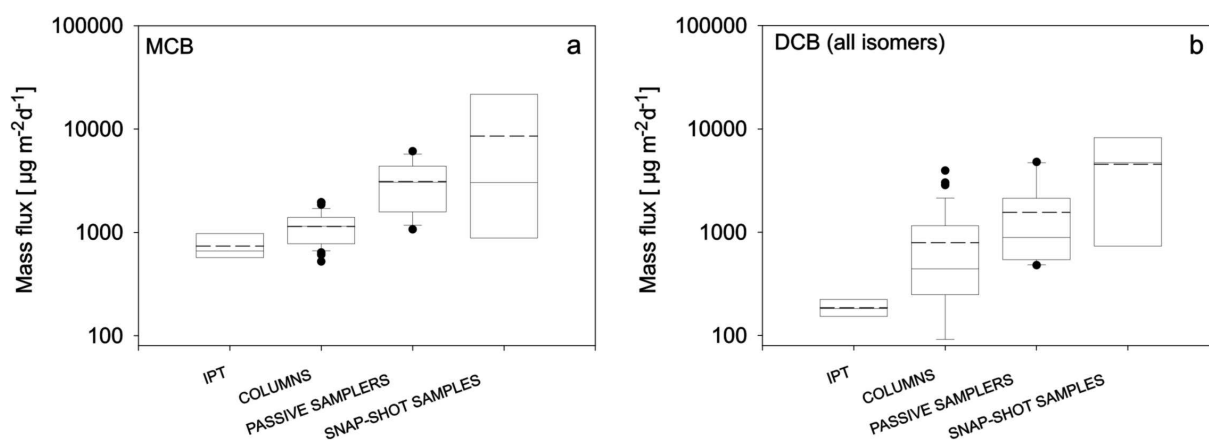


Figure 4.6. Range of estimated mass fluxes of MCB (a) and DCB (b) from the aquifer (IPT) and the streambed (Columns, Passive samplers, Snap-shot samples). Shown are the absolute outliers (dots), the 5. and 95. percentile (whiskers), the 25. and 75. quartiles (boxes), the median (solid line) and the arithmetic mean (dashed line).

4.7. Conclusions

At the Schachtgraben site at the fringe of the regionally contaminated area Bitterfeld-Wolfen, we investigated the contaminant mass fluxes at a stream-streambed-aquifer system using IPT, streambed temperature mapping, passive sampling and column experiments. The results indicated that the study site is characterized by a diffuse groundwater contamination rather than a distinct, concentrated plume. The aqueous contaminant concentrations in the shallow aquifer are significantly lower than in the streambed revealing that the streambed acts as contaminant source for the overlying stream water. Both, inputs from the groundwater and the streambed sediment represent a considerable contaminant source. However, a reliable quantification of mass fluxes from the streambed was difficult. Uncertainties of mass flux estimations may arise on the one hand from the potential deviation of sampled resident concentrations compared to the effective flux concentrations. On the other hand, the uncertainties can be a result of small scale variations of water fluxes that are beyond the resolution of the observation. Hence, to reduce these uncertainties there is need for estimating contaminant fluxes with direct methods.

Typically, the interface between groundwater and surface waters is considered to contribute to retardation and biodegradation and thus lead to a reduction of the mass flux of organic contaminant plumes. In our case, the streambed was potentially contaminated from direct inputs into the stream water. In combination with the contaminated groundwater discharging through the streambed, the site shows complex source and transport patterns. The observation that the streambed is an additional contaminant source is perhaps less prevalent compared to other sites. But this example shows that knowledge regarding the history of a site supports the set up of a conceptual model and will also help to make predictions on the contaminant transport.

Chapter 5

Time-scales of mass reduction of chlorobenzene in streambed sediments.

5.1. Abstract

Streambed sediments can act as long-term storage zones for organic contaminants. Until the early 1990s, the small man-made stream, subject of our study, in the industrial area of Bitterfeld (Germany), was used for waste water discharge from the chemical industry nearby. We investigated the long-term mass release of monochlorobenzene (MCB) from the streambed to the overlying stream water driven by advection of groundwater and diffusion from the contaminated streambed layer. The influence of the magnitude of groundwater discharge was studied in column experiments. The experimental results were inversely modelled applying standard single mass transfer rate models and in addition, a multiple rate mass transfer approach was used. The multiple rate model fitted the data much better than the single rate models. Alternatively, the contaminant transport in the streambed was conceptualized as diffusion into and out of a semi-infinite layer. The results of the long-term predictive modeling revealed that the time required to reduce the remaining mass fraction of MCB in the sediment to 50% of the initial value will be in the scale of decades to centuries. Further, the results did not show a systematic relation between the magnitude of advection in the streambed and the time required to reduce the remaining mass fraction in the sediments.

5.2. Introduction

Streambed sediments often act as long-term storage zones for organic contaminants and metals. The occurrence of contaminants in the streambed is a result of advection, diffusion as well as particle facilitated deposition and sorption to sediments. Contaminants may enter the streambed either by infiltration of stream water into the sediments (e.g.: Zaramella 2006, Wörmann 1998) or by discharging groundwater (e.g. Chapman et al. 2007; Conant Jr. et al., 2004). When the streambed sediments are permeable enough, hyporheic exchange and groundwater discharge drive advective transport within the streambed. Besides advection, diffusion of contaminants into bed sediments of streams and lakes can result in a sediment contamination (e.g. Formica et al. 1988, Richardson and Parr, 1988).

After the source areas at contaminated sites have been cleaned up and the water quality improves, the contaminants stored in the streambed sediments, originating either from the surface water or from groundwater plumes, may be released from the sediments back to the stream and may represent a dominant, long-term contamination source for downstream areas. Processes that contribute to the release of contaminants back to the surface water include bioturbation, sediment erosion, molecular diffusion and pore-water advection due to

groundwater discharge and hyporheic exchange (Thibodeaux et al. 2001, Erickson et al. 2005, Lick 2006).

This chapter aims to estimate the time-scales of the release of organic contaminants from streambed sediments picking monochlorobenzene (MCB) as example. The studied stream is located in the industrial area of Bitterfeld-Wolfen (Germany). In a previous study (Schmidt et al. 2008; and Chapter 4) we found that the streambed is characterized by considerably higher contamination levels than the stream water and the groundwater in the adjacent aquifer. The total contaminant mass fluxes entering the stream will decay with time because contaminants will be successively removed. Prediction of contaminant transport from the streambed towards the stream is difficult because long time periods of contamination resulted in an aged contamination that is released in low rates. Therefore, transport parameters such as retardation and mass transfer rates may be different from those obtained in the laboratory with freshly contaminated sediments (Sharer et al. 2003). At our study site, the streambed was exposed to organic contaminants over a time period in the order of decades. The direct inputs to the stream water were stopped about 15 years ago. Although this time appears to be relatively long, the streambed sediment is still contaminated. To elucidate the release behaviour of MCB, we conducted column experiments at flow rates that were in the range of the groundwater discharge rates observed in the studied stream reach.

5.3. Study site and background

The study was carried out in the industrial area of Bitterfeld/Wolfen, about 130 km south of Berlin, Germany. The region is one of the oldest centres of chemical industry in Germany (Heidrich et al. 2004a, b). One century of chemical production has resulted in a regional groundwater contamination with an estimated extent of 25 km² (Weiß et al., 2001). The main contaminants are volatile halogenated hydrocarbons, monoaromatic hydrocarbons such as BTEX or chlorinated benzenes and phenols, hexachlorocyclohexanes (HCH), polychlorinated biphenyls, dioxins, and a variety of other substances.

The investigations were conducted along a 220 m long reach of the Schachtgraben. The stream is part of the Mulde River system which is a tributary to the Elbe River. The Schachtgraben was man-made and had originally been constructed for mine water discharge from open-cast lignite mines. Later on, it was also used for waste water discharge from the chemical industry, resulting in the contamination of the streambed. Historic topographic maps from 1962 and 1984 revealed that the course of the Schachtgraben was changed at our investigated reach between those two dates. At the beginning of the 1990s, large parts of the chemical industry closed down. Early monitoring programmes during that time revealed a rapid decline of organic contaminants between 1990 and 1992 in the streams and rivers downstream of the study site, particularly in the Mulde River (LSA, 1993). In 1993, chlorinated benzenes were the substances with highest individual concentrations observed in the Mulde River with, for example, MCB concentrations up to 31 µg L⁻¹ (LSA, 1993). The

period when contaminated waste water influenced the sediments at our study site can therefore be constrained to approximately 10 to 30 years.

The contamination of the streambed was also assisted by the hydraulic conditions that were presumably different from those observed today. During the 1970s and 1980s the regional groundwater table was lowered by extensive open cast lignite mining and, moreover, the streamflow in the Schachtgraben was higher than today. Although we can not reconstruct whether the Schachtgraben was gaining or losing groundwater, it might have been rather losing. Today, the water table in the aquifer is generally higher than the water level in the stream. Hence, the Schachtgraben can be classified as a gaining stream. The magnitudes of groundwater discharge were observed along a 220 m long reach by Schmidt et al. (2006) and ranged between -10 and $455 \text{ L m}^{-2} \text{ d}^{-1}$. After the close-down of major parts of the chemical industry and the implementation of new environmental regulations and waste water treatment facilities, the contaminant release from streambed sediments and the discharge of contaminated groundwater became the dominant contamination source for the streams and rivers at the site, which is persisting until today.

The initial conditions in the streambed, when the contamination decreased in the early 1990s, are not known. Information about contamination levels during that time is not available, neither in the water nor in the sediment. Hence, for predictions we can only rely on current data.

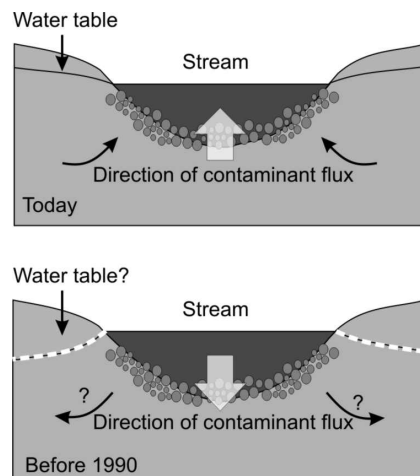


Figure 5.1. Direction of water and contaminant fluxes today and the potential situation before 1990.

The streambed of the Schachtgraben consists of a 0.6 m thick layer of crushed rock. The pore space of the crushed rock layer is filled with autochtone, sandy, fluvatile material. The stream is about 3 m wide and has an average water depth of 0.6 m. It partially penetrates a Quaternary alluvial aquifer. To characterize the interaction between the groundwater and the stream, Schmidt et al. (2006) recorded 140 streambed temperature profiles in the summer of 2005. The water fluxes through the streambed can be estimated based on observed streambed temperatures (Conant Jr. 2004, Schmidt et al. 2007). At the study site, the water fluxes ranged from $455 \text{ L m}^{-2} \text{ d}^{-1}$ of groundwater discharge to $10 \text{ L m}^{-2} \text{ d}^{-1}$ of stream water entering the

streambed (Schmidt et al. 2006). Preliminary investigations showed that the contamination level of pore water in the streambed sediments was significantly higher than in the alluvial aquifer (Schmidt et al. 2008 and Chapter 4, Kalbus et al. 2007).

5.4. Experimental section

5.4.1. Column experiment

In situ observations of long-term removal of contaminants from the streambed sediments are not readily possible. Thus, we set up a column experiment that simulates groundwater discharge to study the release of MCB from the streambed under controlled laboratory conditions. Six columns were packed with aliquots of a mixed sample of the fine grained fraction. The crushed rock was not included since its grain size is too big to fit into laboratory columns of the streambed sediment. The flow rates through the columns were chosen such that they corresponded to the observed range of groundwater discharge to the stream. They were set to range between 15 and 204 mL d⁻¹ which is equivalent to a vertical groundwater flux of 33 to 439 L m⁻² d⁻¹ (see Schmidt et al, 2006 and Chapter 3). The columns were the same as those described in Chapter 4 (30 cm long, 2.44 cm diameter). The effluents were directly collected into glass vials to minimize sorption to plastic tubes. The effluent samples were analyzed with GC-MS (see chapter 4 for details of the analytical method). Initially, the columns were sampled every 24 hours. Later, when the concentrations did not vary significantly on the daily time-scale, the sampling interval was increased to 168 h (one week). To obtain an estimate of the contaminant mass that was initially sorbed to the sediment, the remaining material from the sediment samples was analysed for sorbed MCB concentrations. In total, 8 samples with a weight between 5.7 and 9.0 g were extracted for one hour in an ultrasonic bath with a volume of acetone in mL that was three times the weight in g. The supernatants were analysed with GC-MS (Finnigan GC-MS, GC Type 9001, MS Type GCQ TM, Column: Chrompack Zekrosil-8-CB, 30 m, ID 0.25 mm, FD 0.25 µm, injection volume 1 mL splitless). For quantification, deuterated MCB was added as internal standard.

5.4.2. Batch sorption experiment

The purpose of the sorption experiments was to determine the sediment-water distribution coefficient in equilibrium as input for the subsequent transport models presented in this study. The sorption experiments were conducted with streambed sediment samples from the Schachtgraben in order to represent the field conditions. In total, 9 aliquots of 5.8 to 6.7 g of wet sediment were weighed into glass vials (Supelco 40 mL) and 20 mL of purified water were added. The applied aqueous concentrations of MCB ranged from 0 to 2000 µg L⁻¹. The vials were shaken for 5 days in an overhead shaker. After sedimentation, 250 µL of the supernatants were sampled into head-space vials filled with 10 mL of purified water. The supernatants were analysed with the same GC-MS method as used in Chapter 5.4.1.

The results of the batch sorption experiment are shown in Figure 5.2. The final concentrations in the solid phase were determined experimentally by solvent extraction with acetone. For the extraction procedure the sediment samples from the sorption experiment were extracted for one hour in an ultrasonic bath with a volume of acetone in mL that was three times the mass of the sediment samples in g. The extracts were analysed using the same method as in Chapter 5.4.1 (column experiment). Additionally, the final solid concentrations were calculated by mass balance, taking the difference between the initial and the final aqueous concentration as the amount that was sorbed to the sediment. Both, the estimated and the measured linear sorption isotherm provide similar results. The linear isotherm model provides a good fit to the data with a coefficient of determination of 0.978. The obtained partitioning coefficient (K_D) of 2.1 L kg⁻¹ was used as input for the transport models for all columns.

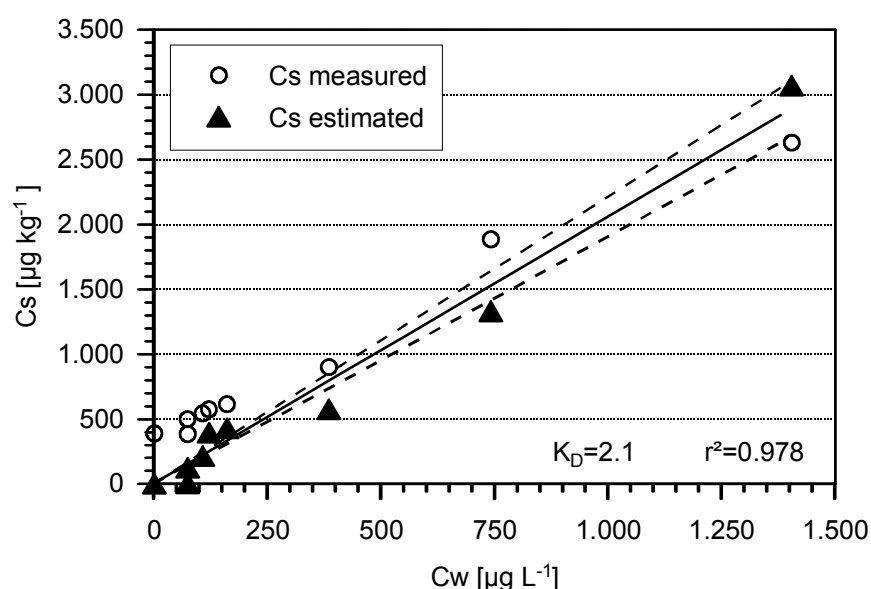


Figure 5.2. Linear sorption isotherm of MCB. C_w is the aqueous concentration, C_s is the concentration in the solid phase. C_s measured was obtained by solvent extraction and GC-MS analysis and C_s estimated was obtained from mass balance calculations. The dashed lines mark the 95% confidence bounds.

5.5. Column experiment analysis using CXTFIT

The effluent concentration time series were inversely modeled with the code CXTFIT. The programme solves the one-dimensional mobile-immobile advection-dispersion equation and is often used to analyse column experiments. Full details on CXTFIT are given in Toride et al. (1999). The modelling was performed to derive parameter sets to describe and to predict the outflow and the remaining sorbed concentration of MCB. The measured MCB effluent concentrations, expressed as relative concentrations, were fitted by using two conventional first-order models: a one-site chemical non-equilibrium model (“one-site model”) and a two-region physical non-equilibrium conceptual model (“two-region model”). For the sake of completeness, a simple equilibrium transport model was additionally fitted to the effluent

concentration time-series to test whether similar quality of fit can be obtained. CXTFIT uses non-linear least square fitting to optimize the model parameters.

In equilibrium transport models, mass transfer is conceptualized as an instantaneous partition of the substance between the solid and the liquid phase of the porous medium. Equilibrium models assume that the rate of mass transfer between the solid and the liquid phase is much faster than the rate of advection in the fluid. The only parameter that was fitted to the data was the hydrodynamic dispersion coefficient (D).

The mass transfer in standard chemical one-site and physical two-region non-equilibrium transport models is formulated as a first-order process where k is the mass transfer rate constant between a mobile and an immobile domain. In a one-site non-equilibrium model the immobile domain is conceptualized by kinetic sorption of a contaminant to the solid phase of the porous medium. In this simplest non-equilibrium model the mass transfer between the solid and the liquid phase is expressed with a first-order rate coefficient k (1/time). In our simulations D and k were fitted to the data. Additionally, a set of one-site model was also run allowing the retardation coefficient (R) to be fitted. In physical non-equilibrium models are conceptualized by dividing the liquid phase into mobile regions where the water is flowing and into immobile regions with stagnant water. The mass transfer between the mobile and immobile zone is modeled as a first-order process. The parameters D , k and β were fitted. The β expresses the ratio of the mobile and immobile porosity regions. The fraction of equilibrium sites was set to 0.5 for all columns. Mathematically, the two first-order models are identical (Haggerty and Gorelick 1995). Practically, for fitting the model to the observed concentrations, the two-region model has an additional fitting parameter (β) compared to the simpler one-site model.

In all models (equilibrium, one-site and two-region non-equilibrium) the hydrodynamic dispersion coefficient D was fitted using a constrained parameter estimation procedure. The range of the dispersion coefficient corresponds to values of longitudinal dispersivity of 0.001-0.1 m.

The Darcian flow velocity v was experimentally determined for each column and the retardation coefficient R was derived from the partition coefficient K_D which was estimated from the sorption experiment described in Chapter 5.4.2.

As initial and boundary conditions we assumed an initially constant, equilibrium MCB concentration in the columns of $c/c_0=1$. A constant input of solute-free water was applied as flux boundary condition.

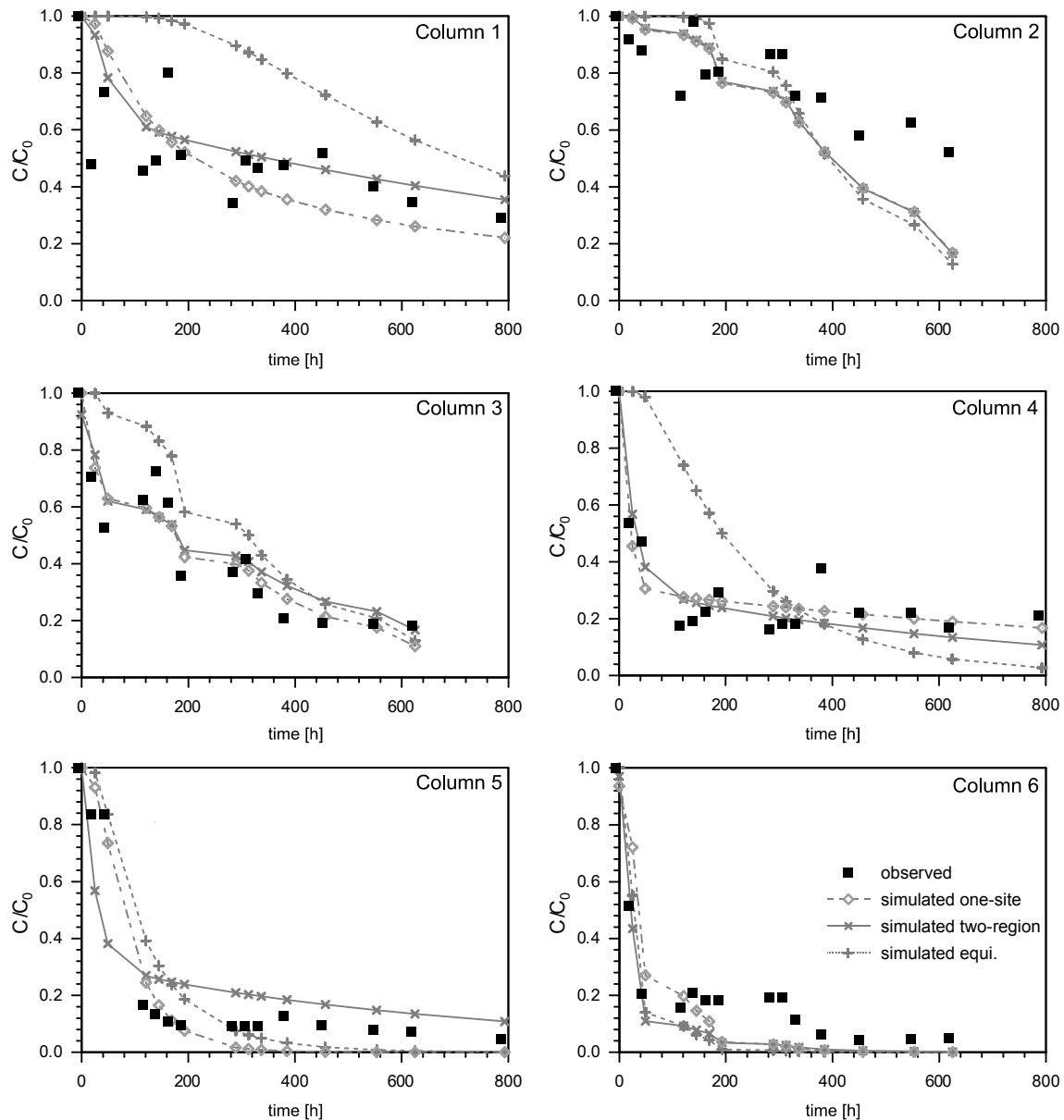


Figure 5.3. Observed and modelled MCB concentration time-series for Column 1-6. The concentrations were modelled with CXTFIT for equilibrium, chemical one-site non-equilibrium and physical two-region non-equilibrium conditions. The legend for all subplots is provided in the subplot of Column 6.

The effluent concentration time-series of the six columns were inversely modelled with CXTFIT. For each dataset, the equilibrium model, the one-sitemodel and the two-region model were fitted. For each column, the observed and the simulated effluent concentrations are displayed in Figure 5.3. The estimated parameters and the quality of fit are summarized in Table 5.1. In general, the differences in the quality of fit were larger between the different columns than between the models. In other words, for columns where only poor fits for one model were achieved, the fits for the other models were also poor and vice versa. Poor fits were obtained for column 1 and column 2 with estimated coefficients of determination below 0.4. For column 2, meaningful coefficients could only be obtained when R was optimized. For $R = 12.16$, as estimated from the experimental data, the coefficients of determination were

below 0.2. Higher flow rates tend to result in better fits. The data of column 5 always resulted in the best fits ranging between 0.90 and 0.98 (Table 5.1).

Table 5.1. Parameters of the best fit CXTFIT models: v is the flow velocity, R is the retardation coefficient, k is the desorption rate constant, D is the hydrodynamic dispersion coefficient, β is the capacity coefficient.

	Experimentally determined parameters		Fitted parameters						
	ν	R	k	D	β	r^2			
	cm h ⁻¹	-	h ⁻¹	cm ² h ⁻¹	-				
Equilibrium									
Column 1	0.39	12.16		3.917		<0.2			
Column 2	0.70	12.16		2.481		<0.2			
Column 3	0.82	12.16		8.204		0.40			
Column 4	1.44	12.16		14.368		<0.2			
Column 5	2.83	12.16		28.285		0.90			
Column 6	5.22	12.16		52.236		0.77			
Parameter set with additionally fitted R									
Non-equilibrium one-site						D	k	R	r ²
Column 1	0.39	12.16	0.0012	3.917	0.37	3.92	0.0016	10.29	0.37
Column 2	0.70	12.16	0.0122	0.358	<0.2	0.66	0.0028	24.79	0.77
Column 3	0.82	12.16	0.0027	0.082	0.86	0.07	0.0047	9.219	0.92
Column 4	1.44	12.16	0.0019	7.603	0.86	8.24	0.0009	19.98	0.87
Column 5	2.83	12.16	0.5109	28.285	0.90	18.45	0.2656	8.64	0.94
Column 6	5.22	12.16	1.5600	61.452	0.77	52.24	1.0616	17.24	0.81
Non-equilibrium two-region									
Column 1	0.39	12.16	0.0067	3.917	0.1	0.31			
Column 2	0.70	12.16	0.0517	0.421	0.1	<0.2			
Column 3	0.82	12.16	0.0182	8.204	0.19	0.89			
Column 4	1.44	12.16	0.0079	14.368	0.17	0.85			
Column 5	2.83	12.16	0.0066	0.283	0.41	0.98			
Column 6	5.22	12.16	0.0131	7.823	0.64	0.83			

It was reported in the literature (Bajracharya and Barry 1997, Haggerty et al. 2004) that values of k may correlate with the flow velocity. In an analysis of literature data, Haggerty et al. (2004) found a stronger correlation with the advection time (LR/v , where L is the length of the column) than with the flow velocity alone. We observed a relationship between velocity and k as well as for advection time and velocity and k for columns 3, 5 and 6 for the one-site model. Column 4 was characterized by very low values of k . Similar observations can be made for the two-region model. An obvious difference between the estimated values of k is that the observed range is larger for the one-site model (three orders of magnitude) than for the two-region model (one order of magnitude) (Table 5.1). The results imply that there is no clear correlation between v and k of contaminant release. Thus, the magnitude of groundwater discharge may not control the release of MCB under field conditions. In the two-region model, the capacity coefficient β is a measure of the fraction of mobile water. the total porosity increases with increasing flow velocity from about 0.1 for column 1 and 2 to 0.64 for column 6. In CXTFIT large values of β refer to a large fraction of mobile porosity. The implication is that with increasing flow velocity an increasing pore fraction is subject to

advection. However, still the fraction of immobile porosity remains large and thus can contribute to the tailing of the effluent concentration. Generally, the model results tend to underestimate the observed late-time concentrations. The reason for this behaviour may be the increasing desorption resistance of the remaining mass fraction. The fractional mass of MCB that remains in each column over the course of the experiment was calculated for the non-equilibrium models from the mean and the 95% confidence bounds of the initial sorbed concentration of MCB and the cumulative mass that has left each column (Figure 5.4). It is apparent that the observed release of MCB from the columns is very unefficient. After ~1000 h, a maximum fraction of 20% was released (column 6). A weak trend can be observed that the released fraction increases with increasing flow rate. The model results, however, indicate a much faster mass release leading to a fraction of 50-100% of MCB mass released over the course of the experiment. It seems that there is no systematic deviation between the one-site and the two-region model. For column 2, the results of the two models were nearly identical, while for columns 4, 5 and 6 the one-site model predicted a faster mass release. Conversely, for columns 1 and 3 the two-region model showed a faster mass release.

Predictions of the time-scales of mass reduction in the streambed based on the obtained parameter sets would be subject to a high degree of uncertainty. Moreover, the fractional mass that remains in each column was significantly underestimated and deviated substantially from the observed values. One reason may be that the applied non-equilibrium models conceptualize mass transfer with a single rate constant. In natural porous media, mass transfer rates are influenced by a variety of factors. The most relevant factors that control the mass transfer and thus the release of contaminants from sediments are the distribution of organic materials, the type and distribution of minerals and the geometry and distribution of low-permeability zones such as clay lenses. Given the variety of factors, mass transfer may be better described by models that account for multiple mass transfer rates (Haggerty and Gorelick, 1995). The partly poor fits of the models to the observed concentration time series may also be attributed to the consideration of only a single mass transfer rate. Additionally, even when the experimental data is well represented in a single-rate model (e.g. Column 5), predictions of the estimated apparent rate constant may be influenced by the duration of the experiment. Haggerty et al. (2004) found that the observed effective mass transfer rates decrease with the duration of the experiment. Longer experimental time-scales allow to fit the tailing of the concentration time series and thus will result in lower effective mass transfer rates. This implies that the time-scales of contaminant release estimated from the column experiment with the non-equilibrium single-rate models will be underestimated compared to the true release time-scale in the field.

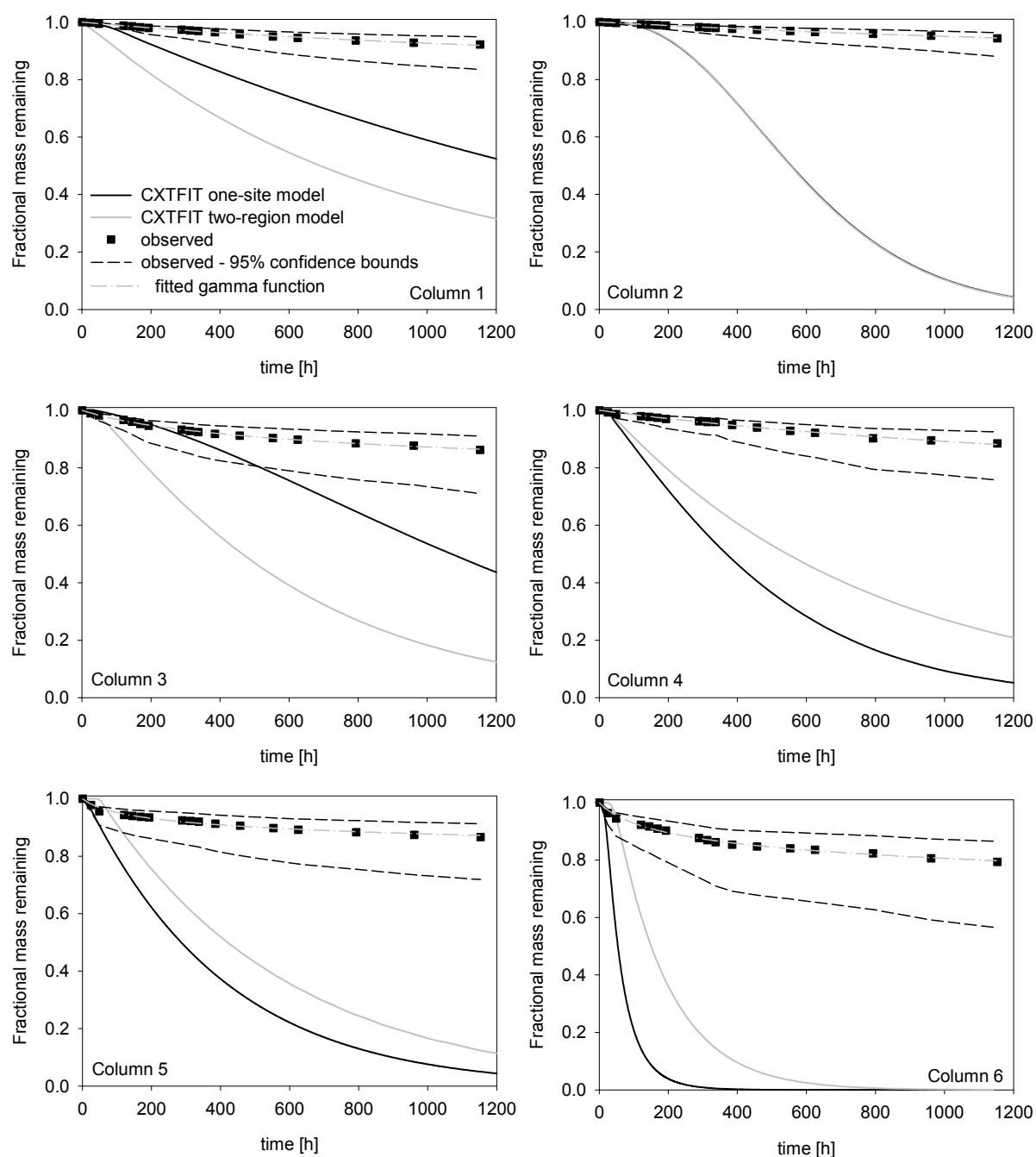


Figure 5.4. Fractional mass remaining in the column as a function of time. Plotted are the observed values, the results from the CXTFIT models (best fit to the effluent concentration) and the multiple-rate model. The legend for all subplots is provided in the subplot of Column 1.

5.6. Column experiment analysis using a multiple-rate model

Giving the deviations between the observed and the modeled remaining mass fraction, it becomes obvious that conventional transport models may not be capable to predict rate limited transport and are not suitable to describe the long-term mass release of MCB from aged contaminated streambed sediments. Thus, an alternative approach is needed to further constrain the time-scales of MCB release from streambed sediments. One alternative to

conventional first-order models are multiple rate models. Here, the first-order mass transfer coefficients are described by a continuous statistical distribution.

We applied the gamma distribution of rate coefficients to fit the column data. Gamma distributions were used by several authors to describe multiple-rate coefficients (Connaughton et al. 1993, Culver et al. 1997, Deitsch et al. 1998, Deitsch et al. 2000, Haggerty et al. 2000). The gamma density function of first-order desorption rate coefficients is:

$$p(k) = \frac{k^{\eta-1} \gamma^\eta}{\Gamma(\eta)} \exp(-\gamma k) \quad [5.1]$$

where γ is the scale parameter, η is the shape parameter and Γ is the gamma function. Following Connaughton et al. (1993), the mass that remains in a column with contaminated streambed sediment after time t is:

$$m_{col}(t) = \int_0^\infty m_{col,i} p(k) \exp(-kt) dk = m_{col,i} \left(\frac{\gamma}{\gamma + t} \right)^\eta \quad [5.2]$$

The fraction of mass that has left the columns after time t is then:

$$1 - \frac{m_{col}(t)}{m_{col,i}} = 1 - \left(\frac{\gamma}{\gamma + t} \right)^\eta \quad [5.3]$$

To obtain the time-scales of MCB release from the columns, a multiple mass transfer rate model was fitted to the data of the fractional mass released from the columns. The fits were in general very good (Table 5.2). The coefficients of determination varied between 0.9818 (Column 5) and 0.9984 (Column 2). Interestingly, the data from Column 5, to which the best fit by the single-rate models was achieved, exhibit the worst fit for the multiple-rate model.

Table 5.2. Parameters for the multiple-rate gamma distribution model

	Gamma distribution parameters			η	lower and upper 95% confidence bounds of η		r^2
	γ	lower and upper 95% confidence bounds of γ					
Column 1	891.4	676.2 1107		0.09386	0.07658 0.1111		0.9975
Column 2	1423	1079 1766		0.1059	0.08493 0.1269		0.9984
Column 3	178.9	154.4 203.4		0.06678	0.06182 0.07175		0.9981
Column 4	1126	624.8 1627		0.1971	0.1274 0.2669		0.9929
Column 5	42.68	25.32 60.04		0.03781	0.03195 0.04368		0.9818
Column 6	56.51	40.65 72.37		0.06778	0.05996 0.0756		0.9912

In Figure 5.4 the fitted data is plotted as mass fraction remaining in the columns. The release time-scales, expressed as the time at which 50% of the initial sorbed mass has been released from each column (t_{50}), varied in a wide range between 7 (Column 4) and > 2500 years (Column 5). The results for the other columns, as well as the 95% prediction bounds, are displayed in Table 5.2. Apparently, the fitted t_{50} is independent of the flow rate which is increasing from column 1 to column 6. Although the gamma distribution of rate coefficients provides excellent fits to the experimental data, it does not necessarily represent the true

processes that control the desorption behaviour of MCB in our sediment. The long tails of the fitted gamma distributions introduce very long desorption time-scales that may be artificial (Cunningham et al. 2005). Other authors also observed long-tailed desorption behaviour (e.g. Deitsch et al. 2000) applying a gamma distribution of rate coefficients. Long-tailed behaviour of desorption can also be observed for other two-parameter distributions such as the log-normal distribution of mass transfer coefficients (Cunningham et al. 2005). Additional uncertainty arises from the small mass fractions that were removed from the columns over the course of the experiment of ~ 1000 hours (Figure 5.4). A longer time-series of experimental data would help to reduce the prediction uncertainty of fitted models.

Table 5.3. Times required to remove 50 % of the initial MCB mass from each column according to the multiple-rate model.

	t_{50} (years)	lower and upper 95% confidence bounds		fraction released after 15 years (=131400 h)	lower and upper 95% confidence bounds	
Column 1	262	939	98	0.375	0.335	0.415
Column 2	180	609	72	0.382	0.338	0.425
Column 3	2080	1052	570	0.357	0.341	0.372
Column 4	7	20	4	0.610	0.513	0.706
Column 5	>2500			0.262	0.236	0.288
Column 6	285	812	118	0.409	0.382	0.436

The fraction of mass that is potentially released from the columns after 15 years of desorption was estimated to be within the scale of the streambed diffusion model (Chapter 5.7), ranging between 26.2% (column 5) and 61.0% (column 4) (see also Table 5.3). However, column 4 and 5 represent the extremes within the range of time-scales. The other columns are characterized by a released fraction between 0.357 and 0.409. It should be noted that the streambed material used in the column experiment was potentially subject to desorption since the beginning of the 1990s. Thus, the faster desorbing fraction may have already been removed from the sediments and we now observe the release of the very slowly desorbable residual contamination. This could again account for the significance of the very long time-scales of desorption.

5.7. Streambed diffusion model

The transport of contaminants from the stream water to streambed sediments and the release back towards the stream can be described as a diffusive process (e.g. Lick 2006, Richardson and Parr 1988). The vertical concentration profile in initially clean, semi-infinite streambed sediments that were exposed to a constant, homogeneous concentration in the overlying water (c_0) for a certain duration (t_c) can be expressed as:

$$\frac{c}{c_0}(z, t_c) = \operatorname{erfc} \frac{z}{\sqrt{4D_a t_c}} \quad 5.4$$

where z is the depth (m), D_a ($\text{m}^2 \text{s}^{-1}$) the apparent diffusion coefficient of the respective contaminant. The mass that has been accumulated in the streambed per unit area after t_c is:

$$m_c(t_c) = 2c_0\alpha\sqrt{\frac{D_a t_c}{\pi}} \quad 5.5$$

where α is the capacity factor defined by $\alpha = \theta + K_D\rho$ (θ is the porosity, K_D is the sediment water distribution coefficient and ρ is the bulk density). When the concentration in the streamwater suddenly drops, e.g. due to environmental protection measures or like in our case study, the closure of the industries, the contaminants that diffused into the streambed sediments will start to diffuse back to the stream water. The time since the beginning of the decontamination is referred to as t_d (decontamination time). As boundary condition we define that c_0 changes to 0 at time $t_d=0$. The initial condition of the concentrations in the streambed is given with equation 5.4. The mass diffused back to the stream per unit area of the streambed after a certain t_d is (Grathwohl 1998, Bear et al. 1994):

$$m_d(t_d) = 2c_0\alpha\left(1 - \sqrt{1 + \frac{t_c}{t_d}} + \sqrt{\frac{t_c}{t_d}}\right) \quad 5.6$$

Unfortunately, the concentrations in the stream water at the study site during t_c are unknown and therefore, we have no information about c_0 . To circumvent this problem, the mass that has left the streambed after t_d can also be expressed as the mass relative to the mass that was accumulated in the streambed at $t_d=0$:

$$\frac{m_d(t_d)}{m_c} = \left(1 - \sqrt{1 + \frac{t_c}{t_d}} + \sqrt{\frac{t_c}{t_d}}\right) \quad [5.7]$$

The relative mass remaining in the streambed can be subsequently calculated by:

$$1 - \frac{m_d(t_d)}{m_c} \quad [5.8]$$

The relative mass is independent of sorption properties of the contaminant because sorptive compounds diffuse slower into the streambed and, hence, also the initial mass m_c is lower provided that the sorption parameters remain constant over time.

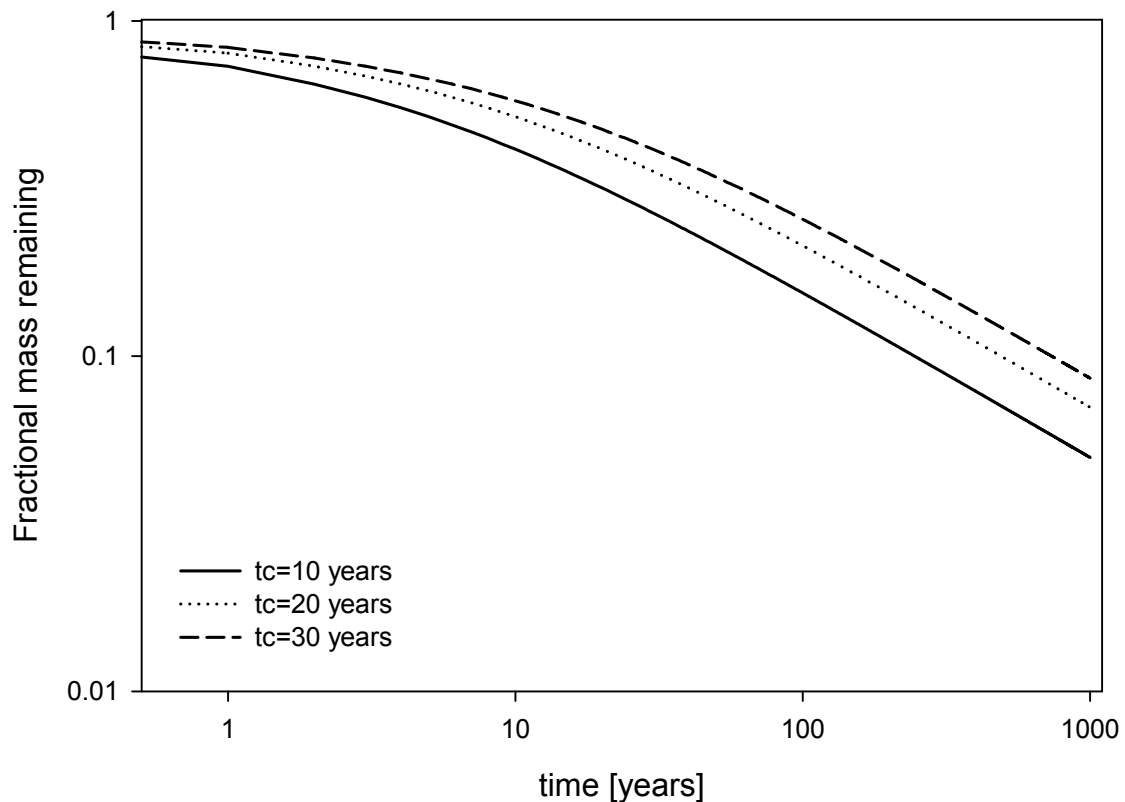


Figure 5.5. Fractional mass remaining per unit area of the streambed from the diffusion model depending on the contamination time.

The time-scale of MCB release from the streambed sediment by diffusion depends on the time period when the sediments were exposed to the contamination in the stream water (t_c). Unfortunately, we were not able to fully reconstruct the contamination history of the Schachtgraben, but we can constrain t_c to be in the range of 10 to 30 years. To test the influence of different contamination times, we calculated the results of the streambed diffusion model for $t_c=10$, 20 and 30 (t_{c10} , t_{c20} , t_{c30}) years, respectively. For each t_c the times required to release 50% and 90% (t_{50} and t_{90}) of the initial mass per unit area of the streambed after the contamination in the stream water dropped were calculated. The calculated values of t_{50} ranged between 5 years and 8 months (= 68 months) for t_{c10} , 11 years and 3 months (= 135 months) for t_{c20} and 16 years and 11 months (= 203 months) for t_{c30} , respectively. The time required to remove 90% of the contaminant mass is in the scale of centuries (246 years for t_{c10} , 490 years for t_{c20} , and 735 years for t_{c30}). A comparison to the multiple rate model shows that t_{90} for the streambed diffusion model is in the order of magnitude of t_{50} of the multiple-rate model. Thus, the time-scale of MCB-release from the columns is much longer than for the streambed diffusion model. This deviation may be an artifact resulting from the fit of the gamma model and does not necessarily have a physical meaning.

Nowadays, it is approximately 15 years since the stream water contamination level rapidly decreased. The mass fractions that have been released from the streambed after 15 years were

estimated with respect to t_c . For t_{c10} , 64.4 % of the initial mass was released after 15 years (t_{c20} : 54.3 %; t_{c30} : 48.2%). The result for t_{c10} shows that the time required for desorption is longer than the contamination time. When the decontamination starts as the concentration in the surface water decreases not all contaminant mass diffuses towards the surface water. Partially, the contaminant continues to diffuse into the layer, resulting in a long decontamination time. In case no other transport processes occurred and degradation is negligible, the desorbed contaminant mass per unit area of the streambed is in the range of 35.6 to 51.8% of the initial mass at the beginning of the 1990s. For long decontamination times, the fraction of mass remaining in the streambed decreases with the square root of time. When plotted in a log-log plot the slope is -0.5 (Figure 5.5) (Grathwohl, 1998). The mass fraction that remains in the streambed is independent of the sorption properties of a particular contaminant provided that the sorptive properties of the sediment remain the same during the contamination and the decontamination period.

Although the results of the streambed diffusion model seem reasonable in terms of the mass fraction that is still present in the sediment, it is a very simple, somewhat unsophisticated estimation. A variety of processes is not considered in this approach which potentially affect the time-scales of contaminant removal. Biodegradation processes in the streambed would reduce the time required to remove the contaminants. In Chapter 3 and in Schmidt et al. (2006) we found that groundwater is discharging through the streambed and thus advection of water will influence the mass transfer from the sediments. Active sediment processes such as bioturbation and sediment turnover can accelerate the release of organic contaminants compared to diffusion alone. Since the streambed is constructed of a crushed rock layer and appears to be stable, we do not expect that the particle mobilization dominates the contaminant transport at the site. The advantage of the selected approach is that the actual release of contaminants can be related to the history of contamination. Therefore, despite the significant simplifications, the streambed diffusion model can help to constrain the potential time-scales of contaminant release from the streambed sediments.

5.8. Conclusions and implications

The streambed sediments of the Schachtgraben were exposed to organic contaminants which were discharged to the stream water for decades. The resulting contamination of the streambed persists until today although the direct contaminant inputs were stopped approximately 15 years ago.

We used column experiments to elucidate the desorption behaviour of MCB which is the major contaminant at the site. The flow rates of the six columns were set to represent the range of observed magnitudes of groundwater discharge. Initially, we hypothesized that the time-scales required to reduce the contaminant mass in the sediment are influenced by the flow velocity. The observed effluent concentrations of MCB decreased faster with increasing flow rates. However, after the initial flushing of the columns, the concentrations decayed practically independent of the flow rate at late times. The concentration time series of MCB

were inversely modelled using standard equilibrium as well as one-site and two-region non-equilibrium transport models. The model results showed an overprediction of the fractional mass removed from the column after a certain time. One reason might be, that in these models only a single first-order rate coefficient of mass transfer is fitted to the observed data, which may result in overpredicting the bulk desorption rate. Thus, it is debatable whether a standard sorption isotherm and the subsequently derived sediment-water distribution coefficient are useful for desorptive transport problems. The fractional mass that remains in the column was much better represented by a multiple-rate model that was fitted directly to the mass rather than to the concentrations. The predicted time required to release 50% of the MCB mass from the columns was in the range of centuries.

Alternatively, the release of MCB from the streambed was described as a diffusion processes into and out of a homogeneous sediment layer. The estimated time required to remove 50% of the initial mass ranged between ~6 and ~17 years. Thus, according to the diffusion model, the mass currently sorbed in the streambed is approximately 50% of the initial value 15 years ago. The time required to remove 90% of the initial mass is in the scale of centuries.

In general, the removal of contaminant mass from the columns and thus from the streambed sediments is very inefficient. Although a relatively large fraction of the initial MCB mass still remains in the sediments, the elution mass fluxes are reduced to a low, tailing level. Consequently, if no significant contaminant degradation occurs, the streambed will remain contaminated for further decades or even centuries. Non-acute but persistent contaminant fluxes out of the streambed will represent a long-term, diffuse contaminant source for the surface water.

Chapter 6

Synthesis and outlook

6.1. Synthesis

In this thesis, we studied spatial patterns of groundwater discharge to streams and their implications on contaminant mass fluxes from the aquifer and streambed sediments towards the stream. The thesis basically comprises two parts. First, we developed, evaluated and applied a temperature-based method to quantify magnitudes of groundwater discharge. Then, we studied the influence of heterogeneous groundwater discharge on the mass fluxes and the release time-scales of organic contaminants from contaminated streambed sediments.

Spatial patterns and magnitudes of water fluxes at the stream-groundwater interface are considered to have significant implications on the transport, distribution and metabolism of solutes, nutrients as well as contaminants on the reach scale and within a watershed. Moreover, the water flow in the streambed forms habitats and controls microbiological processes. However, the magnitude of stream-groundwater exchange also controls the propagation of dissolved organic contaminants between aquifers and streams. Patterns of water fluxes and aqueous contaminant concentrations at the interface are potentially complex and characterized by spatial variations in the scale of metres, often centimetres. When a groundwater plume is approaching a stream, it may be altered in its concentration distribution and composition in the streambed. The contaminant fluxes at spatially distinct high discharge locations can significantly contribute to total contaminant mass entering the stream water. Hence, for a reach-scale analysis of groundwater surface water interactions and associated contaminant transport a meter-scale resolution of fluxes may provide a valuable insight.

In general, it is often challenging in field studies to find the optimal balance between the required temporal and spatial resolution of measurements to gain insight into the processes of interest and the personnel, instrumentation and cost efforts that scientists and practitioners can make to take measurements and collect appropriate data in the field. In this light, it is beneficial to develop effective measurement techniques that can provide an increased resolution on the same extent of observation without increasing the measuring efforts.

Common methods to investigate water fluxes at the stream groundwater interface are based on Darcy's law and require the installation and hydraulic testing of streambed piezometers. Other methods like seepage meters directly estimate magnitudes of groundwater discharge but can not be installed in coarse grained streambed sediments. In a number of studies time-series of streambed temperatures were measured and analysed to estimate water fluxes for both losing and gaining streams. Recording time-series of streambed temperatures requires the deployment of sensors and data loggers. The classical Darcy's law based water flux measurements, direct measurements as well as temperature time-series based methods

may be restricted to a relatively small number of sampling locations because of their considerable equipment or measuring requirements. To increase the spatial resolution of water flux estimates, we propose a temperature based methodology that is referred to as streambed temperature mapping. Streambed temperature mapping is performed by temporarily inserting a temperature probe into the streambed at many locations in the required lateral resolution. The point measurements can be interpolated to generate plan view maps of streambed temperatures. Previous work demonstrated (Conant Jr. 2004) that the mapped streambed temperatures can be empirically related to water flux estimates from independent methods such as hydraulic testing of streambed piezometers. With our approach, we demonstrate that mapped streambed temperatures can be directly, physically-based related to the Darcian velocity of water in the streambed. The suggested methodology assumes vertical, steady flow of heat and water in the streambed and is based on an analytical solution of the heat-diffusion-advection equation.

The method was tested on temperature data-sets mapped in a uniform depth in streambeds of two streams in Ontario, Canada. The water fluxes directly obtained from the temperature data were compared to the flux estimates from seepage meters and streambed piezometers. The results suggest that the temperature based method provides reasonable estimates but tends to underestimate the water fluxes at high groundwater discharge locations. The underestimation may arise from lateral heat diffusion between the often spatially distinct locations of high groundwater discharge and the surrounding lower discharge locations. The spatial patterns of the magnitudes of groundwater discharge, however, can be resolved in a sufficient manner without the need for additional instrumentation.

The concept of streambed temperature mapping implies one key assumption: The observed differences of streambed temperatures in the mapped depth are solely a function of the magnitude of water flux and are not subject to the temporal variability of streambed temperatures over the course of the mapping. However, we know that subsurface temperatures are influenced by diurnal and annual atmospheric temperature oscillations. Also streambed sediments are subject to temperature variations. All methods that use heat as natural tracer to detect the movement of water make use of the fact that the temperatures can significantly differ between the surface and the subsurface. The concept of streambed temperature mapping makes use of the annual differences between the nearly constant, unaffected by surface temperature oscillations, groundwater temperature and the colder (winter) or warmer (summer) surface water. According to experiences, streambed temperature mapping at the reach scale usually requires a few days up to one week. Given the relatively short time, annual temperature oscillations do not affect the observed temperatures. On the annual time-scale streambed temperatures can yet be referred to as being in a quasi steady-state for the time required to perform the mapping. Since streambed temperature mapping at the reach scale usually requires a few days, the streambed is subject to diurnal temperature variations. The depth to which surface temperature oscillations are propagated into the subsurface is a function of the thermal properties of the sediments and moreover of the

wavelength of the temperature signal. Diurnal temperature variations only influence the upper centimetres of the sediment column. We hypothesized that “diurnal disturbances” that affect the quasi steady-state temperatures can be mitigated or ideally excluded from the measurements when the mapping depth is sufficiently deep. Taking time-series of stream temperatures collected during mapping programmes in both winter and summer, we numerically simulated the influences of the real surface water temperature oscillations on the streambed for different groundwater discharge rates. Our results suggest that temperature mapping in a depth of 0.2 m is sufficient to avoid significant deviations from the quasi-steady-state. This result also has implications on methods that are relying on the propagating temperature signal to quantify the water flux based on the phase shift or the amplitude decay. In general, with increased magnitude of groundwater discharge the amplitudes of temperature oscillations in the streambed decrease. For very low groundwater discharge or recharge the diurnal signal is elongated. Under these conditions the mapped temperatures are likely to be not in quasi steady state. However, the consequences for the absolute flux estimations remain small since the practical relevance of groundwater discharge that has been estimated with $10 \text{ L m}^{-2} \text{ d}^{-1}$ is for instance doubled or halved.

To improve the robustness of the water flux estimates from mapped streambed temperatures and to better account for low groundwater discharge rates, we extended the streambed temperature mapping concept. In contrast to mapping streambed temperatures in a single, uniform depth, we simultaneously measured in five depths using a newly constructed temperature probe. On the basis of the mapped, quasi-steady-state streambed temperature profiles, the water fluxes can be obtained by fitting a steady-state analytical model to each observed temperature profile. In the applied configuration, the deepest temperature sensor is placed 0.5 m below the streambed surface. Consequently, the estimated water fluxes become less sensitive to diurnal temperature influences because of the increased observation depth and less sensitive to random errors since the water flux estimates rely on five instead of one temperature measurement.

In this thesis, spatial patterns of groundwater discharge were evaluated from two temperature data sets from one case study in Ontario, Canada and from two case studies in Germany where the measurements were carried out over the course of the thesis. In all case studies that have been performed or evaluated, a few, spatially small high discharge locations contribute the highest proportion of the groundwater discharge along the investigated reaches (Figure 6.1). At the Pine River in Ontario, Canada, the Schaugraben and the Schachtgraben both in Germany, the spatial resolution of water flux data was sufficient to evaluate the distribution of fluxes versus the streambed area. At the Schachtgraben site (Chapter 3) approximately 50% of the streambed area contributes to 80% of the total discharge. For the Pine River site the curvature is less pronounced compared to the Schachtgraben. The inequality of the water flux distribution is lowest at the Schaugraben site. Remarkably, the Schachtgraben streambed was constructed and hence, is characterized by the least heterogeneous sediments of the three sites, but the heterogeneity of the water fluxes is higher

than at the other sites. This suggests that high discharge zones are either correlated with high permeability zones in the aquifer rather than the streambed itself. Thus, the structure of the underlying aquifer may be the key to explain the observed patterns. Consequently, practically as a side effect, mapped streambed temperatures may open up a window to the aquifer heterogeneity adjacent to the stream.

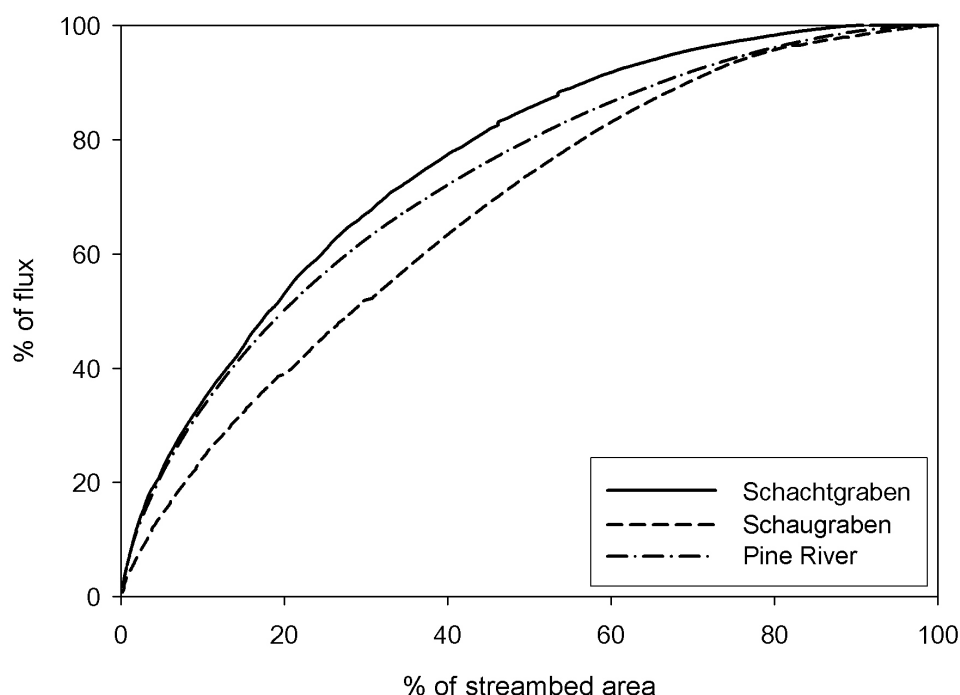


Figure 6.1. Percentage of flux vs. percentage of streambed area for the Schachtgraben (reach length 220 m), the Schaugraben (reach length 750 m) and the Pine River (reach length 60 m). Percentage of flux vs. percentage of streambed area for the Schachtgraben (reach length 220 m), the Schaugraben (reach length 750 m) and the Pine River (reach length 60 m).

At the Schachtgraben site, located in the regionally contaminated area of Bitterfeld-Wolfen, the stream water is polluted with a variety of organic contaminants but mainly with chlorinated benzenes. It is unlikely that the actual contamination originates only from direct inputs into the surface water. The actual contamination of the stream rather results from inputs driven by groundwater discharge and the release of contaminants from streambed sediments. The groundwater in the shallow Quarternary alluvial aquifer adjacent to the stream is characterized by a diffuse contamination with a variety of substances but mainly with chlorinated benzenes. An integral pumping test in the aquifer upstream of the stream with four simultaneously pumped wells revealed that all wells are located within a wide plume without significantly varying contaminant concentrations. Measurements of aqueous concentrations of MCB and DCB in the streambed revealed significantly different concentrations than those observed in the aquifer. The concentrations in the streambed are approximately one order of magnitude higher revealing that the streambed sediments act as contaminant source. Consequently, mass fluxes from the streambed sediments towards the

stream water are higher than those solely estimated from the contaminant concentrations in the aquifer and the average groundwater discharge to the Schachtgraben.

For a period of approximately three decades the Schachtgraben was used for waste water discharge from the chemical industry nearby, resulting in a contamination of the streambed.

The contaminant inputs from the surface water to the streambed discontinued about 15 years ago when major parts of the chemical industry closed. After the closure and the launch of waste water treatment, the surface water quality rapidly improved. Apparently, since then the contaminants in the streambed are likely to be released back to the stream. The release of contaminants is influenced by advection of groundwater through the streambed and diffusion from the sediment to the stream water. The advective transport was simulated with column experiments. The flow rates of the columns represented the range of observed magnitudes of groundwater discharge. The results of the column experiments showed that the removal of contaminant mass is very inefficient. The mass transfer from the sediments is kinetically limited. The desorption rates are slow and thus the fractional mass that remains in the columns remains relatively large although many pore volumes were flushed. After more than 100 pore volumes were exchanged the remaining mass fraction was still 85% of the initial value. This observation helps to explain the occurrence of residual contaminants in the streambed 15 years after the direct inputs decreased. For an assessment of potential remediation and management options, the time-scales that are required to reduce the concentration in the streambed to the regional background level can be a valuable information. To date there is no common theory that predicts mass transfer processes a priori. Consequently, the parameters for predictive models must be obtained by fitting to experimental, site specific data. Thus, although the fitted model may represent the experimental data well, the predictive ability is not necessarily good. In general, the extrapolation of experimental data to time-scales that are much longer than the experiment is subject to high uncertainties. However, we attempted to constrain the time-scales required to remove 50% of the initial contaminant mass from the streambed. A simple diffusion model which conceptualizes the streambed as semi-infinite layer that was exposed to a contamination of the stream water for 10-30 years indicated that the release time-scales for 50% of the initial contaminant mass are in the range of ~ 10-15 years. To remove 90% of the initial mass the time-scale increases to ~250-735 years. The results from the column experiment exhibited even longer time-scales. The predictions are based on a multiple rate mass transfer model that assumes a gamma distribution of desorption rate constants. The time required to remove 50% of the initial contaminant from the columns was in average in the scale of centuries but it may be decades or more than 2000 years.

As in many other studies, the time required for the decontamination of the sediments is longer than the time of exposure to contamination. For the diffusion model the observation results from the fact that the contaminants will partly continue to diffuse into the sediment. The desorption-resistant contaminant fraction observed in the column experiments can be attributed to an aging effect. Aging is related to the length of time period were the sediments

were exposed to contamination and can be attributed to a combination of physical (i.e. diffusion into intraparticle pores) and chemical (sorption to kinetically slow sites) phenomena.

Concluding, the streambed sediments will be a diffuse, long-term source of organic contaminants (mainly MCB and DCBs) at least for decades, potentially for centuries. Because the streambed contamination is rather persistent, the associated contaminant fluxes are relatively low. The longer the time that is required to remove a certain fractional contaminant mass, the lower are the associated contaminant fluxes. We could not clearly determine the influence of the magnitude of groundwater discharge on the contaminant desorption kinetics and the actual mass fluxes. The observed mass flow rates from the columns revealed no dependence on the flow velocity while the mass fluxes estimated based on field data indicated higher mass fluxes at high discharge locations. The predicted time-scales to release 50% of the contaminant mass from the columns were characterized by variations but not systematically associated with the flow rate.

6.2. Outlook

The interface between groundwater and streams has attracted the interest of researches from a great variety of disciplines: ecologists, biologists, engineers and hydro(geo)logists. Because understanding hydraulic and biogeochemical processes in streambeds will be a major step to quantitatively describe the nutrient and carbon cycling in inherently coupled stream-groundwater-systems. Moreover, streambeds are widely regarded as biogeochemically active zones because of steep redox gradients and the potential presence of oxygen. To date, the factors controlling these processes, their spatial patterns and temporal dynamics are not completely understood and practically no tools are available to assess the streambed functioning at the scale of stream reaches and catchments. Beyond the functioning of pristine streams, it is essential to characterize the consequences of contamination and to assess the stability and the resilience of stream-groundwater-systems towards contamination. Recent water management regulations such as the European Union Water Framework Directive demand an integrated view on groundwater and surface water (EU 2000). Understanding the behaviour of contaminants in streambeds will be a central task in order to assess the (bio)degradation and natural attenuation potential of the stream-groundwater interface.

We attempted to add a small piece to a not yet finished puzzle. We believe, although it may sound “hydro-centric”, that transport, transformation and degradation processes in the streambed are essentially controlled and mediated by flowing water. The point of view on stream-groundwater-interactions in this thesis was from the subsurface asking how can patterns of groundwater discharge into a stream be recognized and what are the potential implications on contaminant fate. Knowledge on the complex interplay between the exchange of surface water with the streambed (hyporheic flow) and the superimposed groundwater discharge is limited. The description of flow processes in streambeds and the associated effects on the biogeochemistry should generally account for both hyporheic exchange and groundwater discharge. We propose a simple temperature-based tool to elucidate spatial

patterns of groundwater discharge. Unlike many hydraulic parameters, temperature can be quickly, easily and inexpensively measured. The application of natural temperature gradients as tracer is very promising for studies of groundwater surface water interactions because here the temperature gradients are typically large. Recently, longitudinal temperature measurements along a fibre optic cable were firstly applied in hydrologic research. This new tool enables to measure temperatures simultaneously at distances of kilometers with a spatial resolution ideally down to one meter every few minutes. The work of others (e.g. Stonestrom and Constantz 2003, Conant Jr. 2004) and our work demonstrated that measured streambed temperatures can be interpreted as a function of water flux. Thus, the distributed temperature sensors could also be applied to quantify water fluxes at the stream groundwater interface with fine spatial and moreover temporal resolution providing a quantitative, continuous and dynamic insight into water fluxes between streams and groundwaters.

Measurements of streambed temperatures may also provide a valuable supplement to describe and to quantify aquifer heterogeneities. There is strong evidence relying on field observation and modeling that spatial patterns of water flow between streams and groundwaters are controlled by the distribution of hydraulic conductivities in the aquifer (Conant Jr. 2004, Fleckenstein et al. 2006). High groundwater discharge zones can consequently be interpreted as zones of increased hydraulic conductivities in the underlying aquifer. Thus, aquifer heterogeneities could be inferred from patterns of groundwater discharge or directly from streambed temperatures, respectively (Kalbus et al. 2008). Obviously, this relationship is appealing, since labour intensive coring or slug-testing of the near-stream, shallow aquifers can be omitted. However, the influence of the hydraulic conductivity distribution of the streambed e.g. the effects of a clogging layer should be evaluated first.

At the Schachtgraben site, we studied contaminant mass flow rates entering the stream by discharging groundwater. Our results revealed that the streambed sediments contribute to the contaminant inputs and thus mass fluxes are higher than from the groundwater contamination alone. In our simple analysis of the contaminant release from the sediments, we omitted potentially important processes such as biodegradation, bioturbation of sediments and the particle facilitated transport of sorbed contaminants. In particular, the bioavailability of aged contaminants and the potential biodegradation in the streambed could be studied with respect to high and low groundwater discharge areas and zones of downwelling stream water. When biodegradation rates can be related to different flow conditions in the streambed, a concept can be derived under which hydraulic conditions and morphological structures streambeds optimally act as reactive barrier or reactive layer to mitigate contaminant mass fluxes originating from both groundwater and surface water.

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Appendix 1

Streambed temperature mapping case study Schaugraben

The Schaugraben is a small channel that drains an agricultural used lowland catchment in northern Germany (Figure A1). The discharging nitrate-rich groundwater influences the nitrogen dynamic in the channel. The quantification of the water fluxes is crucial for the understanding the nitrate transport- and turnover in the catchment.

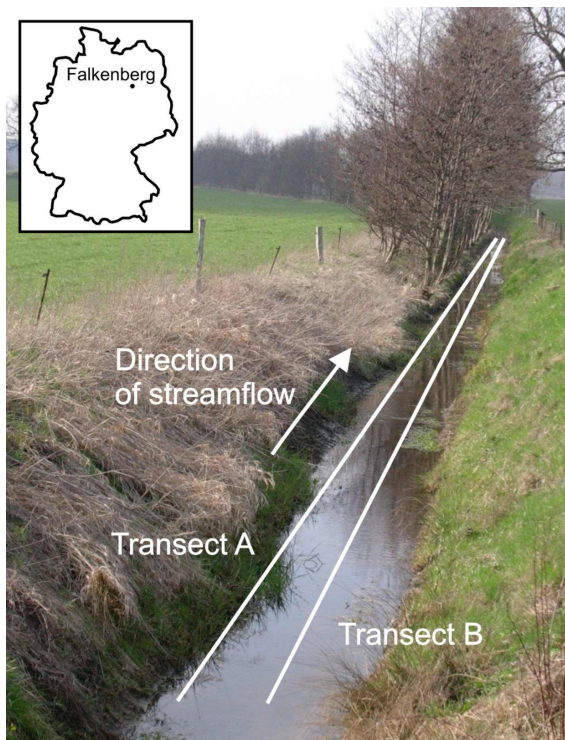


Figure A1. Location of the Schaugraben site, photograph of the stream with the longitudinal transects of temperature measurements.

At the Schaugraben site a streambed temperature mapping survey was performed in winter between February 6 and 10, 2006. The mapped reach was 750 m in length. Streambed temperatures were measured and evaluated to calculate the water fluxes according to the methodology described in Chapter 3 and in Schmidt et al. (2006), respectively. The input parameters used for the water flux calculation are provided in Figure A2.

The Schaugraben site represents the longest reach studied within this thesis comprising 454 temperature profiles. In 0.5 m depth below the streambed the observed temperatures ranged between 4.3 and 10.4 °C. The calculated water fluxes are between -69.2 (downward flux) and 512.8 L m⁻² d⁻¹ with a mean of 128.1 L m⁻² d⁻¹ and a median of 130.3 L m⁻² d⁻¹.

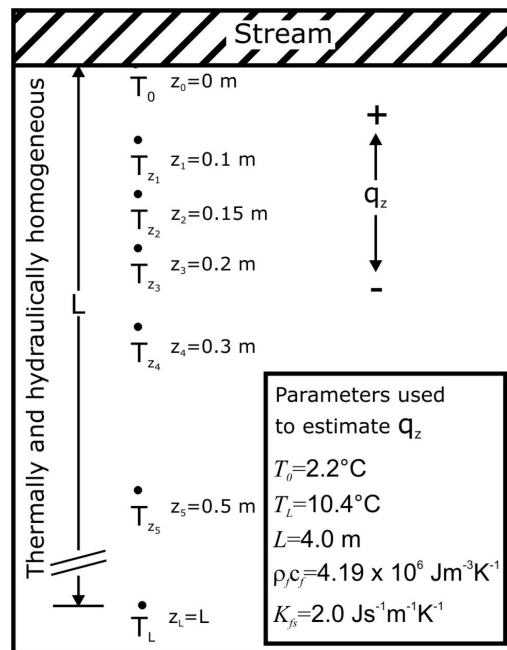


Figure A2. Concept of vertical temperature profiles, boundary conditions and parameters used for the analytical model.

Both transects show very similar temperature patterns and subsequently groundwater discharge patterns. On the approximately first 60 m of the reach nearly no water flux was detected. Then, between 60 and 115 m of the reach (Figure A3) there is a high discharge zone showing the highest observed fluxes along the reach. This zone spatially correlates with coarser sediments which have been detected during an electric resistivity survey (personal communication Joris Spindler, 2007, UFZ). Unfortunately these data is only available for the first 200 m of the studied reach. The second half of the reach (420-750 m) is characterized by relatively few variations of groundwater discharge. In general, the estimated magnitudes of water fluxes are in a reasonable range but were not tested against independent methods in this case study.

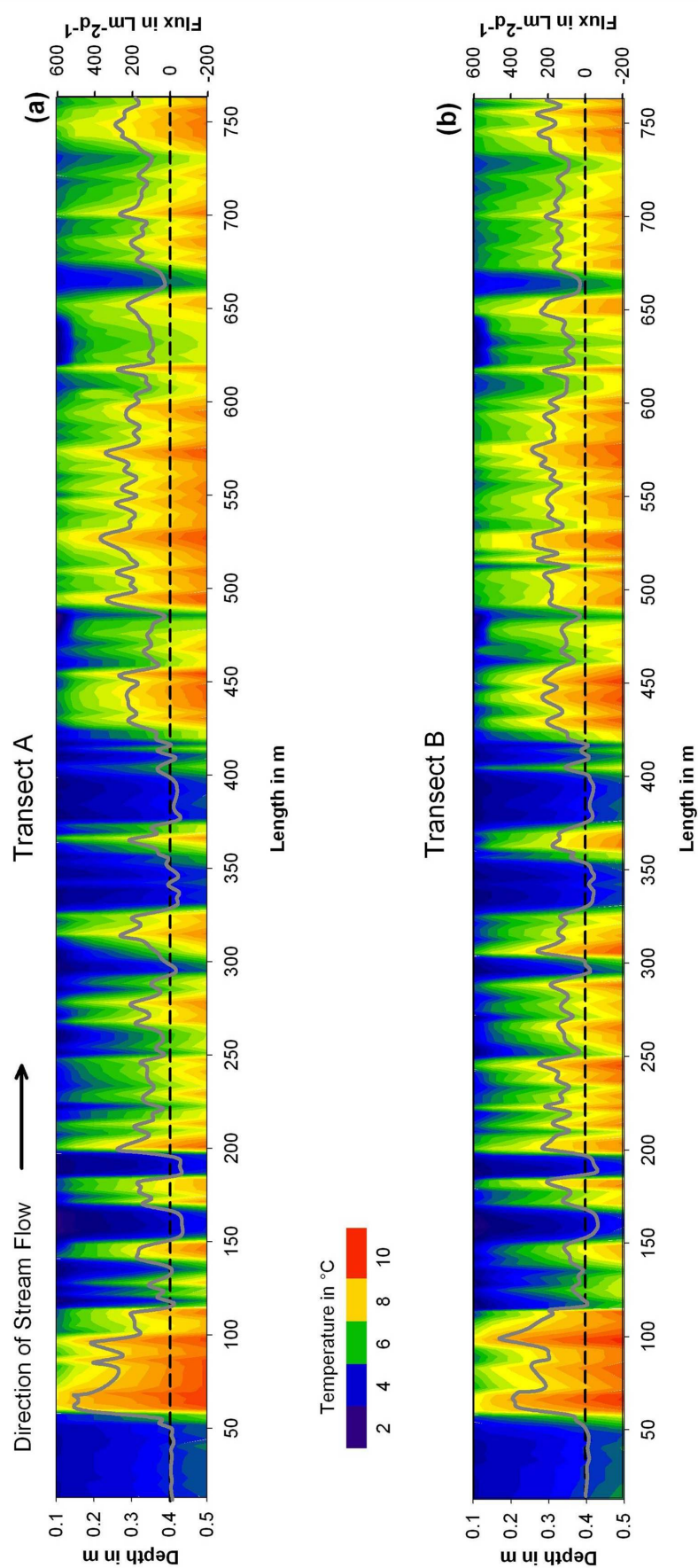


Figure A3. Temperature distribution, temperature based fluxes, along 750 m long transects A (a) and B (b) at the Schaugraben; Note the vertical exaggeration of the longitudinal profiles.