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Application of New Point Measurement Device to Quantify Groundwater-Surface Water Interactions

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Conflict of Interest: None
Abstract

The Streambed Point Velocity Probe (SBPVP) measures in situ groundwater velocities at the groundwater-surface water interface without reliance on hydraulic conductivity, porosity, or hydraulic gradient information. The tool operates on the basis of a mini-tracer test that occurs on the probe surface. The SBPVP was used in a meander of the Grindsted Å (stream), Denmark, to determine the distribution of flow through the streambed. These data were used to calculate the contaminant mass discharge of chlorinated ethenes into the stream. SBPVP data were compared with velocities estimated from hydraulic head and temperature gradient data collected at similar scales. Spatial relationships of water flow through the streambed were found to be similar by all three methods, and indicated a heterogeneous pattern of groundwater-surface water exchange. The magnitudes of estimated flow varied to a greater degree. It was found that pollutants enter the stream in localized regions of high flow which do not always correspond to the locations of highest pollutant concentration. The results show the combined influence of flow and concentration on contaminant discharge and illustrate the advantages of adopting a flux-based approach to risk assessment at the groundwater-surface water interface. Chlorinated ethene mass discharges, expressed in PCE equivalents, were determined to be up to 444 kg/yr (with SBPVP data) which compared well with independent estimates of mass discharge up to 438 kg/yr (with mini-piezometer data from the streambed) and up to 372 kg/yr crossing a control plane on the streambank (as determined in a previous, independent study).

Keywords: groundwater-surface water interactions, contaminant mass discharge, chlorinated ethenes, groundwater velocity, site characterization, streambed
Introduction

Groundwater-Surface Water Interactions and Solute Exchange

The importance of groundwater-surface water exchanges across the groundwater-surface water interface (GWSWI) is well recognized for a variety of hydrological problems (Warnick, 1951; Lee, 1977; Winters and Lee, 1987; Winter et al., 2003; Kalbus et al., 2006; Krause et al., 2009, 2011, 2012). Even a small exchange between groundwater and surface water can deliver a noteworthy contribution of solutes to a surface water body. For example, if a surface water body is gaining, the contribution from groundwater can sometimes affect the flow and chemistry of surface water strongly (Schwartz and Gallup, 1978; Jurley et al., 1985; LaBaugh et al., 1995; Moore, 1999; Holmes, 2000). In principle, the converse can also be true, i.e., losing streams may exert notable effects on groundwater flow and chemistry. Thus, the chemical and physical properties of surface and groundwater are strongly interdependent.

Recently, contaminant mass discharges into a Danish stream, the Grindsted Å, estimated from the analysis of concentration data and groundwater velocities at the stream bank using point velocity probes (PVPs), was compared to mass fluxes in the stream channel water (Rønde et al., 2017). Also recently, a new method of measuring flow across the GWSWI was introduced and evaluated in laboratory tests, based on PVP technology (Cremeans and Devlin, 2017). In this article, the newly adapted PVP probes, temperature gradient measurements, and Darcy calculations are used to conduct a detailed survey of contaminant mass fluxes into the Grindsted Å along a reach receiving groundwater contaminated by chlorinated ethenes.

Methods of Measuring Flow Across the GWSWI

In this work, a goal is to measure flow across the groundwater-surface water interface at the meter scale or less. To achieve this objective, two general approaches have been adopted (1)
measuring indirect metrics that can be converted to discharge rates (e.g. hydraulic heads, temperature profiles, or salinity profiles) (Winter et al., 1988; Bartolino and Niswonger, 1999) and (2) measuring water flux across the GWSWI directly (e.g. with seepage meters, Lee, 1977; Solder et al., 2015). These methods operate on a variety of scales. For example, seepage meters describe flux over the area of a drum (which can be any size but is usually on the order of about a meter in diameter). Mini-piezometers (often used in applications of Darcy’s Law) approach point measurements in scale. Both of these methods focus on specific, small areas of the stream with each measurement. Synoptic gauging (as in Harte and Kiah, 2009), which measures the total change in discharge over a defined reach of a river or stream, gives a much larger scale view of discharge (one that would require many measurements from seepage meters or mini-piezometers to make comparison possible) but does not identify discrete discharge zones are located.

In general, the indirect methods, which can provide detailed spatial patterns of flow, are subject to errors and biases related to the conversion of the measured quantities to flow rates. For example, to obtain accurate estimates of discharge, Darcy calculations rely on accurate estimates of hydraulic conductivity \(K\) and hydraulic gradient values, both of which are associated with high potential error (Molz et al., 1989; Butler et al., 2002; Zemansky and McElwee, 2005; Devlin and McElwee, 2007; Post and von Asmuth, 2013). Several tools and methods for measuring water exchanges across streambeds have been developed using temperature gradients. These commonly rely on analytical solutions that assume one-dimensional flow (Bredehoeft and Papadopolus, 1965; Stallman, 1965) and, sometimes, are restricted to gaining streams (as in Schmidt et al., 2007). Solutions have also been developed to use temperature in two- and three-dimensions and in losing streams (as discussed fully in Anderson, 2005).
The available direct methods of measuring flow across the GWSWI offer independent means of estimating exchanges across the GWSWI, and circumvent many of the sources of error mentioned above. In these cases, estimations of flux tend to depend on calculations involving easily measured properties with comparatively low uncertainties. For example, seepage meters measure discharge \( (Q) \) into a well-defined cross-sectional area \( (A) \) (usually, a steel drum) to permit the direct calculation of specific discharge \( (q = Q/A) \). Naturally, these methods come with their own sources of uncertainty, which tend to arise from the measurements themselves, which can be affected by local heterogeneity of the streambed material and biases introduced during equipment installation. For example, some investigators have seen agreement between measurements made by seepage meters and other methods in flowing streams (Rosenberry and Pitlick, 2009; Kennedy et al., 2010) while others have reported large uncertainties for measurements made in streambeds, or were unable to operate seepage meters at all in these settings (Cey et al., 1998; Zamora, 2006). The reasons for these uncertainties have been attributed to design limitations of the devices (Isiorho and Meyer, 1999; Murdoch and Kelly, 2003; Simpkins, 2006; Rosenberry, 2008), disturbance of flow paths due to instrument installation (Hutchinson and Webster, 1998), velocity heads imposed by waves and moving water interfering with seepage meter operation (Shinn et al., 2002), gas release in bed sediments (Kennedy et al., 2010), improper seals between the drums and the beds (Cey et al., 1998), small-scale spatial heterogeneities (Robinson et al., 1998; Bokuniewicz et al., 2004), and the combined effect of slow seepage rates with a moving streambed, causing scour or burial of the seepage meters (Zamora, 2006). Other methods, such as multiple tracer injections in streambeds (Zellweger, 1994) and the measurement of isotopic and temperature signatures to infer groundwater inflows into streams (Cook et al., 2003) may be similarly influenced by streambed
heterogeneity, difficult installation, and the challenges of working in a continuously evolving system (due to the transport of sediment, temporal variability of flow, etc.).

To gain a better picture of groundwater-surface water exchange, several studies have recommended a combination of two or more methods and datasets to characterize the sediment water interface (Becker et al., 2004; Verruijt, 2007; Ivkovic, 2009; De Smedt, 2014). Nevertheless, there are only a few examples of datasets sufficiently detailed to properly establish the nature of any single exchange zone and to address hydrological and contaminant fate issues (e.g., Conant et al., 2004; Freitas et al., 2014).

To help address the need for reliable, time-efficient, and cost-effective measurements of groundwater velocity, Point Velocity Probe (PVP) technology was developed. The original PVPs were designed to measure centimeter-scale in situ groundwater velocities in aquifers. This technology has been field validated in sand aquifers, a glacial outwash aquifer, and along a stream bank (Labaky et al., 2007; Schillig et al., 2011; Devlin et al., 2012; Rønde et al., 2017). The goal of this work was to adapt PVP technology to measure exchange at the GWSWI for the purpose of estimating contaminant mass discharge. The tool created to meet this goal is referred to as the SBPVP (Cremeans and Devlin, 2017). Previously, the SBPVP was validated in laboratory tests (Cremeans and Devlin, 2017). In this study, the SBPVP was used for high-resolution characterization of flow patterns at the GWSWI of a stream where physical documentation of the interface was necessary to determine the mass discharge of chlorinated ethenes.

Field Site

The Grindsted Å (stream) is located in Jutland, Denmark, proximal to an industrial site from which a plume of dissolved chlorinated solvents originates and subsequently discharges to the
stream (Figure 1). Further information about the site and the stream is reported in Rasmussen et al. (2016), Balbarini et al. (2017), and Sonne et al. (2017). In this study, all measurements were gathered in the streambed of the Grindsted Å, over a reach of the stream instrumented with 26 transects, situated approximately 3 m apart, and oriented perpendicular to the stream flow direction (Figure 1). The transects each comprised three to five evenly spaced measurement locations. The stream bottom consisted of three observed sediment types: silty sand, sand, and gravelly sand, as determined by visual inspection at each measurement location. Mini-piezometers, temperature spears, and the SBPVP were used to estimate groundwater velocity at the GWSWI, at each location.
Figure 1: Grindsted is located centrally in Jutland, Denmark. The field site was a single meander of the Grindsted Å, a stream running through the town of Grindsted, was divided into 26 transects (numbered 0 to 25). Each transect comprised 3 or 5 equally spaced measurements taken along a line perpendicular to the flow direction. The black dots show each measurement location. Temperature gradient and SBPVP measurements were taken on transects 0 to 25, while hydraulic head measurements were limited to transects 0 to 21. Slug testing was conducted at the measurement locations shown as open dots.
Methods

Pore Water Sampling

Samples and replicates, for tetrachloroethene (PCE), trichloroethene (TCE), cis-dichloroethene (cDCE), and vinyl chloride (VC), were collected over several field campaigns from mini-piezometers, which were also used for hydraulic head measurements (Figure 2). Because the plume was previously characterized, and is considered to be in a near steady-state condition (Sonne et al., 2017; Rønde et al., 2017), it was assumed that the plume remained unchanged between sampling efforts. Therefore, this study uses concentration data from sampling campaigns conducted in Oct. 2014, May 2015, June 2016, and September 2016. All velocity data were collected concurrently with the June 2016 campaign. Each water sample was collected by first purging the mini-piezometer with three well volumes and then collecting the samples in 20 to 40 mL glass vials with Teflon lined lids, sealed without headspace. The samples were preserved with 4 M sulfuric acid, and stored at 10º C until analysis. Full analysis was completed within four weeks of collection. Analyses were conducted at the Technical University of Denmark using an Agilent 7980 Gas Chromatograph with an Agilent 5675 C mass-selective detector (GC-MS), following the procedure presented in McKnight et al. (2012). The quantification limits for these analyses were 0.06 µg/L for PCE, 0.043 µg/L for TCE, 0.048 µg/L for cDCE, and 0.0500 µg/L for VC).
Figure 2: Pore water samples were collected from mini-piezometers at various locations in the stream and used to generate a map of contaminant concentrations near the interface of Grindsted stream. All samples were collected from depths between 40 cm and 70 cm, and analyzed for the presence of chlorinated ethenes.
Sediment Characterization

To discern streambed heterogeneity and reduce the errors associated with estimating $K$ for Darcy calculations, the sediment at each measurement location was visually examined and documented. Slug tests were subsequently conducted in the Grindsted Å stream bottom across a representative sample of sediment types, in accordance with the recommendations of Butler (1998) (locations shown in Figure 1). $K$ was measured in duplicate at 5 locations, for a total of 10 in situ tests (two measurement locations for silty sand, two locations for sand, and one location for gravelly sand, all at 40 cm depth). Sediment-type specific values for $K$ were then applied to the location-specific discharge calculations, assuming locally isotropic conditions (discussed in the Results and Discussion section).

Slug tests were conducted using a drive-point piezometer with a 10 cm screen. A pressure transducer (programmed to gather data every 0.5 sec) was placed in the piezometer and the system was left to equilibrate. After equilibration, water slugs of 1 m height were introduced to the piezometer. Data from the tests exhibited a straight line overdamped response. The data from these tests were processed in AQTESOLV (HydroSOLVE, Inc., 2016), where $K$ for each sediment type was calculated with the Hvorslev method (Hvorslev, 1951).

Temperature Gradient Measurements

Temperature surveys can offer a fast, inexpensive method of characterizing the GWSWI in detail. In the Grindsted Å, an Ebro TFN-520 Type K handheld thermometer was deployed using a steel spear to measure temperature gradients in 108 locations (Figure 1). In this study, the approach of Schmidt et al. (2007) was adopted, using the following one-dimensional analytical solution:
\[ q_z = -\frac{\kappa_{fs}}{p_f c_f z} \ln \left( \frac{T_z - T_L}{T_0 - T_L} \right) \]  

where \( q_z \) is Darcy flux in the vertical direction (m s\(^{-1}\)), \( \kappa_{fs} \) is the thermal conductivity of the solid-fluid system (J s\(^{-1}\) m\(^{-1}\) K\(^{-1}\)), \( p_f c_f \) is the volumetric heat capacity of the fluid (J m\(^{-3}\) K\(^{-1}\)), \( z \) is the depth of measurement (m), \( T_z \) is the temperature at depth \( z \) (°C), \( T_L \) is the temperature of the groundwater which is fixed for all calculations (°C), and \( T_0 \) is the temperature at \( z = 0 \) (°C).

The assumptions of this solution, which are also described in Schmidt et al. (2007), are the following: (1) one-dimensional flow in the vertical direction, (2) ascending flow (meaning, the solution is not valid for downward flow (Turcotte and Schubert, 1982), (3) streambed temperatures are in quasi-steady state during the period of measurement, and (4) the properties of the sediment and fluid are assumed to be homogeneous over the entire temperature profile.

The known variables include \( z \) (depth of measurement), which was 40 cm (in this case), \( \kappa_{fs} \) was assumed to be 2.2 J s\(^{-1}\) m\(^{-1}\) K\(^{-1}\) (Hopmans et al., 2002) and \( p_f c_f \) is 4.19 x 10\(^6\) J m\(^{-3}\) K\(^{-1}\). This leaves only the three temperature values unaccounted for in equation 1. \( T_L \) the temperature of groundwater, was determined to be 8.6 °C by averaging samples collected from streambank wells. \( T_0 \) is the temperature at the sediment-water interface. This value was measured along with a surface water measurement \( T_{sw} \) at every measurement location. \( T_z \) is the measurement of temperature at depth \( z \), which was also taken at each measurement location by inserting the temperature spear into the sediment at 40 cm depth, the deepest a probe could be installed without damage (Figure 3). The 40 cm depth was selected in an effort to reach a zone beneath active horizontal hyporheic flow. The measurements were processed using the analytical solution presented above (Eq. 1) coded into an Excel sheet to determine \( q_z \).
Figure 3: Temperature surveys require three measurements at each location, plus a
measurement of the temperature of the groundwater ($T_L$) (not shown above): one in the
surface water ($T_{sw}$), one at the sediment-water interface ($T_0$), and one below the interface (40 cm below, in this study) ($T_Z$). All measurements, except $T_L$, were taken over (or under) the same location on the streambed.
Darcy Calculations

Darcy calculations are commonly applied to the estimation of water flux across the GWSWI (for example, Lee and Cherry, 1979; Baxter et al., 2003; Rosenberry et al., 2008). To apply Darcy’s Law to the Grindsted Å streambed, mini-piezometers were installed in 92 locations across 22 transects (Figure 1). The piezometers were constructed from clear polyvinyl chloride (PVC) pipes (open ended with ~2 cm inner diameter). Each mini-piezometer was installed with a drive-point to a depth of ~40 cm below the streambed, and the hydraulic gradient \( (i = \Delta H/\Delta L) \) was measured between that depth and the stream channel water (therefore, \( \Delta L = 40 \text{ cm} \)). The water levels in the piezometers were allowed to equilibrate for 24 hours before measurements of hydraulic head \( (H \pm 0.7 \text{ cm}) \) were collected. A Solinst Model 101 Water Level Meter was used to measure water levels inside the mini-piezometers and a stilling well was used to determine the water level of the stream channel water (Baxter et al. 2000; 2003) (Figure 4). In all measurement locations, the gradient either indicated upward flow or was not possible to quantify because \( \Delta H \) was less than 0.7 cm, the uncertainty of a head measurement. The groundwater velocities from mini-piezometer data were calculated using the following modification of Darcy’s law:

\[
v = \frac{Ki}{n}
\]

(2)

Based on previous studies of the site, a uniform effective porosity \( (n) \) of 0.3 in the streambed sediments was assumed (Rügge et al., 1999; Lønborg et al, 2006). Estimates of \( K \) were gathered from slug tests, as described above, in the Sediment Characterization section.
Figure 4: The mini-piezometer set-up used in the field. This example shows upward flow, as designated by the arrows and the difference in hydraulic head between the mini-piezometer and the stilling well.
Streambed Point Velocity Probes

The Streambed Point Velocity Probe (SBPVP) was developed to provide high density datasets describing exchange across the GWSWI without reliance on hydraulic gradient or K information. The SBPVP estimates velocity by conducting a mini-tracer test on the surface of a 1-inch diameter drive point probe, which is inserted 7 to 10 centimeters into the streambed (Cremeans and Devlin, 2017). The tracer was chosen on the basis of electrical conductivity contrast with the surrounding water. The SBPVP was installed at 108 measurement locations (Figures 1, 5), at depths of about 7 to 10 cm beneath the sediment water interface (Cremeans and Devlin, 2017). To prevent horizontal hyporheic flow from influencing tests, a hyporheic shield (22 cm outer diameter and 61 cm height) was attached to the instrument (3.6 cm outer diameter and 4.5 cm height), isolating the vertical component of flow for measurement (Figure 5). All tests were conducted with tracer injection volumes ranging from 0.1 mL to 1 mL with tracer concentrations between 1 g/L NaCl and 2 g/L NaCl, as required (Schillig et al., 2014). SBPVP tests lasted from ~3 minutes to ~3.5 hours. All data were processed using VelProbePE (Schillig, 2012).
Figure 5: The SBPVP is installed 7 to 10 cm below the GWSWI, with a hyporheic shield to prevent the influence of non-vertical through-flow on measurements.
Contaminant mass discharge calculations

Visual representations of the in-stream chlorinated ethene mass discharge zones, sediment types, and measured velocity distributions were created with ArcGIS10 using the Inverse Distance Weighting (IDW) interpolation method. IDW is considered a “conservative” interpolator in this case, because low to moderate influence was assigned to empirical measurement points that were far from the interpolated points (a power of 3 with 2 neighbors, and a power of 2 with 12 neighbors, respectively). The application of IDW is described in full detail in the ArcGIS10 documentation (ESRI, 2017). The effect of these choices is that relatively sharp and localized boundaries are defined around the measured points that form localized extremes of the measurement range (high or low). Given the relative sparseness of the pollutant concentration dataset (compared to the SBPVP grid), the IDW scheme used here is expected to err on the side of underestimating pollutant masses, because unsampled areas of high pollutant concentration would be overlooked in the interpolation calculations. By comparison, the velocity data were collected on a denser grid than the water quality samples and, therefore, were less susceptible to interpolation-related errors. Velocity data (from SBPVP, piezometer, and temperature methods) and chemical concentration data were interpolated with IDW at the same cell size (0.171 m²). These interpolated datasets, plus an assumed uniform porosity of 0.3, provide the necessary values to calculate a preliminary mass discharge:

\[ J_{total} = n \times \sum_{i=1}^{m} C_i v_i A_i \]  

(3)

where \( J_{total} \) is the total mass discharge (kg/yr), \( C_i \) is the concentration in each cell (kg/m³), \( v_i \) is the velocity in each cell (m/yr), \( n \) is the effective porosity (dimensionless) in each cell, and \( A_i \) is the area of each cell (m²) (common cell size, given above), \( m \) is the number of cells in the IDW grid. Mass discharges of chlorinated ethenes into the stream are presented in PCE equivalents.
with units of kg/yr. Each compound was converted to a PCE equivalent using the following equation:

\[
PCE \text{ equivalent mass} = \text{Compound mass} \times \frac{PCE \text{ molar mass}}{\text{Compound molar mass}} \quad (4)
\]

Implicit in these calculations is the assumption that the pollutant concentrations and velocity measurements represent the same location near the GWSWI. Given that all measurements were conducted within the top 7 to 70 cm of the stream bottom, the assumption is consistent with obtaining a useful approximation of the discharge patterns. It must be acknowledged, however, that the possibility of horizontal pollutant transport away from the sampling points before discharging to the stream could have occurred in some locations. Also, the possibility of transformations occurring at some locations within the top 70 cm of sediments, cannot be ruled out.

**Results and Discussion**

Concentration data describing the plume of chlorinated ethenes suggested they were present in the streambed throughout the study reach, but were most concentrated near the apex of the meander and near transect 10, immediately upstream of the apex (Figure 6A). The streambed consisted of three observable sediment types: silty sand, sand, and gravelly sand (Figure 6B). Slug tests conducted in each sediment type indicated that the silty-sand sediments were characterized, on average, by \( K = 4.92 \times 10^{-5} \) m/s, the sandy sediments by \( K = 1.05 \times 10^{-4} \) m/s, and the gravelly sand sediments by \( K = 2.51 \times 10^{-4} \) m/s (Table 1). The sediment types were mapped in detail, based on the grid shown in Figure 1, and the range of \( K \) was found to be quite narrow for each type. Therefore, the associated Darcy calculations depending on these data are thought to be quite representative of the site. Nevertheless, the number of slug tests performed was small and could contribute to uncertainty in the calculations in some cases.
### Table 1: Summary of $K$ values measured in the Grindsted A streambed.

<table>
<thead>
<tr>
<th>Location</th>
<th>Test 1</th>
<th>Test 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transect 1 (gravelly sand)</td>
<td>$2.448 \times 10^{-4}$ m/s</td>
<td>$2.564 \times 10^{-4}$ m/s</td>
</tr>
<tr>
<td>Transect 3 (silty sand)</td>
<td>$5.421 \times 10^{-5}$ m/s</td>
<td>$4.938 \times 10^{-5}$ m/s</td>
</tr>
<tr>
<td>Transect 5 (sand)</td>
<td>$1.075 \times 10^{-4}$ m/s</td>
<td>$1.088 \times 10^{-4}$ m/s</td>
</tr>
<tr>
<td>Transect 7 (sand)</td>
<td>$1.043 \times 10^{-4}$ m/s</td>
<td>$9.821 \times 10^{-5}$ m/s</td>
</tr>
<tr>
<td>Transect 14 (silty sand)</td>
<td>$4.722 \times 10^{-5}$ m/s</td>
<td>$4.652 \times 10^{-5}$ m/s</td>
</tr>
</tbody>
</table>
Figure 6: (A) Preliminary assessment of chlorinated ethene distributions in the shallow streambed sediments (40 to 70 cm depth, as PCE equivalents). (B) The stream bottom was also assessed for sediment type. Three main sediment types were established and a series of slug tests was conducted to determine $K$ for each type (Table 1).
To begin the estimation of the groundwater-surface water exchange rate, the temperature gradient method was applied. The temperature-derived pattern of flow reveals relatively low discharges upstream of the meander, with localized regions of higher flow through the meander and slightly downstream (seepage velocities up to 129 m/yr) (Figure 7).
Figure 7: Temperature gradient measurements were the basis for a preliminary assessment of discharge patterns at the GWSW interface. The temperature measurements were made in the stream water column, at the sediment-water interface, and at 40 cm depth below the interface to support the calculations. Note that the scale of groundwater velocity from the temperature data is over an order of magnitude smaller than the scales determined by the other velocity estimation methods.
The streambed was subsequently surveyed using mini-piezometers to obtain hydraulic gradient data (on the same sampling grid). Due to time constraints associated with installation and equilibration of the mini-piezometers, four fewer transects were examined by this method (Figure 8A). The estimated groundwater discharges from the mini-piezometer data (expressed here as velocities for consistency) suggested a pattern of heterogeneous flow that was spatially similar to the temperature data discussed above; the upstream region of the study reach was associated with relatively low discharges and the discharges at the meander apex and downgradient segment were characterized by localized regions of relatively high velocities.
Figure 8: (A) Results of the Darcy method applied to measure exchange, using mini-piezometers. (B) Results of the SBPVP applied to the measurement of vertical streambed seepage velocities. Please note that upper limits are different for the two contour scales due to one measurement outlier (discussed in the text below).

(Figure 8A).
Comparison of the Darcy-derived velocities and the temperature-derived velocities showed major differences (on the order of a factor of 10) in velocity magnitudes (Figures 7, 8A). The velocities were calculated with values of $K$ from slug tests performed in the streambed, which assumed locally isotropic conditions in the sediments. This assumption may have resulted in conservatively large estimates of $v$, since vertical anisotropy was ignored. However, because the sediments were generally sandy, and testing was conducted in a single sediment stratum at each location, factors of anisotropy can reasonably be expected to be low, between 1.3 and 1.6 (Burger and Belitz, 1997), justifying our approximation of isotropic conditions in the streambed. Regardless, anisotropy of the bed sediments does not seem to fully account for the differences in flow magnitudes between the Darcy calculations and the temperature gradient calculations.

The anomalously low flux estimates from the temperature gradient method are explainable by potentially significant horizontal flow in the Grindsted Å streambed, associated with the penetration of stream water into the bed to a depth of at least 40 cm, as discussed in the Introduction (Lautz, 2010; Irvine et al., 2016; Munz et al., 2016). Assuming the Darcy-derived fluxes are representative of the actual vertical flows, this finding is illustrative of a potential limitation of temperature data to calculate groundwater fluxes in streambeds. Other limitations have been documented, such as the seasonal dependence of temperature gradients that limits the times of year when the method is applicable (Irvine et al., 2016). Despite the issues encountered in this work, it is noted that the temperature-based methods represent a fast and useful approach to streambed characterization, complimentary to the other methods used here, and they have been successfully applied in a variety of cases (Lautz, 2010; Lewandowski et al., 2011; Bhaskar et al., 2012; Lu et al., 2017).
The velocities measured using the SBPVP revealed very similar spatial patterns of flow compared to those found by the two preceding methods (Figure 8B). This result verifies the preliminary findings of Cremeans and Devlin (2017) with a more extensive dataset from the same site. Moreover, the velocity magnitudes suggested by the SBPVP data compared very well with those from the Darcy calculations. A linear correlation was found to exist between the two methods’ estimated velocities; the values fell along a line with a slope of 1.08 with a 95% confidence envelope of ±150 m/yr over a velocity range of 0 to ~500 m/yr, and ±550 m/yr for velocities up to 5500 m/yr (Figure 9). The dataset contains one significant outlier which was not included in the 95% confidence interval calculations (shown in Figure 9 as an open circle). The anomalous point occurred at a location where the SBPVP measured a velocity of ~4,500 m/yr while the Darcy calculations led to an estimate of ~6,500 m/yr. In this case, it is thought that a change in the prevailing sediment type at 40 cm depth (noted during piezometer installation) led to the use of an unrepresentative hydraulic conductivity value in the Darcy calculation.

The highest velocity value from the entire data set, measured by the SBPVP, is 9851 m/yr (27 m/day), which seems high but may result from a high convergence of streamlines from the bank to the streambed. The piezometer at this location behaved like a flowing artesian well, and the total hydraulic head there could not be measured. The corresponding point was omitted from Figure 9. The point was, however, included in the mass discharge calculations by using the measured SBPVP velocity value as measured, but assuming total hydraulic head there was at the elevation of the top of the piezometer casing. It is recognized that this approximation caused an underestimation of the Darcy-derived mass discharge at this point.

The Darcy-derived mass discharges were calculated to be within 435.2 to 438.2 kg/yr. Using the SBPVP data, the total chlorinated compound mass discharge (in PCE equivalents) was calculated...
to be between 437.9 and 444.1 kg/yr. In both cases, the lower estimate was calculated with a restrictive Inverse Distance Weighting (IDW in ArcGIS) interpolation of the concentration data (i.e., low influence was assigned to interpolated points far from the empirical points). In this interpolation, an exponent of 3 was assigned and the number of neighbors used was 2. The higher estimate was calculated with a more inclusive IDW interpolation of the chemical data (moderate influence assigned to interpolated points far from the empirical data points) (Figure 10). In this interpolation, the exponent was set at a value of 2 and the number of neighbors used was 12.
Figure 9: A plot of SBPVP velocities compared with Darcy-derived velocities from the Grindsted Å. A single outlier is shown as an open circle. The black dots represent the experimental data, the dot-dash lines represent the error envelope with 95% confidence, based on the measured velocity range of 0 to about 5000 m/yr.
The streambed determinations of chlorinated mass discharge – from Darcy calculations and SBPVP measurements – compared well with similar estimations conducted using data from the northern streambank, as reported by Rønde et al. (2017). Based on Darcy calculations and PVP measurements along a control plane (defined as a plane “oriented perpendicular to the groundwater flow direction and that extends over the entire width and depth of the plume”), they estimated the total chlorinated compound discharge to be between 204 kg/yr and 372 kg/yr. The low value of this range was obtained using PVP data averaged over the control plane (Rønde et al., 2017, pg. 43), raising the possibility that some zones of coincident contamination and high flow rates were not sampled on the control plane. Note that the challenge of sampling the entire plume section is facilitated in the streambed, where flowlines converge. The highest estimate of mass discharge at the stream bank reported by Rønde et al. (2017) was associated with Darcy calculations, which used a geometric mean value of $K (1.8 \times 10^{-4} \text{ m/s})$ from slug tests in streambank wells and a hydraulic gradient normal to the control plane from piezometers installed on the streambank and in the streambed (0.034).

As expected from the water flux calculations, the total contaminant mass discharge calculated with the temperature data yielded a much lower range of total chlorinated ethene discharge than both the Darcy and SBPVP datasets (4.7 kg/yr to 5.1 kg/yr). For reasons previously discussed, and because the mass discharges from the other methods substantially exceeded these values, the temperature-derived estimations are thought to be erroneously low.

With detailed knowledge of the distributions of water discharge and chlorinated ethene occurrence in the streambed, it is possible to calculate mass discharge rates using equations 3 and 4. Most importantly, the resulting pattern of total equivalent PCE mass discharges is not exactly represented by either the water velocity patterns or pollutant concentration patterns in the
streambed (compare Figures 6, 7, 8, and 10). This divergence could occur as a result of either physical or chemical/microbial processes. For example, where the highest flow zones do not coincide with the highest concentration zones, the less aggressively flushed sediments are able to retain the highest levels of contamination for a longer period of time. Alternatively, the divergence could be the result of differential transformation (or biotransformation) rates; sediments with slightly greater water residence times may have maintained the redox conditions necessary for dechlorination reactions that produce cDCE and VC, hence these compounds – which make up the majority of the chlorinated ethene loading at the Grindsted Å – would be associated with the lower seepage velocity zones. Note also that the locations where transformations took place could have been some distance upgradient of the streambed. Regardless of the reasons for the divergence, this phenomenon implies that concentration distributions do on their own reflect the risk associated with mass discharges across the GWSWI. The same implication applies to flow measurements: high groundwater flux estimates do not necessarily correspond to high contaminant mass discharges. Therefore, the results of this study suggest that detailed characterization of both the flow and concentrations may be needed to properly assess risk. Moreover, knowledge of the locations of highest contaminant mass discharges can be used to identify zones of greatest concern and guide highly focused remediation plans, with associated cost and treatment efficiencies.
Figure 10: Contaminant mass discharge \((J)\) was calculated using equation \((3)\) based on concentrations from Figure 6A, and SBPVP data \((v)\) shown in Figure 8B.
Conclusions

Field validation of the SBPVP suggests that it is a useful tool for high resolution monitoring and identification of localized regions of high flow. Spatial patterns of flow distribution (i.e., location of high flow and low flow) tended to be similarly identified from temperature spears, mini-piezometers and the SBPVP suggesting that the patterns of flow are well-delineated by all methods. However, considering the magnitude of a previously reported total mass discharge (across a control plane on an adjoining bank of the stream, 204 to 372 kg/yr), only the SBPVP and mini-piezometer data reflect reasonable mass discharge values, 437.9 to 444.1 kg/yr and 435.2 to 438.2 kg/yr, respectively.

While the Darcy and SBPVP methods were similarly viable in determining mass discharge (and complementary in the type of data they provided), the SBPVP survey was conducted more quickly and with less manpower than the mini-piezometer survey. This outcome presents clear potential advantages for the use of the SBPVP in future investigations at the GWSWI of shallow streams. While the SBPVP can efficiently provide detailed spatial information about flow distribution and magnitude, the results from this work suggest that the temperature gradient method, which is fastest to implement, could be used to great advantage in combination with the SBPVP by identifying or verifying locations of the greatest water fluxes across the GSWSI.
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Highlights

- Darcy, temperature, and PVP used to characterize groundwater-stream water interactions
- Measurements of flow exchanges at the GWSWI used to calculate contaminant mass discharges
- Effects of horizontal hyporheic flow on discharge estimations found to be important