A mixing model analysis of stream solute dynamics and the contribution of a hyporheic zone to ecosystem function*

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SUMMARY

1. We monitored streamwater and streambed sediment porewaters from White Clay Creek (WCC), SE Pennsylvania, for dissolved organic carbon (DOC), dissolved oxygen (DO) and conductivity to investigate organic matter processing within the hyporheic zone. Dissolved organic carbon and DO concentrations were higher in the streamwater than in the porewaters and, in many cases, concentrations continued to diminish with increasing depth into the streambed.

2. Hydrological exchange data demonstrated that the permeability of the stream bed declines with depth and constrains downwelling, effectively isolating porewaters >30 cm from streamwater.

3. End-member mixing analysis (EMMA) based on conductivity documented a DOC source and DO sink in the hyporheic zone. We calculated hyporheic streambed DOC fluxes and respiration from the EMMA results and estimates of water flux. Based upon our calculations of biodegradable DOC entering the hyporheic zone, we estimate that DOC supports 39% of the hyporheic zone respiration, with the remaining 61% presumably being supported by entrained particulate organic carbon. Hyporheic respiration averaged 0.38 g C m$^{-2}$ d$^{-1}$, accounted for 41% of whole ecosystem respiration, and increased baseflow ecosystem efficiency from 46 to 59%.

4. Advective transport of labile organic molecules into the streambed concentrates microbial activity in near-surface regions of the hyporheic zone. Steep gradients in biogeochemical activity could explain how a shallow and hydrologically constrained hyporheic zone can dramatically influence organic matter processing at the ecosystem scale.

Keywords: dissolved organic carbon, ecosystem function, end-member mixing analysis, hydrodynamic exchange, hyporheic zone

Introduction

In stream ecosystems, surface and ground waters communicate through a hydrologic continuum and mix within the hyporheic zone (Orghidan, 1959). Traditionally, the hyporheic zone has been considered from a metazoan (Bretschko, 1992; Danielopol, 1976) or chemical (Triska et al., 1989) perspective. Advances
in hydrodynamic modelling have expanded these views and generated considerable interest in hydrologic exchange processes at the streambed interface (Packman & Bencala, 2000). Within this hydrodynamic context, the hyporheic zone has been described as the streambed layer affected by fine-scale interactions that consist of water exchanges between the streamwater and groundwater that occur within the context of larger-scale exchanges between the stream channel and the catchment (Harvey & Wagner, 2000).

The degree to which the hyporheic zone affects stream ecosystem function has been ascribed to physical dimensions, biogeochemical processing rates, temperature, nutrient and oxygen supply, and to the proportion of the total discharge flowing through the hyporheic zone (Findlay, 1995; Boulton et al., 1998; Kaplan & Newbold, 2000). These concepts are consistent with modelling results (Mulholland & DeAngelis, 2000) and empirical data that show shorter nutrient uptake lengths for phosphate (Mulholland et al., 1997) and nitrate (Valette et al., 1996), and a greater hyporheic zone contribution to whole-stream metabolism (Fellows, Valett & Dahm, 2001), given larger hyporheic zones and greater hydrological exchange.

Our knowledge of hyporheic zone function is strongly biased towards glaciated, arid and coastal plain landscapes. Steep longitudinal gradients and high-porosity streambeds composed of glacial tills result in hyporheic zones that extend from metres to kilometres into the flood plain (e.g. Stanford & Gaufin, 1974; Pusch & Schwoerbel, 1994; Naegeli & Uehlinger, 1997; Battin, 1999). Similarly, high-porosity sandy streambeds result in metres-deep hyporheic zones in the North American Coastal Plain (Fuss & Smock, 1996) and high sediment permeabilities in desert streams that lead to high exchange rates and similar dissolved organic carbon (DOC) concentrations in the streamwater and the hyporheic zone (Jones, Fisher & Grimm, 1996; Fellows et al. 2001). Shallow hyporheic zones of streams draining catchments where clay soils or bedrock constrain the dimensions of stream channels and reduce sediment permeability, have received less attention. This leaves open the question as to whether shallow hyporheic zones can substantially influence stream ecosystem function. Additionally, despite the importance of the hyporheic zone to DOC biogeochemistry, few studies provide data on the temporal variation of hyporheic DOC concentrations (Hendricks & White, 1995; Findlay & Sobczak, 1996; Jones et al., 1996) and even fewer have explored how the interactions between streamwater and groundwater exchange influence DOC metabolism (Battin, 1999, 2000).

In this work we tested two hypotheses related to the structure and function of the hyporheic zone: (1) hydrological exchanges between streamwater and groundwater generate the dominant spatial and temporal patterns of DOC within the hyporheic zone of a third-order piedmont stream, despite seasonal changes in organic matter sources and metabolic activity and (2) highest heterotrophic microbial activities occur near the interface of a hyporheic zone and its organic energy volume, dictates the contribution of a hyporheic zone to stream ecosystem metabolism. We used hydrometric and tracer approaches to characterise the hyporheic zone of a third-order piedmont stream. Spatial and temporal variation in porewater DOC and dissolved oxygen (DO) concentrations were measured from minipiezometers within the streambed. These variables were used in an end-member mixing analysis (EMMA) to explore the dynamics of hyporheic DOC metabolism and respiration. Finally, we compared hyporheic DO fluxes and organic carbon fluxes and transformations with estimates for the whole stream ecosystem to assess the contribution of the hyporheic zone in DOC cycling and stream ecosystem metabolism.

Methods

Study site

The study sites (Fig. 1) are situated in a 725-ha SE Pennsylvania U.S.A. piedmont catchment in the headwaters of the East Branch White Clay Creek (WCC, 39°53′N, 75°47′W; 100–164 m above sea level; Newbold et al., 1997). The catchment is underlain by metamorphic crystalline rock, including gneiss, schist, quartzite and marble. Soils, 1–2 m deep, are unglaciated and primarily typic hapludults, except in the riparian zone, where aquic fragiudults predominate. Land use consists of deciduous woodlands, meadows, pastures and arable agriculture. Annual precipitation averages 1.05 m year⁻¹ and has an even seasonal distribution. Mean stream flow is 113 L second⁻¹, baseflow 75 L second⁻¹ and surface water temperature 10.6 °C. Average stream slope is 8 m km⁻¹ and porosity of the surficial sediment (0–20 cm) ranges from 20 to 30%. Streamwater nutrient concentration ranges from...
Upstream woodland sites A and B are located along a second-order branch that receives water from a spring-fed pond and a first-order stream. These sites are underlain by Cockeysville marble, a carbonate formation that imparts a distinctively high conductivity signature to the groundwater. Sites C, D and E are located along the third-order WCC and have protected riparian zones with deciduous trees and herbaceous woodland plants. Mean sediment particle size averages 0.52 ± 0.20 and 0.58 ± 0.20 mm and sediment organic matter (as ash free dry mass) ranges from 0.98 to 4.36% and from 0.93 to 2.17% for second- and third-order sites, respectively (Bott & Kaplan, 1985).

Minipiezometer installation, sampling, and sample processing

Hyporheic zone water was collected from minipiezometers nested at three depths (10, 30 and 50 cm) per site and installed with three-five replicate minipiezometers per depth. The distance between replicate minipiezometers was typically <1.5 m. Minipiezometers were made from PharMed tubing (Cole Parmer, Chicago, IL, USA) that we perforated near the bottom with millimetre-sized holes and covered with 100 μm mesh Nitex fabric (Wildlife Supply Company, Buffalo, NY, USA) (Lee & Cherry, 1978). We attempted to install the minipiezometers evenly across each stream cross section but, in many cases, our attempts met with resistance, presumably from buried rocks. Water was collected with a Nalgene hand pump from minipiezometers, transferred into glass bottles, stored (4 °C, in the dark) and processed within 4 h. All glassware was precombusted (500 °C, 6 h).

Water for DOC analysis was filtered (Whatman GF/F, precombusted 500 °C, 6 h) and analysed in triplicate with an OI 700 organic carbon analyser (OI Corporation, College Station, TX, USA) (Kaplan, 1994). Subsamples of the water collected at the third-order site E were used to determine concentrations of biodegradable dissolved organic carbon (BDOC) with a suspended inoculum in batch cultures (Kaplan, Reasoner & Rice, 1994), total dissolved saccharides (Gremm & Kaplan, 1997) and absorbance at 254 nm. Absorbance was divided by the DOC concentration to provide specific UV absorption (SUVA) as an indicator of DOC aromaticity (Chin, Aiken & O'Loughlin, 1994). Triplicate field measurements of DO and temperature were performed per minipiezometer with an Orion 840 oxygen probe (Thero Orion, Beverly, MA, USA). Conductivity was measured on unfiltered aliquots in the laboratory (YSI 32 3417 probe (YSI Inc., Youngstown, OH, USA), reference temperature: 25 °C). Bacterial densities in streamwater and porewaters were determined by direct microscopic counts (Hobbie, Daley & Jasper, 1977).

Sediments for particulate organic carbon (POC) analyses were collected from 50 mm diameter cores obtained by driving plastic pipe into the substratum. The organic content was determined as ash free dry mass (APHA, 1998) and converted to units of organic carbon assuming that organic matter is 50% carbon.

Hydrological exchange

We described the hydrodynamics of the WCC streambed from hydrometric data and modelling the dynamics of a conservative solute following its injection. In all minipiezometers (Winter, LaBaugh & Rosenberry, 1988) we estimated pressure heads, \( h \), line refers to the watershed.
with a potentiometer. For each site and date, the average hydraulic head, \( \bar{h} \), was computed from all of the minipiezometers from a given depth (\( z = 10, 30 \) or 50 cm, in which \( z \) is positive downward from the sediment surface). Vertical hydraulic gradients (VHG) were computed from the equation \( \text{VHG} = \Delta h/\Delta z \) in which \( \Delta h \) is the difference in \( h \) between two depths, and \( \Delta z \) is the difference in depths. Thus VHG is reported for depths that are midway between two minipiezometer planes or, for 5 cm, between the sediment surface and the 10-cm plane. Falling head tests were performed with a field permeameter to estimate the sediment hydraulic conductivity, \( K \), in each minipiezometer (Vanek, 1993). Water fluxes were computed according to the Darcy equation (Freeze & Cherry, 1979): \( v = -K\Delta h/\Delta z \), in which \( v \) is the Darcy velocity and is equivalent to the water flux (volume per time) per unit area of streambed. For computations, \( K \) was averaged between adjacent depths, except that the 10-cm permeability was used for the flux between 10-cm and the sediment surface. Because \( z \) is measured downward, a positive VHG represents an upwelling condition (Valett et al., 1994), but yields a negative (upward) Darcy velocity. Following Lee & Cherry, (1978) we henceforth neglect the negative sign in the Darcy equation so that both a positive VHG and a positive Darcy velocity represent upwelling. For the solute injections, we used whole-stream injections of a conservative tracer (Br\(^{-} \)) to estimate the hydraulic exchange between streamwater and the hyporheic zone and obtain mass balance for groundwater flux.

Four injections were conducted in which Br\(^{-} \) was metered into the stream at a constant rate for periods of 24–168 h, during which discharge remained nearly constant. Rising limb, plateau and falling limb Br\(^{-} \) concentrations were monitored at five sites within a 370-m reach of the third-order segment of WCC (between sites D and E, Fig. 1). Bromide concentrations were determined by either an ion-specific electrode or ion chromatography (APHA, 1998). We used trial and error simulations to estimate the parameters of a one-dimensional transport model incorporating transient storage (e.g. Bencala & Walters, 1983) and generalised the transient storage results and piezometric data to the entire channel for carbon and water flux calculations.

We report the rate of transfer of streamwater into the hyporheic zone as a mass transfer coefficient or ‘hydraulic exchange velocity’ (HEV), \( v_{sw} = \alpha d \), where \( \alpha \) is the model-estimated storage exchange coefficient, and \( d \) is the stream depth. We assume that the observed transient storage dynamics represent exchange with the hyporheic zone, rather than with quiescent zones within the water column. This assumption is based on the observation that the rate of postinjection clearance of Br\(^{-} \) in samples taken from minipiezometers agreed much more closely to simulated rates than did clearance from identifiable quiescent zones (I.D. Newbold & S.P. Hendricks, unpublished).

The average flux of groundwater upwelling into the hyporheic zone was calculated from a mass balance analysis that used average annual baseflow and the streambed area upstream of the gauging station on WCC that included all sampling sites (Fig. 1). The gross upwelling from the hyporheic zone to the streamwater was calculated as the sum of the absolute value HEV (representing returning streamwater) and the upwelling groundwater. In our application, the transient storage modelling was hydrologically balanced, in that stream water leaving the stream channel was balanced by water returning to the channel from the transient storage zone. Under these conditions, the velocity describing the movement of water from the channel to the hyporheic zone is equivalent to the velocity describing water returning to the stream channel from the hyporheic zone.

**End-member mixing analysis (EMMA)**

If hyporheic DOC and DO were simply the result of conservative mixing of ground- and streamwater, their concentrations would be between the concentrations of these end-members. Deviations from conservative mixing indicate whether the hyporheic zone is a source or sink for DOC and DO. We conducted an EMMA (Christophersen et al., 1990) to differentiate between sources and sinks of DOC and DO within the streambed. Ambient conductivity was used as a conservative tracer and we assumed, *a priori*, that water at a depth of 10 cm within the streambed was a mixture of downwelling streamwater and upwelling groundwater passing through the 30-cm layer within the streambed. The relative contributions (\( \alpha \) and \( 1 - \alpha \)) of both end-members were computed for each sampling date by solving the equation \( C_{10} = \alpha C_{sw} + (1 - \alpha) C_{30} \) where \( C \) is conductivity and subscripts refer to...
the end-members (streamwater and 30-cm sediment layer) or the mixture of end-members (10-cm sediment layer). Based on these relative fractions and on end-member DOC and DO concentrations, we then calculated predicted DOC and DO concentrations that would result in the 10-cm layer from the conservative mixing of the streamwater and the groundwater (water from 30 cm).

**Carbon fluxes**

Our conceptual model of the organic carbon dynamics in the third-order WCC includes four physically separated compartments: streamwater, benthic interface, hyporheic zone, and groundwater; with exchanges of carbon and water occurring between adjacent compartments. Our calculation of carbon fluxes between compartments involved multiplying the organic carbon concentration within each compartment by the specific water flux between compartments. Water flux (m$^2$ m$^{-2}$ day$^{-1}$), expressed as Darcy velocity and hydraulic exchange rate (m day$^{-1}$) was estimated from mass balance calculations and conservative tracer releases, which integrate over the entire stream reach. The gross DOC outflow from the hyporheic zone was calculated as the product of the gross water upwelling from the hyporheic zone to the stream (see above) and the average concentration of DOC at 10-cm sediment depth. Inputs of BDOC to the hyporheic zone were calculated from the product of BDOC concentrations (available only from site E) in the groundwater and streamwater and the respective hydrologic flux into the streambed. Fluxes of BDOC were subtracted from total DOC fluxes to express fluxes of the refractory DOC (RDOC).

The POC flux to the hyporheic zone from the water column was estimated as the product of the HEV and the average POC concentration in the streamwater. This provides a conservative estimate as we assume that the concentration of particles in the streamwater is the same as the concentration of particles in the laminar zone.

We calculated average hyporheic-zone respiration as the product of EMMA-derived DO residuals and the gross upwelling flux of water from the hyporheic zone to the stream. We used the average dissolved oxygen residuals from sites C and E for this estimate. Dissolved oxygen was converted to units of carbon assuming a respiratory quotient (moles of C: moles of O$_2$) of 1, or 1 g C = 2.67 g O$_2$.

**Statistical analyses**

Data were analysed with SAS (SAS Institute) on a Digital Equipment Corp. MicroVAX 3100 and with SYSTAT (Systat Inc., Evanston, IL, U.S.A.). Analysis of variance and the Tukey multiple range test were calculated to test for effect of site and sediment depth on solutes. We used least square linear regressions to analyse the relationships of solutes from streamwater and porewaters. The variation of DOC and DO residuals was explored with stepwise multiple regression analysis. Step order was forward, $P$ to enter was 0.15, and minimum tolerance for entry into the model was 0.01. Significant differences were determined at an $\alpha$ error level of $P = 0.05$. All data are presented as the mean ± SD of three to six field replicates.

**Results**

*Hydrologic setting of the hyporheic zone*

Generally, sediment permeability and vertical hydraulic gradient decreased with stream bed depth (Table 1). However, within these broad patterns, both hydrologic parameters exhibited considerable heterogeneity within and between sites. Within individual sites, except for site C, permeability at 10 cm exceeded values at 30 or 50 cm depths by 1.7–6.6-fold, and between sites, permeabilities in the 10-cm sediment layers of the third-order sites (C, B and E) were 1.9–3.7-fold lower than those measured upstream (sites A and B). Upwelling dominated the streambed hydrological exchange, accounting for 93% of the points, where VHG were measured ($N = 159$). The Darcy velocity at all sites and depths, where it could be measured was upward, except at the mid-depth (20 cm) at site D where it was 0.95 m day$^{-1}$ downward (Table 1). Although the large standard deviations preclude statistically significant site or depth differences, the upwelling appeared to be greater in the second-order than third-order sites, and greater across the 5-cm plane than across the 20- or 40-cm planes. The mean Darcy velocity of all sites and depths was 0.87 m day$^{-1}$ (upwelling, each site weighted equally), whereas...
the mean across the 20- and 40-cm depths was 0.49 m s\(^{-1}\) (upwelling).

An overall average rate of upwelling can be estimated for baseflow conditions from mass balance considerations by assuming that the base flow (109 ± 19 L s\(^{-1}\) during the period of measurements) originates from upwelling flow distributed evenly over the entire 24 000 m\(^2\) of upstream streambed area (Newbold \textit{et al}., 1997). This approach yields an equivalent Darcy velocity of 0.39 L s\(^{-1}\) which is considerably less than the overall average obtained from the piezometers, but comparable with the piezometer-estimated flux across the 20- and 40-cm planes. Substituting the average annual baseflow of 75 L s\(^{-1}\) in the above calculation yields an estimate for upwelling groundwater Darcy velocity of 0.27 L s\(^{-1}\).

Hydraulic characteristics determined from the transient storage modelling include: stream flow (64 ± 30 L s\(^{-1}\)); velocity (0.10 ± 0.04 m s\(^{-1}\)); depth (0.15 ± 0.014 m); average ratio of storage to stream cross-sectional area, \(A_s : A\) (0.08 ± 0.04); average exchange rate, \(\alpha\) (2.4 \times 10^{-5} ± 1.4 \times 10^{-5} s^{-1}); and transient storage residence time (71 ± 65 min). Based on the average exchange rate (\(\alpha\)) and average water column depth, the average HEV, which refers both to the downwelling of streamwater into the hyporheic zone and to the equal rate of upwelling return flow, was 0.29 ± 0.15 m day\(^{-1}\). Because the net of up- and downwelling, via hydraulic exchange, is zero it should not contribute to the piezometer-based estimates of net Darcy flux.

A theoretical depth of the hyporheic zone of \(\approx 1\) cm was derived from \(A_s : w\) (where \(A_s = 0.05\) m\(^2\) and stream width, \(w = 4.24\) m) which, using a sediment porosity of 20–30% and nearly equal mixing of stream (downwelling HEV of 0.29 m day\(^{-1}\)) and ground waters (upwelling Darcy velocity of 0.27 m day\(^{-1}\)), translates to a hyporheic depth of 6–10 cm in WCC. A downstream Darcy velocity of 0.07 m day\(^{-1}\) for water within the hyporheic zone was estimated from the product of average permeability (\(\approx 1 \times 10^{-4}\) m s\(^{-1}\)) and bed slope (0.008). This velocity translates to a downstream hyporheic flow of \(\approx 23\) L day\(^{-1}\). The ratio of average streamflow to hyporheic flow (\(Q_{\text{surface}} : Q_{\text{hyporheic}}\)) is \(\approx 3 \times 10^5\) (or a \(\log_{10}\) transformed ratio of 5.5, \textit{sensu} Boulton \textit{et al}., 1998). The distance, \(S_{\text{avg}}\) that water travels downstream before entering the hyporheic zone is 4.36 km, calculated as

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### Table 1 Vertical hydraulic gradient and sediment permeability in the White Clay Creek streambed. A gradient is positive when the head increases with depth and thus produces upwelling flow

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Transects</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Vertical hydraulic gradient (cm cm(^{-1}))†</td>
<td>Permeability (cm s(^{-1}) \times 10^{-3})‡</td>
<td>Darcy velocity (m day(^{-1}))§</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>0.04 ± 0.03</td>
<td>0.17 ± 0.11</td>
<td>0.17 ± 0.12</td>
<td>0.15 ± 0.10</td>
<td>0.08 ± 0.14</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>0.18 ± 0.11</td>
<td>-0.07 ± 0.06</td>
<td>0.02 ± 0.06</td>
<td>0.09 ± 0.06</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>0.33 ± 0.06</td>
<td>0.07 ± 0.01</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.03 ± 0.04</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>2.95 ± 2.82</td>
<td>2.13 ± 1.02</td>
<td>1.10 ± 1.27</td>
<td>0.66 ± 0.23</td>
<td>0.80 ± 0.41</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>0.45 ± 0.32</td>
<td>1.22 ± 1.14</td>
<td>0.81 ± 0.89</td>
<td>0.15 ± 0.19</td>
<td>0.24 ± 0.16</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>0.55 ± 0.42</td>
<td>0.78 ± 0.12</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.18 ± 0.22</td>
</tr>
</tbody>
</table>

†Vertical hydraulic gradient (VHG) relate to the plane between installation depths of the minipiezometers, which correspond to the depths used for permeabilities.
‡Permeabilities are the mean ± SD of values computed for each of three to six measurement dates.
§Darcy velocities are the product of the respective vertical hydraulic gradient and permeability converted to units of m day\(^{-1}\). A positive Darcy velocity represents upwelling, as explained in the text. The standard deviation was computed from the standard deviation of vertical hydraulic gradient, and thus reflects temporal variation but not uncertainty in permeability.

*not determined.
the ratio $v_W : \alpha$ (Harvey & Wagner, 2000). This distance is nearly the same as the channel distance from headwaters to site E (4.39 km). By contrast, water that has entered the hyporheic zone would be expected to migrate downstream only 0.034 m (the product of the downstream Darcy velocity and the transient storage residence time) before resurfacing.

**Spatial pattern of solutes**

At all sites we observed a general pattern of higher solute (DOC, DO, BDOC, carbohydrate) concentrations in the streamwater than in the streambed porewater and, in many cases, concentration continued to diminish with increasing depth into the streambed (Table 2). For example, average streamwater DOC concentration ranged from three-fold (site D) to 15-fold (site B) higher than the minimum DOC concentration at depth in the streambed. Dissolved oxygen concentration in the hyporheic zone either declined with depth (sites D and C) or exhibited prominent heterograde profiles with minima in the 10-cm (site E) or 30-cm layer (site A and B). Conductivity followed the general solute pattern of higher streamwater values at the third-order sites E, D and C. Whereas at the second-order sites A and B, where the carbonate geology imparted a high conductivity signal to the groundwater, conductivity was lowest in the streamwater and increased with streambed depth.

Carbohydrate and BDOC concentrations were at least six- and five-fold higher, respectively, in the streamwater than the minimum porewater concentrations (Table 3). The SUVA increased steadily from the streamwater through the streambed to a maximum at 50 cm (Table 3). We found that the streamwater and 10-cm porewater had similar SUVA signatures that were significantly lower than those in deeper porewaters (ANOVA, $P < 0.001$, $n = 52$ and Tukey multiple range test). Furthermore, the SUVA signature at 10 cm correlated with the relative contribution of streamwater ($r^2 = 0.49$, $P < 0.01$, $n = 17$). In site E, bacterial abundance was $4.0 \times 10^8$ cells L$^{-1}$ in the streamwater, increased to $8.8 \times 10^8$ cells L$^{-1}$ in the 10 cm porewater, and then decreased to 3.5 and $1.1 \times 10^6$ cells L$^{-1}$ in the 30- and 50-cm porewaters, respectively.

Table 2 Streamwater and porewater DOC and DO concentrations, conductivity and temperature in White Clay Creek. For each site, depth layers having the same superscripts are not statistically different (ANOVA, Tukey HSD, $\alpha = 0.05$). Data are expressed as the mean ± SD

<table>
<thead>
<tr>
<th>Depth</th>
<th>Site A*</th>
<th>Site B†</th>
<th>Site C‡</th>
<th>Site D§</th>
<th>Site E*</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg C L$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stream</td>
<td>4.716 ± 2.021</td>
<td>2.793 ± 1.241</td>
<td>1.703 ± 0.688</td>
<td>1.682 ± 0.637</td>
<td>1.742 ± 1.005</td>
</tr>
<tr>
<td>10 cm</td>
<td>1.907 ± 0.526*</td>
<td>1.864 ± 0.992</td>
<td>1.190 ± 0.438</td>
<td>0.576 ± 0.252*</td>
<td>0.863 ± 0.323*</td>
</tr>
<tr>
<td>30 cm</td>
<td>0.853 ± 0.945†</td>
<td>0.740 ± 0.103*</td>
<td>0.521 ± 0.137</td>
<td>0.554 ± 0.227*</td>
<td>0.513 ± 0.236†</td>
</tr>
<tr>
<td>50 cm</td>
<td>0.317 ± 0.051†</td>
<td>0.565 ± 0.089*</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.441 ± 0.137*</td>
</tr>
<tr>
<td>DO (mg O$2$ L$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stream</td>
<td>9.2 ± 2.0</td>
<td>9.7 ± 2.4</td>
<td>11.8 ± 2.4</td>
<td>11.1 ± 1.5</td>
<td>11.3 ± 2.2</td>
</tr>
<tr>
<td>10 cm</td>
<td>6.1 ± 1.8*</td>
<td>6.7 ± 0.8*</td>
<td>7.4 ± 2.5</td>
<td>7.1 ± 1.6*</td>
<td>5.1 ± 1.6*</td>
</tr>
<tr>
<td>30 cm</td>
<td>5.7 ± 1.3*</td>
<td>5.7 ± 0.4‡</td>
<td>5.5 ± 1.2</td>
<td>6.6 ± 1.9*</td>
<td>6.8 ± 1.3*</td>
</tr>
<tr>
<td>50 cm</td>
<td>6.0 ± 1.5*</td>
<td>3.0 ± 0.6‡</td>
<td>n.d.</td>
<td>n.d.</td>
<td>6.8 ± 1.3*</td>
</tr>
<tr>
<td>Conductivity (μS cm$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stream</td>
<td>213 ± 30</td>
<td>259 ± 52*</td>
<td>201 ± 14</td>
<td>200 ± 15</td>
<td>193 ± 25</td>
</tr>
<tr>
<td>10 cm</td>
<td>276 ± 28</td>
<td>281 ± 40†</td>
<td>186 ± 13</td>
<td>185 ± 14*</td>
<td>131 ± 28</td>
</tr>
<tr>
<td>30 cm</td>
<td>316 ± 5*</td>
<td>302 ± 10†</td>
<td>171 ± 13</td>
<td>186 ± 16*</td>
<td>115 ± 20*</td>
</tr>
<tr>
<td>50 cm</td>
<td>316 ± 3*</td>
<td>306 ± 8†</td>
<td>n.d.</td>
<td>n.d.</td>
<td>109 ± 15*</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stream</td>
<td>17.4 ± 2.0*</td>
<td>15.5 ± 1.8*</td>
<td>13.8 ± 0.8*</td>
<td>11.1 ± 4.4</td>
<td>10.3 ± 5.1*</td>
</tr>
<tr>
<td>10 cm</td>
<td>16.2 ± 1.7*</td>
<td>15.5 ± 1.6*</td>
<td>13.8 ± 0.4*</td>
<td>11.4 ± 3.7*</td>
<td>10.6 ± 5.2†</td>
</tr>
<tr>
<td>30 cm</td>
<td>14.4 ± 0.9‡</td>
<td>15.1 ± 1.7*</td>
<td>13.8 ± 0.4*</td>
<td>12.2 ± 3.8*</td>
<td>10.8 ± 5.2‡</td>
</tr>
<tr>
<td>50 cm</td>
<td>13.6 ± 0.5‡</td>
<td>15.0 ± 1.7*</td>
<td>n.d.</td>
<td>n.d.</td>
<td>11.1 ± 5.2‡</td>
</tr>
</tbody>
</table>


n.d.: not determined.

Temporal pattern of solutes

Temporal changes in streamwater chemistry were generally transmitted to the 10-cm porewater, and often attenuated towards deeper layers, though there was considerable variability between and within sites (Figs 2 and 3). At the third-order site E, streamwater DOC concentration rose to 6.5 mg C L$^{-1}$ and conductivity declined to 118 lSc m$^{-1}$, at the onset of a February 1995 storm, while porewater DOC and conductivity remained essentially unchanged. In contrast, at the third-order site C, a November 1995 storm doubled porewater DOC concentration at 10 cm and, most dramatically, a late March 1996 storm resulted in a four-fold DOC increase and a two-fold decrease in conductivity at 10 cm in the second-order site A. Under very low baseflow (22 L s$^{-1}$) in September 1995, porewater DOC concentration and conductivity were raised compared with all other porewater data at site E and then reverted to normal values when the drought ended in November.

Dissolved oxygen concentrations were measured with less frequency than either DOC or conductivity, but a clear decline was observed in the summer at site B and the highest concentrations were observed in the third-order sites in the winter. In contrast, little seasonal variation in DO was observed at site A.

Streamwater signatures were rarely detected in the 30- and 50-cm sediment layers, indicating an apparent decoupling of deep porewater chemistry from the overlying water. At site E, 10-cm porewater correlated with streamwater chemistry for DOC concentration ($r^2 = 0.80$, slope = 0.73, $P < 0.001$, $n = 18$) and conductivity ($r^2 = 0.96$, slope = 0.75, $P < 0.001$, $n = 15$), yet no such correlations were found for 30 cm (conductivity: $r^2 = -0.09$, slope = -0.04, $P > 0.05$, $n = 15$; DOC: $r^2 = 0.001$, slope = 0.03, $P > 0.05$, $n = 19$) and 50 cm (conductivity: $r^2 = -0.09$, slope = 0.03, $P > 0.05$, $n = 14$; DOC: $r^2 = 0.17$, slope = 0.04, $P > 0.05$, $n = 18$). While porewater chemistry covaried at 30 and 50 cm, these layers were relatively stable, with average coefficients of variation (CV) of 14 ± 1% for DOC and 2.3 ± 1% for conductivity. In contrast, shallow porewater was much more variable (CV of 53% for DOC and 14% for conductivity in the 10-cm porewater). A similar pattern, though less pronounced, was observed in D.

EMMA

Conductivity and DOC concentrations in the porewaters collected from a depth of 10 cm were predominantly bracketed by the values observed in the streamwater and 30 cm at all sites except D (Fig. 4). The DOC and DO concentrations in 10-cm and 30-cm porewaters were very similar at site D, suggesting little intrusion of streamwater at this location and precluding this site from further consideration with EMMA. At sites A, B, C and E the 10-cm porewater could reasonably be considered as the mixing product of the streamwater and 30-cm porewater end-members. Based on conductivity measurements and the mixing model equation, we computed average contributions from streamwater to the 10-cm porewater (mean ± SD) of 44 ± 23% (site A), 35 ± 20% (site B), 49 ± 10% (site C) and 19 ± 11% (site E). At site E the

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**Table 3** Gross DOC aromaticity (SUVA), biodegradable dissolved organic carbon (BDOC), total dissolved saccharides in the streamwater and porewater of site E in White Clay Creek. Given are means ± SD ($n$)

<table>
<thead>
<tr>
<th>Depth</th>
<th>SUVA (L mg$^{-1}$ m$^{-1}$)</th>
<th>Total BDOC (mg C L$^{-1}$)</th>
<th>% BDOC*</th>
<th>Total dissolved saccharides (nM)</th>
<th>% Saccharides*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stream water</td>
<td>2.99 ± 0.55 (23)</td>
<td>0.679 ± 0.608† (24)</td>
<td>25 ± 5 (24)</td>
<td>3829 ± 2402 (19)</td>
<td>5.7 ± 1.7</td>
</tr>
<tr>
<td>10 cm</td>
<td>3.33 ± 0.84 (24)</td>
<td>0.148 ± 0.054 (4)</td>
<td>14.0 ± 1.8 (4)</td>
<td>123 ± 48 (6)</td>
<td>1.6 ± 0.6</td>
</tr>
<tr>
<td>30 cm</td>
<td>4.06 ± 1.23 (21)</td>
<td>0.094 ± 0.061 (4)</td>
<td>13.8 ± 3.4 (4)</td>
<td>104 ± 61 (6)</td>
<td>2.4 ± 1.3</td>
</tr>
<tr>
<td>50 cm</td>
<td>4.27 ± 1.40 (23)</td>
<td>0.072 ± 0.029 (4)</td>
<td>25.2 ± 8.4 (4)</td>
<td>177 ± 106 (6)</td>
<td>3.2 ± 1.5</td>
</tr>
</tbody>
</table>

*As the percentage of bulk DOC.
†Data from Volk, Volk & Kaplan (1997).
streamwater contribution to the 10-cm layer was as low as 1% in late summer and increased linearly with increasing discharge ($r^2 = 0.45$, $P < 0.01$, $n = 18$). No such correlation was found for A, B and C.

Plotting the EMMA derived predictions of DOC and DO concentrations in the 10-cm layer against the observed DOC and DO concentrations provided a first approximation of whether the hyporheic zone of WCC behaved as a source or sink for the respective solutes (Fig. 5). The variance explained by both end-members can be estimated from the regression of the EMMA derived predictions of DOC and DO concentrations in the 10-cm layer against the observed solute concentrations. Regression analyses between observed and predicted concentrations explained 48–91% of the variance for all sites (Table 4).

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**Fig. 2** Temporal and spatial dynamics of dissolved organic carbon, conductivity and dissolved oxygen in the second-order sites A and B in WCC. Bars represent the SD of the mean of three to six field replicates.
Fig. 3 Temporal and spatial dynamics of dissolved organic carbon, conductivity and dissolved oxygen in the third-order sites C, D and E in WCC. Bars represent the SD of the mean of three to six field replicates.
The model underestimated DOC concentration (positive residuals) at sites A, B and E, and overestimated DO concentration (negative residuals) at all sites.

We used multiple regression analysis to identify factors influencing the DO and DOC residuals from the EMMA results for site E, the most extensively characterised study site. Stream discharge and temperature and SUVA in the hyporheic zone explained 66% ($P < 0.05, n = 13$) of the variance in the DO residuals in site E, with DO residuals more negative (increased respiration) at higher flows and less negative (lower respiration) at higher temperatures. Moreover, DO residuals were positively related to the Darcy velocity (i.e. respiration was lower at high velocities, see Fig. 6) and DO residuals were significantly ($t$-test, $P < 0.01, n = 16$) more negative in autumn and winter ($-5.70 ± 1.14$ mg C L$^{-1}$) than during spring and summer ($-3.85 ± 1.65$ mg C L$^{-1}$). In contrast, DOC residuals correlated only weakly with SUVA ($r^2 = 0.35, P < 0.05$) but no relationship was found with stream discharge, temperature or Darcy velocity.

**Carbon fluxes**

The carbon fluxes calculated for the third-order reach of WCC were based on water fluxes representing the upwelling of groundwater into the hyporheic zone plus the hydraulic exchange between the surface water and the hyporheic zone (Fig. 7). The upwelling groundwater Darcy velocity of $0.27$ m day$^{-1}$ represents the average annual baseflow of $75$ L s$^{-1}$ distributed over the entire $24,000$ m$^2$ of upstream streambed (and is proportionately lower than the $0.39$ m day$^{-1}$ presented earlier for the short-term baseflow of $109$ L s$^{-1}$). The hydraulic exchange consists of the gross downwelling flux of $0.29$ m day$^{-1}$.
and an equal return flux which, added to the net upward flux from groundwater of 0.27 m day\(^{-1}\), yields a gross upwelling from the hyporheic zone to the stream of 0.56 m day\(^{-1}\). The net upwelling from the hyporheic zone to the stream therefore is the same as the upwelling of groundwater, or 0.27 m day\(^{-1}\).

Carbon fluxes based on the gross water fluxes and respective pool concentrations show that the hyporheic zone acts as a net sink for organic carbon in the amount of 0.14 g C m\(^{-2}\) day\(^{-1}\) (Fig. 7). This represents the net sum of DOC fluxes (net sink of 0.07 g C m\(^{-2}\) day\(^{-1}\)) and an estimate of POC advective delivery (0.07 g C m\(^{-2}\) d\(^{-1}\)). The DOC fluxes include downwelling from the streamwater (0.50 g C m\(^{-2}\) day\(^{-1}\)), upwelling from the groundwater (0.14 g C m\(^{-2}\) day\(^{-1}\)), and upwelling from the hyporheic zone into streamwater (0.56 g C m\(^{-2}\) day\(^{-1}\)). Within the hyporheic zone, we have partitioned the DOC into BDOC and RDOC pools, each with the same three fluxes just described for DOC. The net internal flux of BDOC reveals a net sink of 0.15 g C m\(^{-2}\) day\(^{-1}\), while net RDOC flux reveals a net source of 0.08 g C m\(^{-2}\) day\(^{-1}\). We balanced the BDOC portion of the budget by assuming respiratory BDOC consumption of 0.15 g C m\(^{-2}\) day\(^{-1}\) and balanced the RDOC budget by assuming that 0.08 g C m\(^{-2}\) day\(^{-1}\) of POC is hydrolysed to RDOC. The hyporheic respiration rate is estimated at 0.38 g C m\(^{-2}\) day\(^{-1}\) based on the EMMA-derived mean of DO residuals for Sites C and E (Table 4), of which only 0.15 g C m\(^{-2}\) day\(^{-1}\) (39\%\(\)) was accounted for by BDOC consumption. We assumed that the remaining 0.23 g C m\(^{-2}\) d\(^{-1}\) of respiratory consumption was supplied by decomposition of POC, via hydrolysis to BDOC. The total POC hydrolysis rate is therefore estimated at 0.31 g C m\(^{-2}\) day\(^{-1}\) which represents 0.12% per day (turnover time of 2.3 years) of the POC standing stock of 261 g C m\(^{-2}\) (Newbold et al., 1997; assuming POC : POM = 0.5). Advective POC delivery offsets 0.07 g C m\(^{-2}\) day\(^{-1}\), leaving the POC budget with a net depletion of 0.24 g C m\(^{-2}\) day\(^{-1}\). The DOC budget is in steady state whereas, under observed conditions, the POC is slowly depleted and must be resupplied, for example, by burial during storms. We do not have seasonal estimates of hyporheic POC standing stocks in WCC. However, we did measure an increase in hyporheic zone POC at site E (sampled between 5 and 20 cm depth) from a prestorm concentration of

<table>
<thead>
<tr>
<th>Site</th>
<th>Dissolved Organic Carbon (mg C L(^{-1}))</th>
<th>Dissolved Oxygen (mg O(_2) L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Variance explained (%)</td>
<td>Residuals*</td>
</tr>
<tr>
<td>A</td>
<td>91</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>B</td>
<td>84</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>C</td>
<td>73</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>E</td>
<td>69</td>
<td>&lt;0.0001</td>
</tr>
</tbody>
</table>

Difference among sites: *ANOVA, P < 0.01, n = 54; Tukey HSD, α = 0.05; AC, EC; †ANOVA, P < 0.001, n = 54; Tukey HSD, α = 0.05; EC; ‡ANOVA, P < 0.01, n = 33; Tukey HSD, α = 0.05; AE, BE; §ANOVA, P < 0.01, n = 33; Tukey HSD, α = 0.05; AE, BE.

Fig. 6 Relationship between DO residuals of the end-member mixing analysis and the Darcy velocity in the hyporheic zone of WCC.
745 ± 224 (n = 11 cores) to 1145 ± 178 g C m⁻² (n = 6 cores) following a late spring storm. It should also be noted that, because 0.14 g DOC m⁻² day⁻¹ enters the hyporheic zone from groundwater, and because the net consumption of DOC in the hyporheic zone is 0.07 g DOC m⁻² day⁻¹, there remains a net upward DOC transfer of 0.07 g C m⁻² day⁻¹ from the hyporheic zone to the stream. This net transfer can also be seen as the difference between the 0.56 g DOC m⁻² day⁻¹ that upwells to the streamwater from the hyporheic zone and the 0.50 g DOC m⁻² day⁻¹ that downwells from the streamwater.

The net DOC fluxes also can be estimated from the EMMA as the product of the mean residual DOC concentration (Table 4) and the gross upwelling water flux (0.56 m day⁻¹). At site E, the hyporheic zone is a net source of DOC (0.11 g C m⁻² day⁻¹), whereas at site C the hyporheic zone is a net DOC sink (0.04 g C m⁻² day⁻¹), indicating that there is considerable longitudinal heterogeneity within the hyporheic zone. Despite this variability, two results are clear: (1) the hyporheic zone is an important net consumer of BDOC and (2) POC supports a substantial portion of hyporheic respiration and contributes to DOC production.

Discussion

Hydrologic setting of the hyporheic zone

This research describes a shallow and hydrologically constrained hyporheic zone. Diminishing permeability of the streambed with depth confines the downwelling streamwater, isolates porewaters below 30 cm, and renders deep sediments under the control of groundwater. The depth of the hyporheic zone, derived from bromide releases between sites D and E, is consistent with observed vertical patterns in sediment permeability and hydraulic gradients throughout the basin. This supports the scaling-up of discharge measurements at the metre scale to reach-average fluxes and our assumption of homogeneity in hydrologic exchanges implicit when extrapolating data from the bromide releases to the entire stream. Our
estimates of upwelling based on minipiezometer data, particularly those across the 5-cm plane, were higher than upwelling Darcy velocities computed from whole stream mass balance. We are unable to explain this discrepancy. While we cannot rule out the possibility of lateral inflow to the hyporheic zone, we suspect that the discrepancy results from high spatial variability in streambed hydrodynamics. For this reason, we have used the Darcy velocity (0.27 m day\(^{-1}\)) based on whole stream mass balance that averages over the entire streamed for our summary diagram (Fig. 7).

The size of the WCC hyporheic zone (as \(A_e : A\)) is approximately at the 50th percentile of the data summarised for 60 streams (range 0.02–5.6) throughout the United States (Harvey & Wagner, 2000). Indeed, shallow hyporheic zones seem to be representative of intermediate and low gradient streams, that while they have the coarse sediments at the surface and within the benthic interface needed to conduct subsurface flow, also have low slopes and lack large roughness features which would otherwise create the pressure distributions needed to generate hydrologic exchange (Harvey & Fuller, 1998). In WCC, local bedrock and high clay content with depth below the surface sands appear to constrain the depth of the hyporheic zone.

The combination of a high ratio of surface water flow to flow through the hyporheic zone (\(Q_{\text{surface}} : Q_{\text{hyporheic}}\)), combined with low \(A_e : A\), suggest that the WCC hyporheic zone contributes little to ecosystem function (Boulton et al., 1998; Fig. 3). Our data suggest just the opposite, however, indicating that frequent fine-scale vertical exchange of streamwater and hyporheic porewater (i.e. transient storage) can be more important than the proportion of downstream discharge occurring via subsurface flowpaths. This interpretation of the importance of the hyporheic zone emphasises hydrodynamics (Harvey & Wagner, 2000) and aerobic biogeochemistry, which determine the functional contribution of the hyporheic zone to the stream ecosystem. Hydrodynamics distinguish the fine-scale vertical exchanges between the hyporheic porewater and streamwater from the nearly continuous mixing of streamwater with the porewaters in the surficial sediments or benthic zone. We cannot say how much of the oxygen depletion that we observed at a 10-cm depth actually occurred closer to the hyporheic zone/benthic zone interface. However, departures of oxygen concentration from the streamwater concentration, by definition, reflect the function of the hyporheic zone.

**Temporal and spatial patterns of hyporheic DOC**

Whereas seasonal (Kaplan, Larson & Bott, 1980; Mulholland & Hill, 1997; Butturini & Sabater, 2000) and diel (Kaplan & Bott, 1982) variations in streamwater DOC concentration have been reported from several streams, little is known about the temporal variation of hyporheic DOC. Our data reveal that fluctuations in stream discharge, rather than seasonality, controls DOC concentration within the WCC hyporheic zone. Hyporheic DOC concentration increased at high flow, a pattern we attribute to enhanced downwelling of streamwater rich in DOC during high flow. Dynamic hydrologic exchange and its impact on hyporheic DOC concentration were particularly pronounced in second-order sites underlain by Cockeysville marble and characterised by high sediment permeability. This condition is similar to that reported for Sycamore Creek, where high exchange rates resulted in a similar DOC concentration in the streamwater and the hyporheic zone (Jones et al., 1996). In contrast, deeper porewater DOC concentration in WCC was largely uncoupled from streamwater and driven by groundwater, characterised by low and seasonally invariate DOC concentration (Kaplan et al., 1980). Thus, while stream and alluvial hydrogeology affect hydrologic exchange (Morrice et al., 1997), our data suggest that hydrogeology also controls patterns of DOC within the hyporheic zone at the catchment scale. These observations contradict predictions that hyporheic zone development is low in headwaters and increases downstream (White, 1993). We tentatively attribute the lack of seasonality in WCC hyporheic DOC concentration to the combined effects of episodic scouring of the streambed during storms and the subsequent replenishment of the detrital POC pool with the year-round presence of benthic algae, mosses and macrophytes.

**EMMA of hyporheic solute dynamics**

The EMMA detected a net hyporheic DO sink, and both sources and sinks of DOC. A decrease in porewater bacterial abundance mimics the vertical
DO profile, suggesting that a decline in microbial biomass and activity is driven by the decline in organic carbon and energy resources. In estimating carbon fluxes, the EMMA provided an elegant tool to study mixing patterns between the streamwater and the streambed and to detect sources and sinks of solutes within the hyporheic zone. Considering the total throughput of organic carbon in the WCC hyporheic zone (1.04 g C m$^{-2}$ day$^{-1}$), including gross hyporheic zone DOC outflow, groundwater DOC input, advective POC delivery, and respiration of DOC generated from POC hydrolysis, we can see that the EMMA-derived net DOC fluxes from the hyporheic zone are at most 10.6% (site E) and as little as 3.8% (site C) of the total. This transfer, however, does not increase DOC concentration in the downstream direction within the third-order WCC, because it is delivered at a concentration (1.00 mg L$^{-1}$) that is less than the streamwater concentration (1.7 mg L$^{-1}$). In fact, the streamwater concentration of approximately 1.2 mg L$^{-1}$ above that of the groundwater (at an inflow of 0.27 m day$^{-1}$) translates to a net DOC production rate of 0.32 g C m$^{-2}$ day$^{-1}$, indicating that the primary source of exported DOC is the superficial sediments. In sum, the estimates of DOC sources or sinks are arguably close to 0, and suggest that DOC fluxes within the WCC hyporheic zones are essentially in balance.

The spatial pattern of DO in the hyporheic zone of WCC differs from a continual, asymptotic decline in DO anticipated for hyporheic zones experiencing a downwelling of DOC enriched surface waters (Kaplan & Newbold, 2000) and reported for a sandy-bed, north-temperate stream in northern Michigan (Hendricks, 1996). The heterograde depth profile of DO at site E suggests that a source of organic matter resides at the oxygen minimum or that the delivery of DO to the 10-cm depth is slower than the metabolic demand at that location. The production of DOC from POC buried within the hyporheic zone has been considered a major factor that supports metabolism in some streams (e.g., Pusch & Schwoerbel, 1994; Pusch, 1996). Our calculated hydrolysis rate, relative to the POC standing stock, yielded a turnover time for hyporheic POC of 2.3 years, considerably shorter than reported for many other streams (typically 10 years, Hedin, 1990). This suggests that the respiration in the confined, near-surface hyporheic zone of WCC is highly dynamic, involving the supply and degradation of labile POC, such as from recently deposited leaf litter, or autchthonous algal production. Below we present three lines of evidence that allochthonous POC entering WCC following leaf fall is the primary organic matter source fuelling respiration and generating the observed oxygen minimum.

First, EMMA revealed higher hyporheic respiration (more negative DO residuals) in autumn and winter than during spring and summer. DOC released from fresh allochthonous POC entering the stream during and after leaf fall should be sufficiently labile to support subsequent metabolism even as water temperatures declined. Second, residence time should influence POC degradation, and we observed a significant relationship between declining Darcy velocity of porewaters and increasingly negative DO residuals. As Darcy velocity through the hyporheic zone decreases, transport residence time of POC and water within the hyporheic zone should increase, and thus enhance POC transformation to DOC, subsequent metabolism, and higher respiration in the hyporheic zone. Third, the positive correlation between DOC residuals and SUVA is consistent with a terrestrially derived carbon source with a notable aromatic signal within the hyporheic zone, as aromatic moieties are higher in terrestrially derived than algal-derived DOC (McKnight & Aiken, 1998). Furthermore, benthic algae stimulate microbial activity on the streambed of WCC (Kaplan & Bott, 1989) and we suspect that algal exudates and algal POC constitute additional resources for hyporheic metabolism. Algal inputs are consistent with the lower DOC gross aromaticity in both the stream and hyporheic waters. Alternatively, upwelling groundwater enriched in aromatic moieties may dilute the aliphatic DOC pool in the shallow sediments.

Respiration in the hyporheic zone of this stream (0.38 g C m$^{-2}$ day$^{-1}$), as derived from the EMMA, is close to the 0.42 g C m$^{-2}$ day$^{-1}$ annual benthic respiration for WCC (Newbold et al., 1997) determined by chamber respirometry, and represents 41% of the annual whole stream metabolism of 0.92 g C m$^{-2}$ day$^{-1}$ estimated from diurnal oxygen changes (T. L. Bott, personal communication). As the whole stream method includes both benthic and hyporheic zone respiration, and the depth of sediment trays (5 cm) used in the chamber method would incorporate some of the hyporheic zone, the similarities of hyporheic and benthic respiration suggest that
these rates are strongly influenced by the same near-surface layers where the bulk of streambed respiration must occur. The rates of hyporheic zone respiration in WCC are lower than those values reported from large hyporheic zones, such as in the Sycamore Creek in the Sonoran Desert (1.53 g C m⁻² day⁻¹, Grimm & Fisher, 1984) and in mountain streams (Steina: 0.64 g C m⁻² day⁻¹, Pusch, 1996; Oberer Seebach: 0.88 g C m⁻² day⁻¹, Battin, 1999; Necker: 0.97–3.3 g C m⁻² day⁻¹, Naegeli & Uehlinger, 1997; Gallina Creek, lower reach: 5.14 g C m⁻² day⁻¹, Fellows et al., 2001). The WCC hyporheic respiration, however, is close to the respiration (short reach: \( R = 0.34 \text{ g C m}^{-2} \text{ day}^{-1} \)) in the shallow hyporheic zone \( (A_s : A = 0.06) \) of Rio Calaveras (Fellows et al., 2001).

As a proportion of total stream ecosystem respiration, the 41% value for WCC is identical to the contribution of the Rio Calaveras hyporheic zone (short reach: 40%, Fellows et al., 2001) and bracketed by values from Sycamore Creek (40–50%, Grimm & Fisher, 1984), the forested Buzzards Branch in the Atlantic Coastal Plain (70%, Fuss & Smock, 1996), and the prealpine Necker River (75–90, Naegeli & Uehlinger, 1997).

We have described the use of an EMMA combined with hydrologic fluxes as a direct, non-destructive approach to estimate hyporheic respiration. In other studies respiration measurements were extrapolated from recirculation chambers to the reach scale (Pusch & Schwoerbel, 1994; Pusch, 1996), or hyporheic respiration was indirectly calculated as the difference of ecosystem and benthic respiration (e.g. Grimm & Fisher, 1984; Naegeli & Uehlinger, 1997). Applying this latter approach to our average data from WCC would result in a hyporheic respiration rate of 0.50 g C m⁻² day⁻¹ which, considering the errors associated with these measurements, is reasonably close to the estimate provided by EMMA. Furthermore, the difference between both estimates is at least partly because of the overlap between measurements of benthic and hyporheic respirations mentioned above.

**Carbon fluxes**

The cycling of organic carbon within the hyporheic zone includes the export and import of DOC and POC, plus respiration. Our carbon budget calculations conclude that the WCC hyporheic zone is a sink for BDOC but a source for RDOC. In this sense, the hyporheic zone of WCC differs from those that function as net DOC sinks that metabolise DOC from downwelling streamwater (Findlay et al., 1993; Jones, Fisher & Grimm, 1995; Hendricks, 1996; Battin, 1999) or purportedly strip organic carbon from upwelling groundwater carrying high DOC loads (Wallis, Hynes & Telang, 1981; Hynes, 1983). The mass balance approach estimated a DOC sink within the hyporheic zone of 0.07 g C m⁻² day⁻¹ which is bracketed by the EMMA-derived estimates of a net hyporheic DOC source of 0.04 g C m⁻² day⁻¹ (site C) and a sink of 0.11 g C m⁻² day⁻¹ (site E). The similarity of these fluxes gives us confidence that our approach is robust.

Nevertheless, the EMMA and budgetary results do differ, and this is partly because of differences in estimates of groundwater contributions to streamwater. The budgetary approach implicitly mixes ground- and streamwater according to the independently estimated porewater fluxes. This is based on influent fluxes of 0.27 m day⁻¹ (the groundwater Darcy velocity) and 0.29 m day⁻¹ (the hydraulic exchange rate from the water column), yielding a mix of 48% groundwater and 52% streamwater, respectively. In contrast, the EMMA approach derives its mixing estimate from the conductivity of hyporheic zone porewaters. The EMMA-estimated averages for streamwater contribution to hyporheic porewater (19–49%) were somewhat lower than the 52% used for the budget calculations.

The hyporheic zone source of DOC estimated from the budget approach represents at most, a relatively small fraction (18%) of the baseflow export of DOC from the stream of 0.39 g C m⁻² day⁻¹. If this were added to the 0.11 g m⁻² day⁻¹ of RDOC supplied from groundwater, a total of 46% of the DOC export would be accounted for, leaving 54% of the baseflow export of DOC to be supplied from benthic sediments. The estimates for WCC are close to the estimates for Creeping Swamp (0.07 g C m⁻² day⁻¹ hyporheic outflow), which accounted for 13% of the total DOC export from that system (Mulholland, 1981). The hyporheic DOC outflows from the streambed in the Mediterranean Riera Major were estimated at 0.07 and 0.16 g C m⁻² day⁻¹ during growing and dormant seasons, respectively, and fall within a similar range (Butturini & Sabater, 2000). Much higher hyporheic zone DOC flux (74.4 g C m⁻² day⁻¹) was estimated for the Allequash Creek hyporheic zone, which is...
notable for its large volume, high upwelling velocity (~11.5 m day⁻¹), and extensive anaerobic zones containing buried large woody debris (Schindler & Krabbenholt, 1998).

Total BDOC entering the hyporheic zone explained 39% of the respiration in the hyporheic zone, with the residual 61% potentially accounted for by POC. In Wappinger Creek, 40% of the hyporheic respiration was attributed to DOC and 60% to POC (Findlay et al., 1993). The importance of POC to streambed respiration was also demonstrated in woodland streams at the Hubbard Brook Experimental forest (Hedin, 1990). The advective delivery of POC to the hyporheic zone in WCC slightly exceeds the baseflow export of POC. This observation underscores the importance of the hyporheic zone in particle retention and presumably the transformation to DOC via solubilization or hydrolysis, and eventual incorporation into microbial biomass, sorption to surfaces, or export to the stream water (Kaplan & Newbold, 2000).

Ecosystem implications

Despite its relatively small size, the hyporheic zone of WCC accounted for 41% of the annual whole stream respiration and clearly plays a significant role in the ecosystem dynamics of WCC. Thus, hyporheic respiration effectively adds 13% to ecosystem efficiency, processing carbon in a place that would otherwise be subject to downstream export and shortening the spiraling length of organic carbon in this system. It is therefore of considerable interest how this relatively small hyporheic zone so effectively processes organic carbon.

We have already noted that one criterion indicative of hyporheic zone significance (its share of the total downstream flow sensu Boulton et al., 1998) is quite small in WCC. However, the flow criterion fails to consider explicitly the vertical exchange of surface and subsurface waters. Harvey & Fuller (1998) proposed a conceptual model wherein the importance of the hyporheic zone depends: (1) on the rate of water exchange, as measured by the transport distance of water, \( S_w \), relative to stream length, \( L \) and (2) on the residence time \( t_s \) of water in the hyporheic zone relative to the reaction time of a substance of interest. They combined these two criteria into a reaction significance factor (RSF), which is given by

\[
\text{BDOC}_{\text{RSF}} = \frac{\lambda_{\text{BDOC}} \ t_s \ L \ S_w^{-1}}{C_0},
\]

in which \( \lambda_{\text{BDOC}} \) is the reaction rate constant. From both the ratio of water turnover length to channel length in WCC (4.36 : 4.39 km) and the approximate equality of rates of downwelling from the water column and upwelling of new water (Fig. 7), we see that water passing any given point in the stream has cycled, on average, once through the hyporheic zone. Thus by the first criterion, the hyporheic zone is potentially significant. Regarding the second criterion, reaction times for BDOC are not known, but according to our BDOC budget (Fig. 7), 65% of the BDOC that crosses the sediment/water interface and enters the hyporheic zone is consumed. This removal occurs within the average residence time of 71 min, generally agrees with our observation that nearly 100% of WCC BDOC is removed from laboratory bioreactors with a residence time of 108 min (Kaplan & Newbold, 1995). The removal of 65% in 71 min yields an estimated reaction rate, \( \lambda_{\text{BDOC}} \), of 0.015 min⁻¹. Using \( S_w = 4.36 \) km, \( L = 4.39 \) km, and \( t_s = 71 \) min, we obtain RSF = 1.07, which is substantially greater than the RSF value of 0.2 that is considered significant (Harvey & Wagner, 2000). Thus, the hyporheic zone of WCC appears to play a very significant role as a BDOC processor. However, we note that the calculated size of the hyporheic zone (\( A_{\text{hyp}} \)) is mathematically (inversely) related to the residence time, so that it is not immediately clear whether one or the other is truly the parameter of interest. We consider it more appropriate to conclude that as degradation of BDOC is a function of microbial utilisation, the roughly 6–10 cm-depth of the hyporheic zone, when supplied by oxygenated water, provides sufficient microbial habitat to degrade the majority of BDOC produced in the stream.

The degradation of BDOC in WCC accounted for only 39% of the hyporheic respiration and 16% of the whole stream respiration. Thus, while the Harvey & Fuller (1998) criteria correctly identify the significance of the hyporheic zone in BDOC processing, it is neither the exchange nor the residence time of water that accounts for the majority of carbon processing within the hyporheic zone. Rather, the role of the hyporheic zone, which involves the degradation of POC, is to trap and process POC that would otherwise be lost to downstream export. In this sense the hyporheic zone directly enhances the efficiency of the ecosystem by shortening the distance between
input and utilisation in the classical way envisaged by the spiralling concept.

In conclusion, our results demonstrate that important processes can occur even in a shallow but hydrologically dynamic hyporheic zone. Although a majority of the metabolic activity in the stream (primary productivity, respiration and net DOC production) remains associated with sediments at the benthic interface, a substantial amount of respiration is associated with hyporheic sediments. We suspect that the most active regions of the WCC hyporheic zone are constrained to the first few centimetres that constitute the interface between nutrient-enriched and nutrient-depleted zones. This is probably a general phenomenon for hyporheic zones and helps explain dramatic influences on organic matter processing at the ecosystem scale. An early description of the hyporheic zone, based on water chemistry and mixing models, was of a spatial compartment within the streambed containing less than 98% but greater than 10% stream water (Triska et al., 1989). This has been a very useful conceptual model, though our work on WCC reveals that much of the hyporheic zone dynamics are confined to a narrow zone or interface. We suggest that incorporating new information on the spatial distribution of aerobic biogeochemical processes and vertical gradients of nutrients, energy and oxygen extends the utility of the conceptual model.

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