

ADVOCATE bulletin

CL:AIRE's ADVOCATE bulletins describe practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater. This bulletin describes the current scientific understanding of water fluxes across the hyporheic zone and discusses methods to quantify them.

Copyright © CL:AIRE (Contaminated Land: Applications in Real Environments).

Delineating groundwater-surface water interaction

1. Introduction

The hyporheic zone (HZ) is the transition zone between an aquifer and a surface water body, also called the groundwater-surface water interface (GSI). This zone provides various ecological services including a habitat for interstitial organisms, a spawning ground for fish and a rooting zone for aquatic plants (Buss *et al.*, 2009). Local hydrological conditions determine groundwater-surface water mixing patterns in the HZ and thus the exchange of carbon, nutrients, oxygen and energy between aquifers and streams. The mixing process can lead to an increase in organic carbon, which in turn could trigger increased biogeochemical activity in HZ sediments in comparison to the aquifer. The HZ of lowland rivers is therefore thought to have an increased potential for natural attenuation of contaminants. This potential can be actively stimulated for the attenuation of certain contaminant groups. Therefore, the awareness of HZ-specific characteristics has become of interest in the management of coupled groundwater-surface water systems as well as riverine ecosystem studies.

In CL:AIRE technical bulletin TB15, Ibrahim *et al.* (2011) outlined flow and transport processes in the HZ and discussed the interplay between biological activity, hydrology and the fate of contaminants. In this bulletin we will briefly outline the current scientific understanding of water flow across the HZ and discuss important methods to quantify them. A special focus will be put on using heat as an environmental tracer. The last section of this bulletin provides conclusions and take-away messages.

2. Description of Water Flow in the Hyporheic Zone

Flow in the HZ can be categorised into (1) gravity-driven flow, (2) pressure-driven flow and (3) capillary flow. Gravity-driven flow is the downward flow due to the gravitational force. Pressure-driven flow occurs due to differences in stream stage and hydraulic head in the connected aquifer, causing a pressure gradient that may overcome elevation head. It can also be caused by stationary or moving geomorphologic features (bedforms) of the streambed (i.e. dunes, anti-dunes, pool-riffle sequences and ripples), turbulent stream flow or surface waves (Elliott and Brooks, 1997; Higashino and Stefan, 2011). Capillary flow or flow against gravity is mainly driven by streambed grain size characteristics and other effects causing differences in the soil matric potential.

Water flow in the HZ can be divided into hyporheic exchange flow (HEF), i.e. stream water entering the HZ upstream and discharging back into the stream at some point downstream, and groundwater-surface water (GW-SW) exchange flow, i.e. flow across the HZ (Hannah *et al.*, 2009). Actual flow patterns in the HZ are difficult to delineate as the HZ comprises a mix of surface water and groundwater, and has often ill-defined borders. Thus many studies do not distinguish between HEF and GW-SW exchange flow when quantifying water fluxes (i.e. the flow per unit area). Depending on pressure head differences between aquifer and stream, flow in the HZ can occur from stream to aquifer (losing or downwelling conditions), from aquifer to stream (gaining or upwelling conditions), horizontally or laterally to the streambed as can be seen in Figure 1.

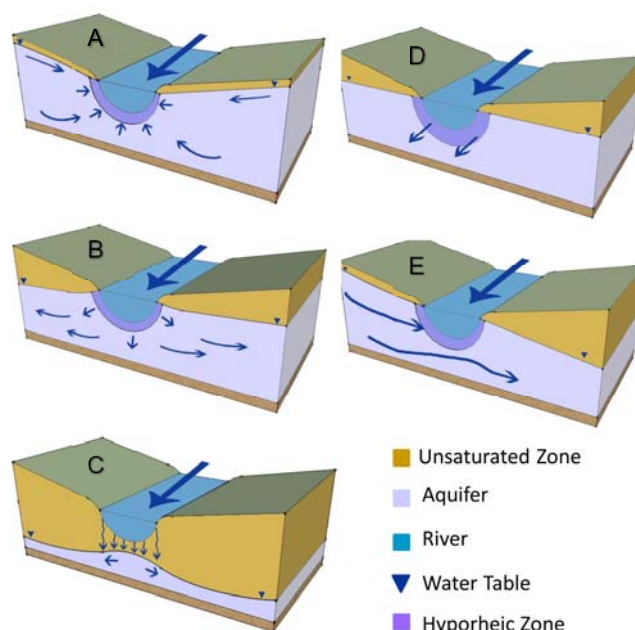


Figure 1. Stream-aquifer connections: A: Gaining stream; B: losing stream; C: disconnected stream; D: parallel flow, and E: throughflow. Modified after Winter *et al.* (1998) and Woessner (2000).

In most settings, flow through the HZ can be described similar to saturated or unsaturated aquifer flow with the Darcy equation (1) or the non-linear Richards equation (2), respectively.

$$q = -Ki \quad (1)$$

ADVOCATE bulletin

$$\frac{\partial \theta(h)}{\partial t} = \nabla[K(h)\nabla h] - s(h) \quad (2)$$

Here, q [LT^{-1}] is the specific discharge or in our case the exchange flux between streams and aquifers, K [LT^{-1}] is the hydraulic conductivity, h [L] is the hydraulic head, i [-] is the hydraulic gradient, $s(h)$ [LT^{-1}] represents a source/sink term and θ [-] represents the volumetric water content.

3. Flow at Different Spatial Scales

HZ flow can vary in space and time due to various natural and anthropogenic factors shown in Figure 2. It is commonly studied on three distinct scales: the catchment, reach (1 to several 10 m) and sediment scale (below 1 m). Flow paths can vary in length from several cm to more than one km as shown in a modelling study by Poole *et al.* (2008).

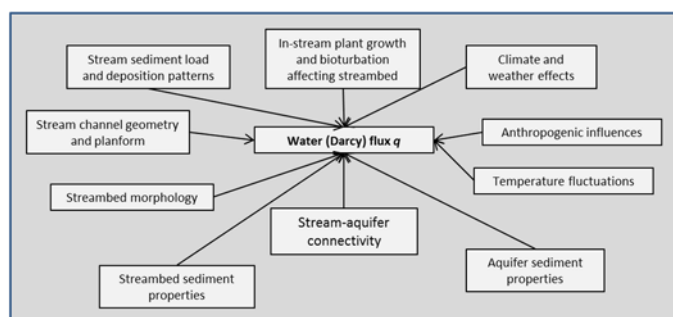


Figure 2. Water fluxes in and across the HZ and the parameters they are connected to.

At the catchment scale, one can often find downwelling conditions in the upper stream reaches due to unsaturated subsurface conditions. In mid-reaches groundwater contribution to stream flow (baseflow) increases and streams are mostly gaining and perennial. In lower reaches gradients are often small and more parallel flow occurs resulting in less net exchange flux between streams and streambeds/aquifers. However, this flow behaviour strongly depends on local geography. Stream flow and bedform are influenced by catchment scale runoff and drainage processes determining sediment and organic matter load as well as basin-channel connectivity. In general, stream sediment depositional patterns lead to an accumulation of more coarse-grained sediments like pebbles and gravel in the upper reaches while in the lower reaches the sediment bed structure is mostly defined by fine sands, silts and higher organic matter content. These depositional patterns are mainly caused by changes in the longitudinal hydraulic gradient, that decreases downstream as well as by channel geometry and planform.

On the reach scale, flow conditions vary depending on stream width to depth ratio, wetted perimeter, local distributions of hydraulic conductivity, channel planform, streambed morphology as well as local characteristics of the connected aquifer and hydrostatic pressure conditions (Buss *et al.*, 2009). Flow conditions are more typically effluent, when the stream width to depth ratio becomes smaller or when streams follow a more meandering path. Exchange flows can also be created by stream bank structures (bars) reaching into the channel and changing local hydrostatic pressure conditions. Streambed morphology influences exchange flows and discharge patterns mainly by pool-riffle sequences (Tonina and Buffington, 2007). At local elevation highs in the streambed water tends to flow

downwards (downwelling zones), passing through the streambed sediments and exiting at local elevation lows (upwelling zones). Climatic conditions may influence reach-scale flow patterns, e.g. through the occurrence of heavy rainfall, which can cause local inundation and subsequent recharge of the surrounding floodplain sediments leading to changes in hydraulic head differences between aquifer and stream.

At the sub-reach and sediment scale, flow patterns are mainly defined by sediment physical properties. Grain size, shape and packing directly influence permeability and hydraulic conductivity, leading to the formation of preferential pathways. They might also influence flow patterns as differences in surface roughness cause pressure differences at the upper streambed sediment boundary, which creates exchange flow to a depth of several cm (Packman *et al.*, 2004). Given a sufficient pore throat width, a larger sediment surface area to volume ratio could increase microbial growth, which in turn leads to a reduction in local porosity and hydraulic conductivity as biofilm and gas produced may decrease pore space (Buss *et al.*, 2005). Flow patterns can also be influenced by morphological features such as dunes, ripples or simply by objects acting as obstacles like wood, pebbles, litter or anthropogenic features. These so-called small-scale bedform structures cause small variations in pressure gradients across the sediment interface and allow surface water to penetrate the HZ.

Minor factors influencing HZ flow include daily and seasonal temperature variations, which directly affect fluid density, viscosity and thus the hydraulic conductivity of the HZ. An increase in water temperature from e.g. 10°C to 12°C would lead to an increase in kinematic viscosity by 6% and a slight decrease in hydraulic conductivity and flux. This effect would however only be of importance in shallow streams exposed to strong daily or seasonal temperature fluctuations, where the streambed would also be strongly heated by direct radiation from the sun.

Stream sediment load can play a crucial role as fine sediments can be deposited on top of the streambed by gravitational settling (depending on grain size and flocculation capability). This process is called colmation (Brunke and Gonsler, 1997), and can induce clogging of the HZ by reducing the available pore space (Sear *et al.*, 2008). Sediment deposition can also be affected by vegetation growth, which often varies seasonally. In areas with dense in-stream vegetation, flow velocities are reduced and finer sediments can settle forming local low permeability areas with increased organic matter content. Flow patterns can also be influenced by bioturbation, i.e. the destruction or alteration of natural sediment structures by aquatic plants rooting in the streambed as well as by animals. Changing water volumes and flow velocities as well as increased turbulent flow in the stream channel on the other hand can cause erosion of the colmated layer of the streambed also changing local permeability patterns.

Anthropogenic influences include stream channel engineering procedures and landuse. A canalisation of a stream leads to a loss in connectivity with the aquifer and to changes in stream velocity, sediment load, sedimentation processes and finally hydraulic properties. Landuse procedures influence recharge and drainage patterns, sediment and contaminant load in the stream and the connected aquifer, and as such sedimentation processes and hydraulic properties.

ADVOCATE bulletin

4. Why Quantify Streambed Fluxes?

The reliable quantification of water flow in and across the HZ has become an integral part in the study of coupled GW-SW water systems, which is mandated e.g. by the European Water Framework Directive (2000/60/EC). Exchange fluxes and their variability in space and time can be an indicator for stream-aquifer connectivity, for geological heterogeneity of streambed and HZ sediments, for the potential of contaminant mass fluxes or for local ecosystem composition. In modelling studies they can be used as a parameter for model calibration and as input to study flow, transport and attenuation processes. In combination with additional field data exchange fluxes can also be used to infer hydraulic conductivity or thermal parameters of the soil.

5. Field Methods Aiding in the Quantification of Exchange Fluxes

Based on Kalbus *et al.* (2006), Table 1 summarises measurement techniques adapted for use in the determination of water fluxes between streams and aquifers. Each method is classified according to the property or parameter used and the spatial scale where the method can be applied. The most important literature is also provided for the different methods.

A direct quantification of GW-SW exchange fluxes at the metre scale can only be performed with seepage meters. Seepage meter designs range from simple half-barrels using a flexible plastic bag to capture seepage (Figure 3) to fully automated devices using heat-pulse (Taniguchi *et al.*, 2003), electromagnetic (Rosenberry and Morin, 2004) or ultra-sonic (Paulsen *et al.*, 2001) signals to measure discharge over time. Rosenberry and LaBaugh (2008) provide more information regarding design, handling and error sources.



Figure 3. Half-barrel seepage meter installed in the bed of a lowland stream with a low flow velocity.

All other methods determine exchange fluxes indirectly. At catchment/reach scale exchange fluxes can be quantified via hydrograph separation or incremental stream flow discharge. Incremental stream flow discharge can be quantified using either velocity gauging or dilution gauging or a combination of both methods. In velocity gauging, the stream velocity over a flume, weir or stream section with a known cross-section is measured, from which the discharge can then be inferred. In dilution gauging a solute tracer is injected upstream and breakthrough curves are deduced for several stream cross-sections to determine discharge. The latter method helps to determine surface water inflow/outflow to/from the considered section whereas the former method is used to determine the net gain/loss of water in the section considered. Combining both methods ideally allows for separating the water of a stream section into its surface water and groundwater components (Harvey and Wagner, 2000; Kalbus *et al.*, 2006).

Table 1: Assessment methods of HZ properties determining flow

| Property | Assessment method | Explanation | Review literature | Scale |
|----------------------------|--|--|---|-----------------------|
| Water (Darcy) flux | Seepage meter measurements | Bag-type or automated seepage meters | (Rosenberry and LaBaugh, 2008) | Sediment |
| | Tests with conservative and environmental tracers | Artificial tracers such as fluorescent dyes and saline solutes or environmental tracers such as heat or stable & radioactive isotopes can be used. | (Berryman, 2005) | Reach |
| | Incremental streamflow | Determination of stream flow discharge through subsequent cross sections. | (Harvey and Wagner, 2000) | Reach to catchment |
| | Hydrograph separation | Estimation of groundwater contribution to streamflow. | (Hornberger <i>et al.</i> , 1998) | Reach to catchment |
| Hydraulic gradient | Water level measurements in (multilevel) piezometers | Assessment of vertical and horizontal gradients possible, from which water (Darcy) flux can be determined. | (Rosenberry and LaBaugh, 2008; Buss <i>et al.</i> , 2009) | Sediment |
| | Grain size analysis | K derived using empirical methods on sieved sediment samples. | (Vienken and Dietrich, 2011) | Sediment |
| Hydraulic conductivity K | Pumping tests | K calculated from observations on water level drawdown and recovery in pumping and observation wells. | (Fetter, 2001) | Sediment to sub-reach |
| | Slug and bail tests | K determined from analyzing recovery of water level in piezometer after initial displacement. | (Butler, 1998) | Sediment |
| | Permeameter tests | K derived from constant or falling head tests applied on sediment samples. | (Freeze and Cherry, 1979) | Sediment |
| | Constant head injection tests | K (horizontal) can be calculated from injection rate and test geometry. | (Cardenas and Zlotnik, 2003) | Sediment |
| Porosity | Laboratory tests on sediment samples | Determined by relating dry mass to the total volume. | (Fetter, 2001) | Sediment |

ADVOCATE bulletin

In hydrograph separation a stream hydrograph obtained using a gauging station is separated into its different runoff components. Groundwater contribution (discharge) to stream flow is mostly considered to equal the baseflow in the hydrograph. Although this technique is probably the most common one applied in catchment management, it only provides fluxes averaged over larger stream reaches. Additionally, it is prone to produce inaccurate results in case of bank storage, wetlands, snow or other factors contributing additional stream flow (Halford and Mayer, 2000).

Based on equations (1) and (2), exchange fluxes can be estimated by quantifying other relevant hydraulic parameters such as hydraulic conductivity or hydraulic gradients. Piezometers or monitoring wells have been used to determine vertical and horizontal hydraulic gradients and water fluxes across the HZ via water level measurements (Figure 4). They can also be used to conduct slug or pumping tests to determine hydraulic conductivity, to take water samples for the assessment of natural hydrochemical or biological parameters and for tracer tests. Dense networks of multilevel monitoring wells have been used regularly to collect detailed information regarding the spatial and temporal variability of gradients and additional parameters governing flow and transport (e.g. Conant *et al.*, 2004; Rivett *et al.*, 2008; Schmidt *et al.*, 2008).



Figure 4. A piezometer nest comprising three piezometers, installed in different depths in the streambed to determine the hydraulic gradient and monitor pressure heads as well as water quality parameters. A seepage meter is installed to the right of the three piezometers.

Hydraulic conductivity can be determined in the field via slug and bail tests or pumping tests. In slug/bail tests a known volume of water or a solid object is either introduced into or rapidly removed from a monitoring well and the subsequent water level response over time is measured. Depending on aquifer and monitoring well properties a variety of analytical solutions exist (see Butler, 1998) that allow for a determination of the hydraulic conductivity along the filter screen. In pumping tests, monitoring wells are used as pumping and/or observation wells to observe the water table drawdown over time. By means of a variety of analytical solutions (see e.g. Fetter, 2001) parameters such as hydraulic conductivity, transmissivity or specific storage can then be determined. Compared to slug tests, pumping tests provide information on K for a larger aquifer volume and as such with less detail.

6. Quantifying Exchange Fluxes Using Heat as a Tracer

Another indirect method for the quantification of exchange fluxes is the use of heat as an environmental tracer. With this method, temperature as a measure of heat is used in combined water flow and heat transport models to deduce the flow of water from a measured temperature distribution in the HZ. Main advantages of this method are that temperature is an easily, cheaply and accurately measurable property, and that the thermal parameters needed for the coupled model have a very limited range. Heat transport through a streambed is governed by

- i) Advection or heat transport by water moving through the streambed and
- ii) Diffusion, which is the combined conductive heat flow through the sediment-fluid matrix and thermal dispersion caused by intra-pore space velocity variations (Anderson, 2005);

Additionally, streambeds can receive direct heat input from solar radiation, especially if the stream is shallow.

For the determination of water fluxes across the HZ, advection and diffusion are the most important heat transport mechanisms and are described by the partial differential heat transport equation (3) that shows many similarities to the equation describing contaminant transport through a porous medium:

$$\frac{\partial T}{\partial t} = \nabla \cdot (D \nabla T) - v \nabla T \quad (3)$$

where $T[\Theta]$ is the temperature variable over time $t[T]$, $v[LT^{-1}]$ is the thermal front velocity and $D[L^2 T^{-1}]$ denotes the thermal dispersion coefficient or diffusivity. The thermal front velocity is

$$v = \bar{q} \frac{\rho_w c_w}{\rho c} \quad (4)$$

with $\bar{q}[LT^{-1}]$ being the Darcy flux or specific discharge vector (the same as in equation (2)), while $\rho_w c_w$ and $\rho c[ML^{-1} T^{-2} \Theta^{-1}]$ are the volumetric heat capacities of water and the water-sediment mixture, respectively. Through the total porosity n these volumetric heat capacities are connected to that of the solids $\rho_s c_s$ via

$$\rho c = n \rho_w c_w + (1 - n) \rho_s c_s \quad (5)$$

Table 2 provides thermal properties of selected materials and porous media. Variations in $\rho_w c_w$ are negligible in most hydrological settings. The thermal diffusivity is given as

$$D = \frac{\kappa}{\rho c} \quad (6)$$

with $\kappa[ML T^{-3} \Theta^{-3}]$ as the bulk thermal conductivity that connects the thermal conductivity of water κ_w to that of the solids κ_s . This bulk thermal conductivity can depend on the porosity or water content, mineral type, grain size distribution as well as on structure effects, i.e. grain shape and the degree of cementation (Côté and Konrad, 2009). The most common approach relating κ to κ_w and κ_s so far is a geometric mean model (e.g. Cote and Konrad, 2005; Rau *et al.*, 2014) where

$$\kappa = \kappa_w^n \kappa_s^{1-n} \quad (7)$$

ADVOCATE bulletin

An alternative approach is provided by Anderson (2005) and Tarnawski *et al.* (2011) based on the series-parallel model put forward by Woodside and Messmer (1961) with

$$\kappa = n\kappa_w + (1 - n)\kappa_s \quad (8)$$

For the range of thermal conductivities found in laboratory experiments for fluvial and alluvial deposits (Table 2) the difference between both models is very small.

Similar to solute transport studies a dimensionless thermal Péclet number Pe can be defined that relates conductive to convective heat transport as (e.g. Anderson, 2005)

$$Pe = \frac{\rho_w c_w \vec{q} L}{\kappa} \quad (9)$$

with L [m] as a characteristic length, over which heat transport is considered. For $Pe > 1$ convective heat transport dominates over the conductive one and vice versa. According to Bons *et al.* (2013) and Rau *et al.* (2014), L is usually chosen as the average grain size diameter.

Eq. 6 can be expanded to include thermal dispersion due to the movement of water as (Roshan *et al.*, 2012)

$$\mathbf{D} = \frac{\kappa}{\rho c} + f(\psi, \vec{q}) \quad (10)$$

with f as a function of the thermal dispersivity ψ [L] and the Darcy velocity. Mostly, this function is assumed linear. However, the significance of ψ on overall heat dispersion at different spatial scales is an ongoing dispute in the scientific literature (see Rau *et al.*, 2014 for a discussion).

Rau *et al.* (2012) also showed in their experiments that conductive heat transport is faster than solute diffusion and that convective heat

transport is retarded compared to advective solute transport. A thermal retardation R_T factor with respect to \vec{q} exists as (Vandenbohede and Lebbe, 2010)

$$R_T = \frac{\rho c}{\rho_w c_w} \quad (11)$$

For the same Darcy velocity, Péclet numbers for solute and heat can vary significantly and e.g. heat transport can be dominated by conduction while solute transport is dominated by advection.

When thermal parameters in Eq. (3) are known, exchange (Darcy) fluxes can be quantified from temperature time series. More commonly however, heat transport through the subsurface is modelled and temperature data is used to optimise these parameters.

7. Measuring Temperatures in Streambeds

To study heat transport in the HZ, streambed temperatures can be monitored by stationary or mobile temperature loggers placed in the streambed or by fibre-optics based distributed temperature sensing equipment (FO-DTS).

Due to the improvement of measurement devices and their relatively low costs, measuring temperature time series by means of loggers embedded in the streambed and the HZ has become a standard procedure. The idea behind these loggers is that the temperature is measured at the streambed top and at least one depth in vertical direction. As such, information regarding the vertical propagation of the temperature signal can be obtained. Depending on aquifer-stream connectivity, the temperature signal is distributed through the streambed and gradually attenuated with depth.

Temperature measurements have been used to quantify fluxes on the reach scale by Anibas *et al.* (2011) and Schmidt *et al.* (2006). They

Table 2: Thermal properties of selected single phases and soils based on a meta-study of Stonestrom and Constantz (2003, and references therein). Thermal properties of selected minerals can be found in Cote and Konrad (2005).

| Single Phase | (Bulk) Density (10^6 g/m^3) | Porosity ($V_{\text{pores}}/V_{\text{bulk}}$) | (Liquid) Water Content | Volumetric Heat Capacity ($10^6 \text{ J/m}^3 \text{ }^\circ\text{C}$) | Thermal Conductivity ($\text{W/m }^\circ\text{C}$) | Thermal Diffusivity ($10^{-6} \text{ m}^2/\text{s}$) |
|---------------------------|--|--|------------------------|---|---|---|
| Air | 0.001 | | | 0.001 | 0.024 | 19 |
| Liquid water | 1 | | | 4.2 | 0.6 | 0.14 |
| Ice | 0.9 | | | 1.9 | 2.2 | 1.2 |
| Quartz | 2.7 | | | 1.9 | 8.4 | 4.3 |
| Average of soil minerals | 2.7 | | | 1.9 | 2.9 | 1.5 |
| Average of clay minerals | 2.7 | | | 2 | 2.9 | 1.5 |
| Average of organic matter | 1.3 | | | 2.5 | 0.25 | 0.1 |
| Porous Medium | | | | | | |
| Sand | 1.83 | 0.31 | saturated | 2.6 | 2.2 | 0.85 |
| Sandy loam | 1.38 | 0.48 | saturated | 3.2 | 1.8 | 0.55 |
| Clay loam | 1.21 | 0.54 | saturated | 3.2 | 1.4 | 0.42 |
| Sand | 1.5 | 0.43 | dry | 1.3 | 0.25 | 0.18 |
| Silt loam | 1.3 | 0.51 | dry | 1.1 | 0.26 | 0.23 |
| Clay | 1.16 | 0.56 | dry | 1.2 | 0.18 | 0.15 |

ADVOCATE bulletin

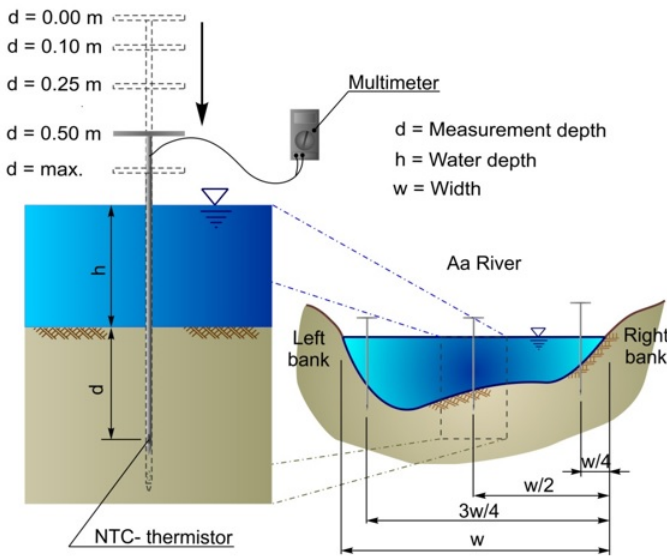


Figure 5. Mobile temperature lance used by Anibas *et al.* (2011) to map streambed temperatures at the Aa River in Belgium.

used different versions of mobile probes, which were inserted into the streambed (Figure 5). Each measurement took several minutes and numerous transects could be mapped. Schmidt *et al.* (2008), Kalbus *et al.* (2007) and Conant *et al.* (2004) used information from temperature probes in combination with other measurements (e.g. integral pumping tests) to study contaminant mass fluxes across the HZ. Essaid *et al.* (2008) deployed loggers in piezometers installed in several creeks in the US to study GW-SW interactions. However, direct contact of the temperature sensor with the streambed sediment should be preferred as in piezometers convection can occur in times when no strong thermal gradient exists. Vandersteen *et al.* (2015) used stationary multi-level temperature sticks to simultaneously obtain temperature-time series at several locations in a streambed in Belgium (Figure 6).

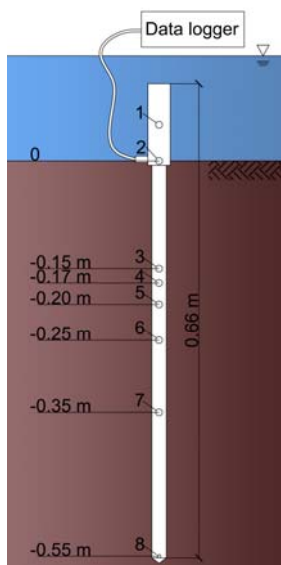


Figure 6. Stationary multi-level temperature stick from UIT, Dresden, Germany (after Schmidt *et al.*, 2014).

To acquire continuous temperature data of much higher spatial resolutions than achievable with normal loggers, FO-DTS systems as described by Selker *et al.* (2006) have been used (Figure 7). Such a system consists of one or more fibre-optic cables, along which pulsed laser light is sent and Raman scattering effects are measured. When the incident light strikes matter, some of it is backscattered with frequencies above (anti-Stokes backscatter) and below (Stokes backscatter) the original one. Nowadays, instruments with a spatial resolution of ≤ 1 m and a temporal resolution of seconds to hours are commonly used. With proper instrument calibration temperature changes of 0.01°C can be observed. Instrument design and performance as well as cable options

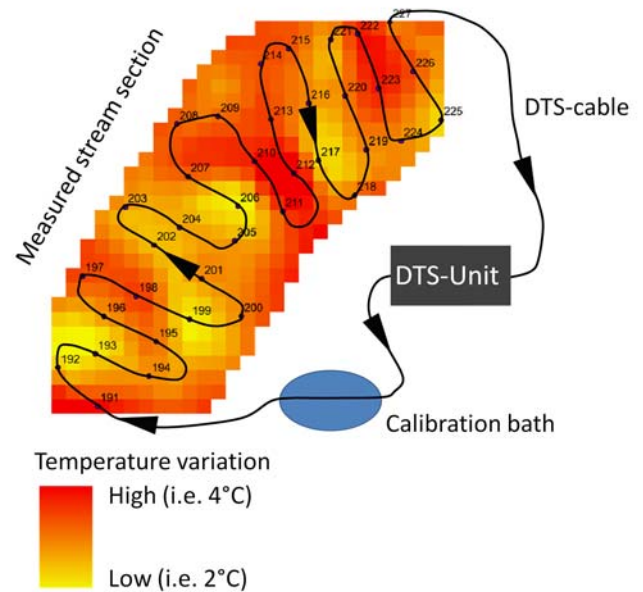


Figure 7. A FO-DTS system deployed in the Biebrza River, Poland measures temperatures at the streambed top.

for hydrological environments are discussed profoundly in Tyler *et al.* (2009). The main advantage of the FO-DTS over other temperature loggers is its capability to continuously obtain temperatures at many locations along the cable at the same time. Used alone or in combination with other measurements this makes a concurrent estimation of exchange fluxes possible with high detail as has been demonstrated by Krause *et al.* (2012), Lowry *et al.* (2007) and Vogt *et al.* (2010).

The aforementioned methods passively use the natural temperature distribution in the HZ to deduce fluxes. Recently Lewandowski *et al.* (2011) and Angermann *et al.* (2012) developed an active methodology where a heat pulse is emitted into the streambed and an array of 24 temperature sensors is used to monitor the resulting heat plume (Figure 8). With this tool magnitude and direction of the water flux can be derived.

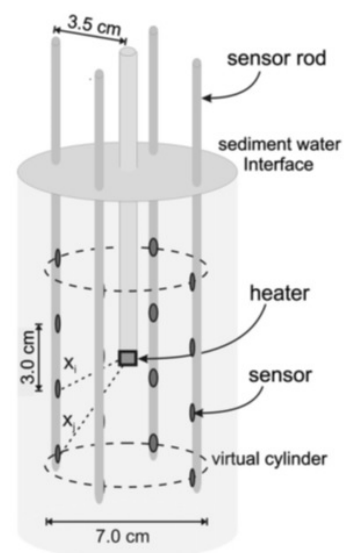


Figure 8. Heat pulse sensor that actively injects heat into the streambed and measures the temperature response of the subsurface (Angermann *et al.*, 2012).

In any measurement campaign aiming at the quantification of fluxes it is recommended to combine different methods. Temperature measurements for example may be accompanied by monitoring of surface water and background groundwater temperatures, as well as hydraulic gradients in piezometers.

ADVOCATE bulletin

8. Using Temperature Time Series Information in Models

Numerous model codes have been developed to solve the heat transport equation (3) and quantify fluxes. These solutions are either based on numerical or analytical modelling techniques. Table 3 lists the most frequently used analytical and numerical codes to solve for heat transport in the HZ. Numerical methods are often applied for more complex scenarios with fluid flow and heat transport under transient conditions in three dimensions. They use separate equations for fluid flow and heat transport and are applied mostly at reach and catchment scales. Numerical models can couple a variety of relevant processes and can besides fluxes also estimate other relevant hydraulic or thermal parameters, with temperature data serving as an additional constraint. However, numerical models are often complex in setup and handling and need a considerable amount of input data to produce meaningful results.

Table 3. List of commonly used model codes to study heat transport and quantify exchange fluxes.

| Numerical heat transport codes | |
|---|--|
| SUTRA | (Voss and Provost, 2008) |
| VS2DH | (Healey and Ronan, 1996) |
| HYDROGEOSPHERE | (Therrien <i>et al.</i> , 2010) |
| FEMME-STRIVE | (Anibas <i>et al.</i> , 2009) |
| FEFLOW | (Diersch, 2014) |
| SEAWAT | (Langevin <i>et al.</i> , 2007) |
| MODFLOW with MT3DHeat | (Hecht-Mendez <i>et al.</i> , 2010) |
| HYDRUS | (Šimůnek <i>et al.</i> , 2006) |
| Analytical solutions | |
| Steady state solution for constant temperature conditions | (Bredehoeft and Papadopoulos, 1965) |
| Steady state solution for upwelling conditions only | (Schmidt <i>et al.</i> , 2007) |
| Transient methods with an upper sinusoidal temperature boundary. Methods use information on amplitude differences and phase shifts between temperature signals collected at two depths. | (Suzuki, 1960; Stallman, 1965; Goto <i>et al.</i> , 2005; Hatch <i>et al.</i> , 2006; Keery <i>et al.</i> , 2007; Luce <i>et al.</i> , 2013) |
| Transient method using wavelet analysis to extract amplitudes and phases. | (Onderka <i>et al.</i> , 2013) |
| GUIs to analytical solutions | |
| Ex-Stream | (Swanson and Cardenas, 2011) |
| VFLUX | (Gordon <i>et al.</i> , 2012) |

Analytical models provide exact solutions to the heat transport equation and are easier to use, however, they are subject to the following restrictions:

i) Fluid flow is considered steady and uniform

ii) Streambed materials are spatially homogeneous and isotropic

iii) A local thermal equilibrium is assumed, i.e. water and solids have the same temperatures at all times

These limitations have so far restricted the use of analytical models to vertical 1D flux estimates. Here the assumption is that the input temperature signal at the streambed surface is transmitted through the stream where it is attenuated with long wave signals penetrating deeper than short wave signals. The most pronounced signals have been found to be diel (day-night) and seasonal ones. Under ideal flow conditions daily or seasonal temperature variations form a so-called envelope in the streambed sediment as shown in Figure 9. However, in nature, flow conditions are usually non-ideal due to a heterogeneous streambed, which can lead to considerable errors in calculated exchange fluxes (Rau *et al.*, 2014). Thus, studies recently have begun to quantify uncertainties of measurements (Soto-Lopez *et al.*, 2011), model parameters and model structure (Shanafield *et al.*, 2011; Vandersteen *et al.*, 2015). However, uncertainties of the underlying processes have not yet been quantified.

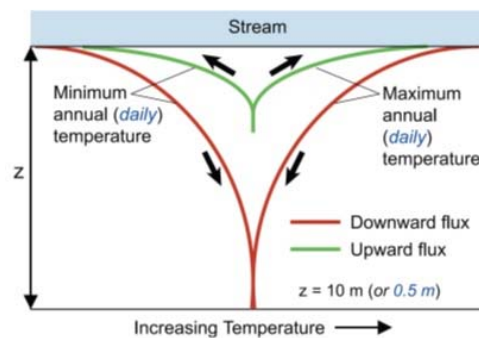


Figure 9. Temperature envelopes formed in streambed sediments (Constantz, 2008) .

9. Conclusions and Take Away Message

The quantification of exchange fluxes has become an integral part in many research studies dealing with GW-SW interactions. It is also increasingly important for river management and in the assessment of the fate of contaminants at operational sites. A variety of techniques exist to measure exchange fluxes or hydraulic parameters relevant for flux quantification. As exchange flux can also be linked to heat transport in the HZ, field and modelling techniques using heat as a natural or induced tracer have received particular attention within the scientific community. As the research is ongoing, special focus will be put on improving the assessment of associated uncertainties to better understand the impact of modelling results. With improved process understanding and model codes, future research will also increasingly focus on simulating exchange flows at the catchment scale.

This bulletin briefly highlighted and discussed the following aspects:

- The net exchange flux between a surface water body and a connected aquifer is a major parameter of interest in studies on water flow, contaminant transport and attenuation in the HZ.
- The net exchange flux is divided into a hyporheic flow component and a flow component across the HZ also considered GW-SW exchange flux. However, a distinction between both flow types is often difficult and commonly not done.

ADVOCATE bulletin

- Magnitude and direction of the exchange flux depends on a variety of factors, most importantly the local and regional flow patterns as well as various stream (width, planform, sediment load) and streambed sediment characteristics.
- The exchange flux can be quantified by a variety of techniques, one of which is the application of heat as an environmental tracer.
- Variations in streambed temperatures in space and time can be measured easily by means of mini divers, temperature lances or fibre-optic DTS systems. These techniques can accurately log temperatures at various ranges of spatial and temporal resolution.
- To quantify exchange fluxes from temperature time-series a variety of analytical and numerical models have been developed. Through numerous studies it has been found that analytical models under most circumstances quantify flux with sufficient accuracy. However, while analytical models are easier to set up and need less computing efforts, they make certain assumptions (1D vertical steady and uniform flow, local thermal equilibrium, homogeneous and isotropic streambed) that do not always hold true in reality. In those cases the application of numerical models is advised.
- Information on the exchange flux can be used to calibrate numerical models or to directly quantify other parameters such as hydraulic conductivity.

10. Acknowledgements

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013 under grant agreement n°265063).

11. References

- Anderson MP. 2005. Heat as a ground water tracer. *Ground Water*, 43: 951-968. DOI: 10.1111/j.1745-6584.2005.00052.x.
- Angermann L, Krause S, Lewandowski J. 2012. Application of heat pulse injections for investigating shallow hyporheic flow in a lowland river. *Water Resour. Res.*, 48: W00P02. DOI: 10.1029/2012wr012564.
- Anibas C, Buis K, Verhoeven R, Meire P, Batelaan O. 2011. A simple thermal mapping method for seasonal spatial patterns of groundwater-surface water interaction. *J. Hydrol.*, 397: 93-104.
- Anibas C, Fleckenstein JH, Volze N, Buis K, Verhoeven R, Meire P, Batelaan O. 2009. Transient or steady-state? Using vertical temperature profiles to quantify groundwater-surface water exchange. *Hydrol. Process.*, 23: 2165-2177. DOI: 10.1002/Hyp.7289.
- Berryman CJ. 2005. Tracer tests for investigating flow and transport in the hyporheic zone. In: *Science Report SC030155/8*, Environment Agency, pp: 41.
- Bons PD, van Milligen BP, Blum P. 2013. A general unified expression for solute and heat dispersion in homogeneous porous media. *Water Resour. Res.*, 49: 6166-6178. DOI: 10.1002/Wrcr.20488.
- Bredehoeft JD, Papadopoulos IS. 1965. Rates of vertical ground-water movement estimated from the Earth's thermal profile. *Water Resour. Res.*, 1: 325-328.
- Brunke M, Gonser T. 1997. The ecological significance of exchange processes between rivers and groundwater. *Freshwater Biology*, 37: 1-33. DOI: 10.1046/j.1365-2427.1997.00143.x.
- Buss SR, Cai Z, Cardenas MB, Fleckenstein JH, Hannah DM, Heppell K, Hulme PJ, Ibrahim T, Kaeser D, Krause S, Lawler DM, Lerner DN, Mant J, Malcolm IA, Old G, Parkin G, Pickup RJ, Pinay G, Porter J, Rhodes G, Richie A, Riley J, Robertson A, Sear D, Shields B, Smith JWS, Tellam JH, Wood P. 2009. *The Hyporheic Handbook - A handbook on the groundwater-surface water interface and hyporheic zone for environmental managers*. In: *Environment Agency Science Report SC050070*, Environment Agency, pp: 280.
- Buss SR, Rivett MO, Morgan P, Bemment CD. 2005. Attenuation of nitrate in the subsurface environment. In: *Science Report Environment Agency*, pp: 108.
- Butler JJ. 1998. *The Design, Performance, and Analysis of Slug Tests*. Lewis Publishers.
- Cardenas MB, Zlotnik VA. 2003. A simple constant-head injection test for streambed hydraulic conductivity estimation. *Ground Water*, 41: 867-871.
- Conant B, Jr., Cherry JA, Gillham RW. 2004. A PCE groundwater plume discharging to a river: influence of the streambed and near-river zone on contaminant distributions. *J Contam Hydrol*, 73: 249-279. DOI: 10.1016/j.jconhyd.2004.04.001.
- Constantz J. 2008. Heat as a tracer to determine streambed water exchanges. *Water Resour. Res.*, 44. DOI: 10.1029/2008wr006996.
- Côté J, Konrad J-M. 2009. Assessment of structure effects on the thermal conductivity of two-phase porous geomaterials. *International Journal of Heat and Mass Transfer*, 52: 796-804. DOI: 10.1016/j.ijheatmasstransfer.2008.07.037.
- Cote J, Konrad JM. 2005. A generalized thermal conductivity model for soils and construction materials. *Can. Geotech. J.*, 42: 443-458. DOI: 10.1139/T04-106.
- Diersch H-JG. 2014. *FEFLOW - Finite Element Modeling of Flow, Mass and Heat Transport in Porous and Fractured Media*. Springer.
- Elliott AH, Brooks NH. 1997. Transfer of nonsorbing solutes to a streambed with bedforms: Theory. *Water Resour. Res.*, 33: 123-136.
- Essaid HI, Zamora CM, McCarthy KA, Vogel JR, Wilson JT. 2008. Using heat to characterize streambed water flux variability in four stream reaches. *Journal of environmental quality*, 37: 1010-1023. DOI: 10.2134/jeq2006.0448.
- Fetter CW. 2001. *Applied hydrogeology*. 4 Edn., Pearson Education.
- Freeze RA, Cherry JA. 1979. *Groundwater*. Prentice-Hall.
- Gordon RP, Lautz LK, Briggs MA, McKenzie JM. 2012. Automated calculation of vertical pore-water flux from field temperature time series using the VFLUX method and computer program. *J. Hydrol.*, 420: 142-158. DOI: 10.1016/j.jhydrol.2011.11.053.
- Goto S, Yamano M, Kinoshita M. 2005. Thermal response of sediment with vertical fluid flow to periodic temperature variation at the surface. *J Geophys Res-Sol Ea*, 110. DOI: 10.1029/2004jb003419.
- Halford KJ, Mayer GC. 2000. Problems associated with estimating ground water discharge and recharge from stream-discharge records. *Ground Water*, 38: 331-342. DOI: 10.1111/j.1745-6584.2000.tb00218.x.
- Hannah DM, Malcolm IA, Bradley C. 2009. Seasonal hyporheic temperature dynamics over riffle bedforms. *Hydrol. Process.*, 23: 2178-2194.
- Harvey JW, Wagner BJ. 2000. Quantifying hydrologic interactions between streams and their subsurface hyporheic zones. In: *Streams and ground waters*, Jones JB, Mulholland PJ (eds). Academic Press, pp: 3-44.
- Hatch CE, Fisher AT, Revenaugh JS, Constantz J, Ruehl C. 2006. Quantifying surface water-groundwater interactions using time series analysis of streambed thermal records: Method development. *Water Resour. Res.*, 42. DOI: 10.1029/2005wr004787.
- Healey RW, Ronan AD. 1996. Documentation of computer program VS2DH for simulation of energy transport in variably saturated porous media -- Modification of the U.S. Geological Survey's computer program VS2DT. In: *Water Resources Investigations Report 90-4025*, U.S. Geological Survey, pp: 125.
- Hecht-Mendez J, Molina-Giraldo N, Blum P, Bayer P. 2010. Evaluating MT3DMS for heat transport simulation of closed geothermal systems. *Ground Water*, 48: 741-756. DOI: 10.1111/j.1745-6584.2010.00678.x.
- Higashino M, Stefan HG. 2011. Non-linear effects on solute transfer between flowing water and a sediment bed. *Water Research*, 45: 6074-6086. DOI: 10.1016/j.watres.2011.09.004.
- Hornberger GM, Raffensberger JP, Wiberg PL, Eshleman KN. 1998. *Elements of Physical Hydrology*. The Johns Hopkins University Press.
- Ibrahim T, Lerner D, Thornton S. 2011. Accounting for the groundwater-surface water interface in contaminated land assessments. In: *Technical Bulletin TB 15*, CL:AIRE, pp: 8.
- Kalbus E, Reinstorf F, Schirmer M. 2006. Measuring methods for groundwater - surface water interactions: a review. *Hydrology and Earth System Sciences*, 10: 873-887.
- Kalbus E, Schmidt C, Bayer-Raich M, Leschik S, Reinstorf F, Balcke GU, Schirmer M. 2007. New methodology to investigate potential contaminant mass fluxes at the stream-aquifer interface by combining integral pumping tests and streambed temperatures. *Environmental Pollution*, 148: 808-816. DOI: 10.1016/j.envpol.2007.01.042.
- Keery J, Binley A, Crook N, Smith JWN. 2007. Temporal and spatial variability of groundwater-surface water fluxes: Development and application of an analytical method using temperature time series. *J. Hydrol.*, 336: 1-16. DOI: 10.1016/j.jhydrol.2006.12.003.
- Krause S, Blume T, Cassidy NJ. 2012. Investigating patterns and controls of groundwater up-welling in a lowland river by combining Fibre-optic Distributed Temperature Sensing with observations of vertical hydraulic gradients. *Hydrology and Earth System Sciences*, 16: 1775-1792. DOI: 10.5194/hess-16-1775-2012.

ADVOCATE bulletin

- Langevin CD, Thorne DT, Dausman AM, Sukop MC, Guo W. 2007. SEAWAT Version 4: A Computer Program for Simulation of Multi-Species Solute and Heat Transport. In: Techniques and Methods 6-A22, U.S. Geological Survey pp: 39.
- Lewandowski J, Angermann L, Nutzmann G, Fleckenstein JH. 2011. A heat pulse technique for the determination of small-scale flow directions and flow velocities in the streambed of sand-bed streams. *Hydrological Processes*, 25: 3244-3255. DOI: 10.1002/Hyp.8062.
- Lowry CS, Walker JF, Hunt RJ, Anderson MP. 2007. Identifying spatial variability of groundwater discharge in a wetland stream using a distributed temperature sensor. *Water Resour. Res.*, 43. DOI: 10.1029/2007wr006145.
- Luce CH, Tonina D, Gariglio F, Applebee R. 2013. Solutions for the diurnally forced advection-diffusion equation to estimate bulk fluid velocity and diffusivity in streambeds from temperature time series. *Water Resour. Res.*, 49: 488-506. DOI: 10.1029/2012wr012380.
- Onderka M, Banzhaf S, Scheytt T, Krein A. 2013. Seepage velocities derived from thermal records using wavelet analysis. *J. Hydrol.*, 479: 64-74. DOI: 10.1016/j.jhydrol.2012.11.022.
- Packman A, Salehin M, Zaramella M. 2004. Hyporheic exchange with gravel beds: Basic hydrodynamic interactions and bedform-induced advective flows. *J. Hydraul. Eng. -ASCE*, 130: 647-656. DOI: 10.1061/(ASCE)0733-9429(2004)130:7(647).
- Paulsen RJ, Smith CF, O'Rourke D, Wong TF. 2001. Development and evaluation of an ultrasonic ground water seepage meter. *Ground Water*, 39: 904-911. DOI: 10.1111/j.1745-6584.2001.tb02478.x.
- Poole GC, O'Daniel SJ, Jones KL, Woessner WW, Bernhardt ES, Helton AM, Stanford JA, Boer BR, Beechie TJ. 2008. Hydrologic spiralling: The role of multiple interactive flow paths in stream ecosystems. *River Research and Applications*, 24: 1018-1031. DOI: 10.1002/Rra.1099.
- Rau GC, Andersen MS, Acworth RI. 2012. Experimental investigation of the thermal dispersivity term and its significance in the heat transport equation for flow in sediments. *Water Resour. Res.*, 48. DOI: 10.1029/2011wr011038.
- Rau GC, Andersen MS, McCallum AM, Roshan H, Acworth RI. 2014. Heat as a tracer to quantify water flow in near-surface sediments. *Earth-Science Reviews*, 129: 40-58. DOI: 10.1016/j.earscirev.2013.10.015.
- Rivett MO, Ellis R, Greswell RB, Ward RS, Roche RS, Cleverly MG, Walker C, Conran D, Fitzgerald PJ, Willcox T, Dowle J. 2008. Cost-effective mini drive-point piezometers and multilevel samplers for monitoring the hyporheic zone. *Q. J. Eng. Geol. Hydrogeol.*, 41: 49-60. DOI: 10.1144/1470-9236/07-012.
- Rosenberry DO, LaBaugh JW. 2008. Field techniques for estimating water fluxes between surface water and ground water. U.S. Geological Survey pp: 128.
- Rosenberry DO, Morin RH. 2004. Use of an electromagnetic seepage meter to investigate temporal variability in lake seepage. *Ground Water*, 42: 68-77. DOI: 10.1111/j.1745-6584.2004.tb02451.x.
- Roshan H, Rau GC, Andersen MS, Acworth IR. 2012. Use of heat as tracer to quantify vertical streambed flow in a two-dimensional flow field. *Water Resour. Res.*, 48. DOI: 10.1029/2012wr011918.
- Schmidt C, Bayer-Raich M, Schirmer M. 2006. Characterization of spatial heterogeneity of groundwater-stream water interactions using multiple depth streambed temperature measurements at the reach scale. *Hydrology and Earth System Sciences*, 10: 849-859.
- Schmidt C, Buttner O, Musolf A, Fleckenstein JH. 2014. A method for automated, daily, temperature-based vertical streambed water-fluxes. *Fund Appl Limnol*, 184: 173-181. DOI: 10.1127/1863-9135/2014/0548.
- Schmidt C, Conant B, Bayer-Raich M, Schirmer M. 2007. Evaluation and field-scale application of an analytical method to quantify groundwater discharge using mapped streambed temperatures. *J. Hydrol.*, 347: 292-307. DOI: 10.1016/j.jhydrol.2007.08.022.
- Schmidt C, Kalbus E, Krieg R, Bayer-Raich M, Leschik S, Reinstorf F, Martienssen M, Schirmer M. 2008. Contaminant mass flow rates between groundwater, streambed sediments and surface water at the regionally contaminated site Bitterfeld. *Grundwasser*, 13: 133-146. DOI: 10.1007/s00767-008-0076-7.
- Sear DA, Frostick LB, Rollinson G, Lisle TE. 2008. The significance and mechanics of fine sediment infiltration and accumulation in gravel spawning beds. In: *Salmon Spawning Habitat in Rivers; Physical controls, biological responses and approaches to remediation.*, Sear DA, DeVries P (eds.) AFS, pp: 149-174.
- Selker JS, Thevenaz L, Huwald H, Mallet A, Luxemburg W, de Giesen NV, Stejskal M, Zeman J, Westhoff M, Parlange MB. 2006. Distributed fiber-optic temperature sensing for hydrologic systems. *Water Resour. Res.*, 42. DOI: 10.1029/2006wr005326.
- Shanafield M, Hatch C, Pohll G. 2011. Uncertainty in thermal time series analysis estimates of streambed water flux. *Water Resour. Res.*, 47. DOI: 10.1029/2010wr009574.
- Šimůnek J, M. J. van Genuchten T, Šejna M. 2006. The HYDRUS Software Package for Simulating Two- and Three-Dimensional Movement of Water, Heat, and Multiple Solutes in Variably-Saturated Media. In: *Technical Manual, Version 1.0*, PC Progress, pp: 241.
- Soto-Lopez CD, Meixner T, Ferre TPA. 2011. Effects of measurement resolution on the analysis of temperature time series for stream-aquifer flux estimation. *Water Resour. Res.*, 47: WT2602.
- Stallman RW. 1965. Steady one-dimensional fluid flow in a semi-infinite porous medium with sinusoidal surface temperature. *Journal of Geophysical Research*, 70: 2821-2827.
- Stonestrom DA, Constantz J. 2003. Heat as a Tool for Studying the Movement of Ground Water Near Streams. In: *Circular 1260*, U.S. Geological Survey, pp: 105.
- Suzuki S. 1960. Percolation Measurements Based on Heat Flow through Soil with Special Reference to Paddy Fields. *Journal of Geophysical Research*, 65: 2883-2885. DOI: 10.1029/Jz065i009p02883.
- Swanson TE, Cardenas MB. 2011. Ex-Stream: A MATLAB program for calculating fluid flux through sediment-water interfaces based on steady and transient temperature profiles. *Computers & Geosciences*, 37: 1664-1669. DOI: 10.1016/j.cageo.2010.12.001.
- Taniguchi M, Burnett WC, Smith CF, Paulsen RJ, O'Rourke D, Krupa SL, Christoff JL. 2003. Spatial and temporal distributions of submarine groundwater discharge rates obtained from various types of seepage meters at a site in the Northeastern Gulf of Mexico. *Biogeochemistry*, 66: 35-53. DOI: 10.1023/B:Biog.0000006090.25949.8d.
- Tarnawski VR, Momose T, Leong WH. 2011. Thermal Conductivity of Standard Sands II. Saturated Conditions. *Int J Thermophys*, 32: 984-1005. DOI: 10.1007/s10765-011-0975-1.
- Therrien R, McLaren RG, Sudicky EA, Panday SM. 2010. *HydroGeoSphere A Three-dimensional Numerical Model Describing Fully-integrated Subsurface and Surface Flow and Solute Transport*. Groundwater Simulations Group, University of Waterloo, Canada, pp: 483.
- Tonina D, Buffington JM. 2007. Hyporheic exchange in gravel bed rivers with pool-riffle morphology: Laboratory experiments and three-dimensional modeling. *Water Resour. Res.*, 43. DOI: 10.1029/2005wr004328.
- Tyler SW, Selker JS, Hausner MB, Hatch CE, Torgersen T, Thodal CE, Schladow SG. 2009. Environmental temperature sensing using Raman spectra DTS fiber-optic methods. *Water Resour. Res.*, 45. DOI: 10.1029/2008wr007052.
- Vandenbohede A, Lebbe L. 2010. Parameter estimation based on vertical heat transport in the surficial zone. *Hydrogeology Journal*, 18: 931-943. DOI: 10.1007/s10040-009-0557-5.
- Vandersteen G, Schneidewind U, Anibas C, Schmidt C, Seuntjens P, Batelaan O. 2015. Determining groundwater-surface water exchange from temperature time series: Combining a local polynomial method with a maximum likelihood estimator. *Water Resour. Res.*, 51. DOI: 10.1002/2014wr015994.
- Vienken T, Dietrich P. 2011. Field evaluation of methods for determining hydraulic conductivity from grain size data. *J. Hydrol.*, 400: 58-71. DOI: 10.1016/j.jhydrol.2011.01.022.
- Vogt T, Schneider P, Hahn-Woernle L, Cirkpa OA. 2010. Estimation of seepage rates in a losing stream by means of fiber-optic high-resolution vertical temperature profiling. *J. Hydrol.*, 380: 154-164. DOI: 10.1016/j.jhydrol.2009.10.033.
- Voss CI, Provost AM. 2008. SUTRA - a model for saturated-unsaturated variable-density ground water flow with solute or energy transport. In: *Technical report Water-resources Investigations Report 02-4231* U.S. Geological Survey, pp: 270.
- Winter TC, Harvey JW, Franke OL, Alley WM. 1998. *Ground Water and Surface Water A Single Resource*. In: U.S. Geological Survey Circular, U.S. Geological Survey, pp: 79.
- Woessner WW. 2000. Stream and fluvial plain ground water interactions: Rescaling hydrogeologic thought. *Ground Water*, 38: 423-429. DOI: 10.1111/j.1745-6584.2000.tb00228.x.
- Woodside W, Messmer JH. 1961. Thermal Conductivity of Porous Media. I. Unconsolidated Sands. *Journal of Applied Physics*, 32: 1688.

For more information on the ADVOCATE Project, please visit:
www.theadvocateproject.eu

If you have any questions about this bulletin or would like further information about other CL:AIRE publications please contact us at:
 Email: enquiries@claire.co.uk Website: www.claire.co.uk