Biogeochemistry **43:** 157–174, 1998.

The hyporheic zone as a source of dissolved organic carbon and carbon gases to a temperate forested stream

JOHN E. SCHINDLER[1,2] & DAVID P. KRABBENHOFT[1]
[1] *U.S. Geological Survey, Water Resources Division, 8505 Research Way, Middleton, WI 53562, USA;* [2] *University of Wisconsin – Madison, Center for Limnology, Trout Lake Station, 10810 County Highway N, Boulder Junction, WI 54512, USA*

Accepted 19 February 1998

Abstract. The objective of this study was to examine chemical changes in porewaters that occur over small scales (cm) as groundwater flows through the hyporheic zone and discharges to a stream in a temperate forest of northern Wisconsin. Hyporheic-zone porewaters were sampled at discrete depths of 2, 10, 15, 61, and 183 cm at three study sites in the study basin. Chemical profiles of dissolved organic carbon (DOC), CO_2, CH_4, and pH show dramatic changes between 61 cm sediment depth and the water-sediment interface. Unless discrete samples at small depth intervals are taken, these chemical profiles are not accounted for. Similar trends were observed at the three study locations, despite each site having very different hydraulic-flow regimes. Increases in DOC concentration by an order of magnitude from 61 to 15 cm depth with a corresponding decrease in pH and rapid decreases in the molecular weight of the DOC suggest that aliphatic compounds (likely organic acids) are being generated in the hyporheic zone. Estimated efflux rates of DOC, CO_2, and CH_4 to the stream are 6.2, 0.79, 0.13 moles m^2 d^{-1}, respectively, with the vast majority of these materials produced in the hyporheic zone. Very little of these materials are accounted for by sampling stream water, suggesting rapid uptake and/or volatilization.

Key words: carbon, geochemistry, groundwater, hyporheic zone, streams

Introduction

Characterization of the interactions between groundwater and surface water is of primary importance for balancing chemical budgets of watersheds. Of particular interest recently, are better evaluations of carbon transformation processes and transport processes in watersheds. Streams receive and export terrestrially fixed particulate and dissolved carbon by overland and subsurface flows. A critical area to evaluate when assessing fluxes in streams is at the groundwater/surface water interface, commonly referred to as the hyporheic zone (shallow, saturated sediments below or to the sides of the stream bottom). Most of the explicitly hyporheic literature cited in this paper define the hyporheic zone as that area in which surface water and subsurface waters mix

(Triska et al. 1989; Hendricks & White 1995; White 1993). However, due to the enormous variation in the nature of hyporheic zones from stream to stream, many investigators (e.g. White 1993; Palmer 1993) have pointed out that there is still no single definition or conceptual framework for delineating the hyporheic zone, and researchers should explicitly state their own working definitions. The hyporheic zone, defined here as the point at which distinct chemical changes in upwelling water begin to appear (61 cm), is a region of concentrated microbiological activity, in which porewaters generally have very different geochemistry than groundwater below or surface water above (Findlay et al. 1993; Fiebig & Lock 1991). Depending on hydrologic conditions, which can vary temporally and spatially, groundwater may discharge to the stream or recharge from the stream. In either case, water passing through the hyporheic zone can undergo significant chemical change over relatively small distances (cm scale). If these changes are overlooked or not examined at the proper scale, erroneous process rates at the sediment-water interface can result.

Dissolved organic carbon is involved in many biogeochemical processes that are vital to the integrity of many aquatic ecosystems. The sources and fates of DOC are important in the complexation and transport of metals and many environmental nutrients and toxins. Benthic bacteria and fungi commonly metabolize DOC and are responsible for most metabolic activity in small streams (Findlay et al. 1993). Availability of labile DOC to a stream ecosystem has been found to be the primary control on seasonal variation of heterotrophic activity of planktonic microbial populations (McKnight et al. 1993). The quantity and quality of DOC in the hyporheic zone may therefore have a major effect on the activity and abundance of the microbial communities, and thereby strongly regulate the biogeochemical changes in through-flowing water.

Most previous work has identified the hyporheic zone as a sink for DOC. Ford and Naimen (1989) estimated that 70 percent of the DOC is removed as groundwater passes through the hyporheic zone and across the sediment-water interface. Findlay et al. (1993) found a 50 percent reduction of stream-water DOC as it passed through the hyporheic zone under a gravel bar. Field and laboratory experiments have indicated that sediments with active microbial communities efficiently immobilize DOC passing through hyporheic sediments (Fiebig et al. 1990; Fiebig & Lock 1991). Other researchers, however, have determined that the hyporheic zone is a seasonally important source area of DOC for streams (Hornberger et al. 1994; Crocker & Meyer 1987).

Most studies of the hyporheic zone have focused on chemical change in stream water as it infiltrates and moves laterally through the benthic sedi-

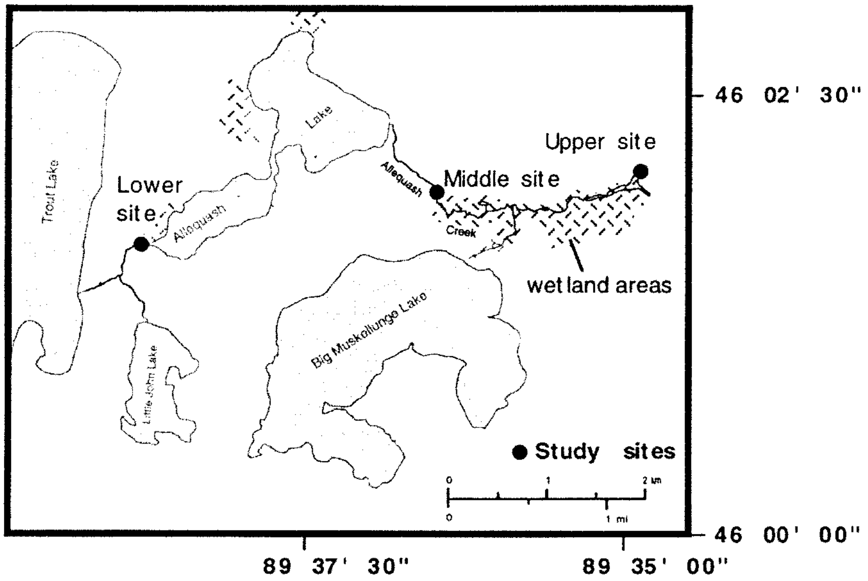

Figure 1. Location of study area in northern Wisconsin, with the specific sites of investigation indicated along Allequash Creek.

ments from pool to pool under a riffle or laterally under a point bar (Hendricks & White 1995; Findlay 1995, Harvey & Bencala 1993; Vervier et al. 1993). We examine vertical flow and chemical change by small-scale (cm) sampling of porewater as it moves upward into a stream of a northern temperate forest. In this paper we attempt to answer three questions: Is the hyporheic zone in this type of stream a source or sink of DOC and carbon gases? How does the quantity and quality of DOC vary in porewaters of the hyporheic zone in relation to depth? If the hyporheic zone is a source or a sink for DOC and carbon gases, what are the flux rates of these materials into or out of the stream?

Site description

The Allequash Creek watershed is the study site of the U.S. Geological Survey's Water, Energy, and Biogeochemical Budgets (WEBB) North Temperate Lakes project. The project focuses on the study of processes controlling the flux of water, solutes, and energy into and out of watersheds.

Allequash Creek is a first order perennial stream draining 22 km^2 in the lake district of northern Wisconsin (Figure 1). The catchment is nearly pristine, as much of the drainage is located within the Northern Highlands State Forest. Forest cover is a mix of pine and hardwoods, and the morphology of the basin ranges from steeply sloping forested hillslope (30 to 50 m relief) to riparian wetland. The soil consists of a thin humic layer (about 5–15 cm) covering approximately 50 m of sandy, glacial-outwash sediments that overlie Precambrian crystalline bedrock (Okweueze 1983). The streambed sediments are heterogeneous, consisting of alternating layers of sand, gravel, and silty sand, and occasional woody debris.

Allequash Creek is typical for a forested stream in the low-relief glacial-outwash terrain of northern Wisconsin. Average discharge during the period of this study (May through November, 1994) was 0.34 m^3 s^{-1}, and ranged from 0.24 m^3 s^{-1} to 0.42 m^3 s^{-1}. Overland runoff is negligible because of the presence of highly permeable soils. From the springs that form at the headwaters of the watershed (Figure 1), Allequash Creek flows through 4.5 km of riparian wetland before it discharges into Allequash Lake, a shallow (maximum depth 8 m) 168 hectare lake. The creek discharges from Allequash Lake at its surface outlet and terminates 1.7 km downstream at Trout Lake, the regional discharge point.

Methods

During May-November 1994, stream water and sediment pore waters in the stream bed of Allequash Creek were sampled for dissolved inorganic carbon (DIC), DOC, CO_2, CH_4, pH, temperature, alkalinity, and specific ultraviolet absorption (SUVA). Three sites were sampled (Figure 1): the headwater basin (upper site), a transect across the creek at the approximate midpoint of the streams length (middle site), and a transect approximately 100 m down stream from Allequash Lake (lower site). Field efforts for this study primarily focused on the middle site, but the upper and lower sites were each sampled once during July base flow conditions as a means of comparison. All sampling was done at least 4 days after any significant precipitation ($>$ 0.5 inch) to minimize the effects of transient hydrological conditions.

At the middle site, where the stream is about 2 m wide, porewater samples were taken in profile approximately once a month during the study period (sample depths 2, 10, 15, 61 and 183 cm) at three points: near each stream edge and in the stream center on each sampling date. The 183 cm sampling depth is considered to be beyond the hyporheic zone and representative of local groundwater; water samples from this depth will be referred to as "groundwater". The 61 cm sampling point is considered the lower limit of the hyporheic zone, defined here as the point at which distinctive geochemical changes in porewaters appear. Extensive sampling by the WEBB project for water isotopes (oxygen-18 [^{18}O] and deuterium[D]) at 55 fixed points below the stream bed and from piezometers installed on adjacent hill slopes at the

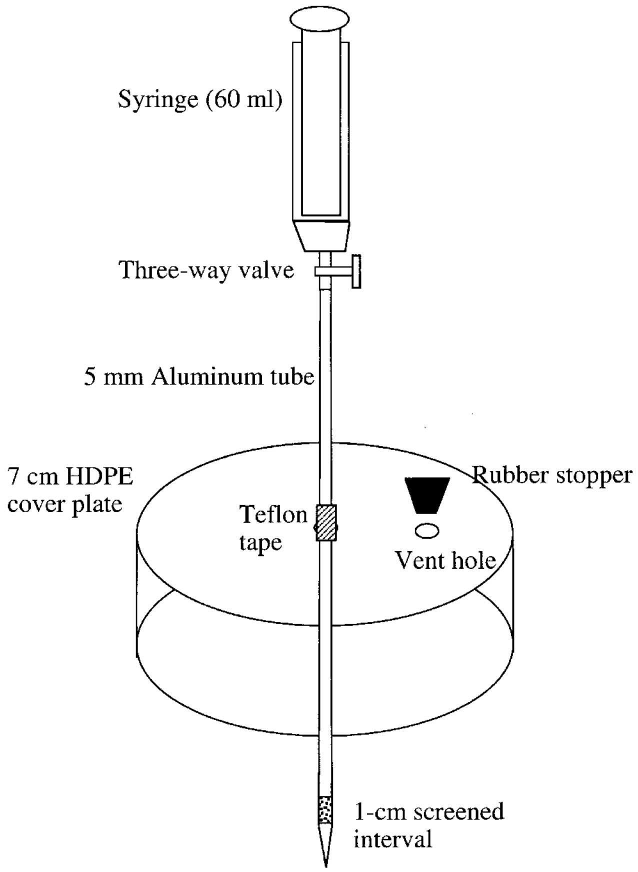

Figure 2. Diagram of a streambed sampler. The cover plate is secured in position to assure that the screen at the end of the aluminum tube is at the desired sampling depth when the cap is pressed flush against the stream bed.

middle site has revealed that groundwater discharging through the hyporheic zone at this location is from regional groundwater flow and not shorter flowpaths originating on the hillslopes (John F. Walker, U.S. Geological Survey, personal communication). Due to the longer residence time and travel distance in the regional aquifer, DOC in this water is expected to be recalcitrant compared to DOC contributed by groundwater over short flowpaths near the stream (Schiff et al. 1990).

Porewater samples were collected by vacuum extraction using a 5 mm diameter aluminum tube with a screened end and a 7 cm diameter high-density polyethylene (HDPE) cover plate (Figure 2). The cover plate was pressed against the top of the sediments to prevent migration of stream water into the sediments after the vacuum was applied. A hole drilled into the cover plate allowed stream water to escape as it is pressed flush against the stream bottom. This hole was sealed with a rubber stopper, and then a 60 ml syringe was attached to the upper end of the aluminum tube. Porewater was slowly drawn into the syringe (total volume of 50 ml extracted over two minutes). Samples were immediately filtered through sterile syringe filters (pore size 0.45 μm) directly into sample bottles, with the exception of dissolved gas and pH samples, which were not filtered.

In the spring of 1995, an additional sampling for the ^{18}O content of stream and pore waters was conducted to test the suitability of this sampler for eliminating downward leakage of stream water. Due to evaporative fractionation of ^{18}O, stream and groundwater are isotopically distinguishable, and thus we can document possible sample dilution by stream water (Krabbenhoft & Webster 1995; Krabbenhoft et al. 1996). Results for ^{18}O analysis are presented in delta (δ) notation relative to the international standard Vienna Standard Mean Ocean Water (VSMOW) in units of per mil (‰)(Baertschi 1976).

Samples from the 61 and 183 cm depths were collected from fixed mini-piezometers using a peristaltic pump and were filtered in-line using 0.45 μm filters. After filtration, samples were placed in a cooler and kept dark and chilled until analysis. Samples were analyzed for pH immediately upon return from the field. Headspace equilibration of CO_2 and CH_4 samples was performed in the field using equal volumes of sample and ambient air and vigorously shaking in a 60 ml syringe for one minute (Kratz et al. 1995). Headspace gas was drawn off into a 20 ml nylon syringe for transport to the lab. Samples were also taken of the ambient air used for the headspace equilibrations. Carbon dioxide and methane were analyzed by gas chromatography with a flame-ionization detector and an in-line methanizer. Concentrations of the CO_2 and CH_4 in water were calculated using gas partial pressures and Henry's Law constant with corrections for temperature. Analysis of DIC and DOC were performed within one week of collection using a OI Corp. model 700 carbon analyzer that employs acidification and persulfate ultraviolet oxidation.

SUVA was measured on samples at 280 nm using a 5 cm analysis cell. Measurements of SUVA have been shown to be an effective estimator of gross aromaticity and weight averaged molecular weight (M_W) of DOC (Chin et al. 1994). Here, we use SUVA values to estimate the relative amount of aromatic and aliphatic compounds of the total DOC in water samples. Greater relative absorptivity of a sample corresponds to a greater amount of aromatic compounds and M_W of the DOC. We estimated M_W of the DOC by using the relation of Chin et al. (1994):

$$M_W = (3.99e + 490)/1000 \text{ (k Daltons)}.$$

Epsilon (e) is the measured value of SUVA normalized to the concentration of DOC (mole L^{-1}) in that sample and the measurement cell path length:

$$\varepsilon = \frac{SUVA_{(280nm)}}{DOC{*}5}$$

The direction of groundwater flow at each site was established by measuring hydraulic head in mini-piezometers (Lee & Cherry 1978) installed in the streambed and in the riparian wetland adjacent to the stream. The WEBB project has installed over 150 mini-piezometers at the upper, middle and lower study sites along Allequash Creek. To estimate the vertical advective velocity of water passing through the hyporheic zone at the middle site we used Darcy's Law:

$$\mathrm{v} = -\mathrm{K}(\mathrm{h}/\mathrm{l})$$

Where v is the advective velocity of water discharging into the stream, –K is the hydraulic conductivity estimated at 0.1 cm/s for fine sand (Domenico & Schwartz 1990), h the difference in hydraulic head between the sediment water interface and the 61 cm sampling point, and l the distance between the sediment water interface and the 61 cm sampling point (61 cm).

To quantify the vertical transport velocity of groundwater (advection + dispersion) discharging to the stream at the middle site, a dye injection tracer test was performed along with a measurement of hydraulic head during April of 1995. A small amount (50 ml) of Rhodamine WT dye was injected into a mini-piezometer (installed in the middle of the stream bed) with a 1 cm screen centered at 61 cm depth, and the time required for visual discharge of the dye out of the stream bed was recorded.

Result and discussion

Porewater Chemical Profiles from the Middle Site. As presented later, all three of our sampling sites have groundwater upwelling rapidly into the stream, eliminating or minimizing any mixing with streamwater. Even though the measured hydraulic head in all 55 piezometers at the middle site indicate upward groundwater flow, the shallow depth of sampling and *in situ* suction method of sampling brings into question whether sample dilution by downward leakage of stream water might occur. Porewater samples taken at the mid-stream site in June of 1995 at the 2, 10, and 15 cm depths as well as stream water had δ^{18}O values (mean ± SE of 0.1 per mil) of –11.4, –11.5, –11.2, and –9.2‰, respectively. The porewater results were very similar to previous samplings of deeper groundwater (groundwater mean –11.51‰,

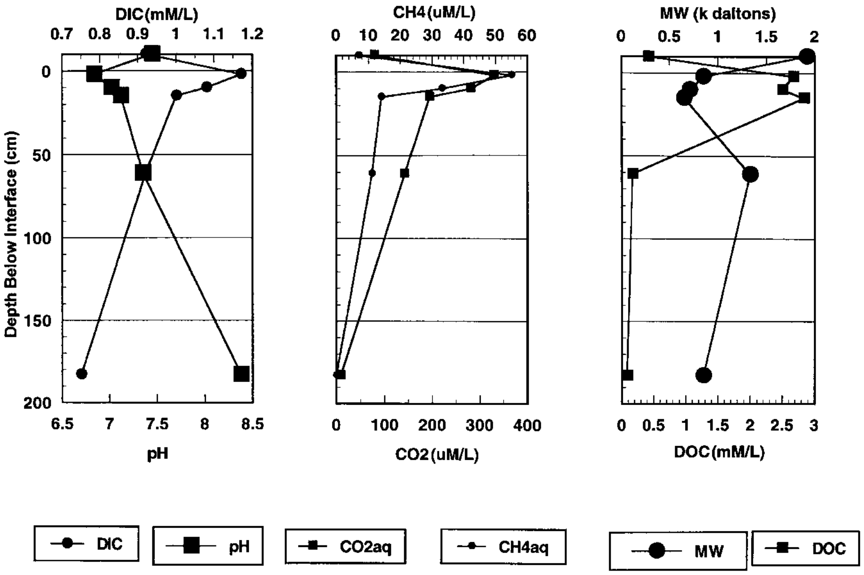

Figure 3. Relationship between depth and carbon-related chemical parameters in the hyporheic zone at the middle site. The zero cm depth marks the sediment-water interface, stream samples are plotted at –10 cm. Connections of CO_2, CH_4, pH, DOC, and weight averaged molecular weight (M_W) are averages of measurements made at the same depth at the three sampling points across the width of the stream. Analytical errors for each constituent are less than or equal to the symbol size plotted.

with a range of –11.37 to –11.72‰, n = 7) and the stream water results were similar to earlier stream water O^{18} values (mean 9.46‰, with a range of –9.08 to –10.51, n = 21) at this site, and demonstrate the effectiveness of our sampler to prevent leakage. Recent studies that have that not employed a cover plate when collecting porewater samples by suction have demonstrated substantial sample dilution by surface water (Krabbenhoft & Webster 1995).

The chemistry of the groundwater flowing through the hyporheic zone and discharging to the stream at the middle site exhibited dramatic changes in most measured parameters (Figure 3). No clear temporal trends were observed, and the overall shape of this profile did not change throughout the study period. Leaf fall occurred during early October, yet our November sampling did not show any significant change in the individually measured constituents. Chemical concentrations at the 61 and 183 cm depths were fairly constant during the study period, while at the shallower depths (< 15 cm) more variation was observed, most likely due to the extreme heterogeneity of the streambed sediments (Figure 6). Samples taken on the same date from the same depth taken a few cm apart above 15 cm had more variation than was seen between sampling dates. Therefore parameters presented are averages

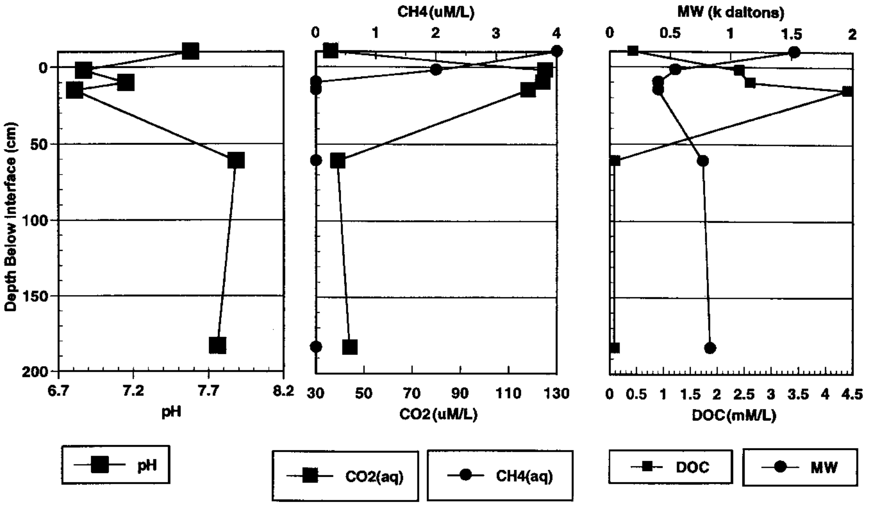

Figure 4. Relationship between depth and carbon-related chemical parameters at the upper site. The zero cm depth marks the sediment-water interface, stream samples are plotted at –10 cm. Analytical errors for each constituent are less than or equal to the symbol size plotted.

of measurements made at the same depth across the stream channel. Similar profiles in all of these measured parameters have also been observed in the groundwater discharge zone of Pallette Lake (about 4 km north of the study site) during all seasons. Earlier studies of microbial populations in the benthic sediments of the Red Deer River in Alberta (Baker et al. 1992; Baker 1986) have shown that microbial activity is fairly constant throughout the year.

DIC showed a rapid increase in concentration over the last 61 cm, and can almost be completely attributed to increases in dissolved $CO_2(H_2CO_3)$. Alkalinity in the stream and in porewater was essentially constant (within analytical uncertainty), whereas pH showed a mirror-image profile of DIC, declining by an average of 1.3 units at the middle site for each sampling period (Figure 3).

The middle site showed the clearest and most consistent trends in CO_2 and CH_4 profiles (Figure 3). Concentrations of CO_2 increased from the groundwater source average of 12 μmole L^{-1} to 330 μmole L^{-1} at the 2 cm depth (with the most rapid rate of increase occurring between 15 and 2 cm). Methane showed a very similar trend, starting below the detection limit in the groundwater, but increasing to an average concentration of 11 μmole L^{-1} at the 61 cm depth, and 55 μmole L^{-1} at 2 cm. Carbon dioxide and CH_4 both exhibited a near linear, step function from 183 to 15 cm, and then from 15 to 2 cm. When compared to the considerable buildup of these two gases in porewaters, the stream CO_2 and CH_4 concentrations are quite similar to

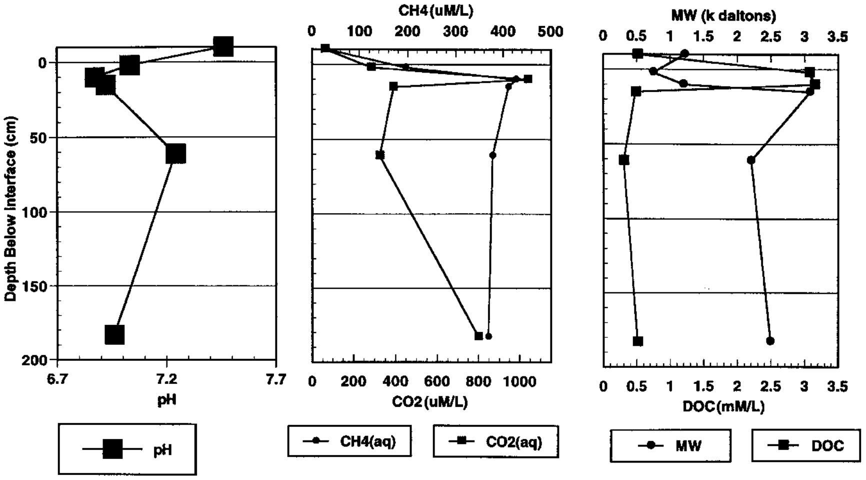

Figure 5. Relationship between depth and carbon-related chemical parameters at the lower site. All values are from the sampling location near the southern edge of the stream where groundwater discharge occurs. The zero cm depth marks the sediment-water interface, stream samples are plotted at –10 cm. Analytical errors for each constituent are less than or equal to the symbol size plotted.

groundwater (average values of 79 μmole L^{-1} [1462 ppmv] and 7 μmole L^{-1} [314 ppmv], respectively).

Atmospheric CO_2 averaged 371 ppmv, and atmospheric CH_4 was always $<$ 2 ppmv. The stream was therefore supersaturated in CO_2 and CH_4 with respect to the atmosphere, but had a much lower concentration than the hyporheic zone just 2 cm below the sediment-water interface. The apparent loss of CO_2 and CH_4 as the hyporheic porewater discharge to the stream is most likely due to biological uptake, oxidation, and evasion facilitated by the turbulent flow of the stream.

Groundwater DOC concentrations in the Allequash Creek watershed are generally less than 1 μmole L^{-1}. At all our sites, however, DOC levels increased by approximately one order of magnitude as groundwater discharges through the hyporheic zone (Figures 3 and 4); these high concentrations are in sharp contrast to the less than 1 μmole L^{-1} levels observed in the stream.

Porewater Chemical Profiles from the Upper and Lower Sites. Measurements of hydraulic head and results from ^{18}O sampling at the upper and lower sites reveal contrasting hydrologic regimes (Walker et al. 1993). At the upper site, groundwater is recharged by infiltration of precipitation on upland areas, and discharges as springs at the base of hillslopes and as subsurface flows to the pond that marks the originating point of Allequash Creek. The result-

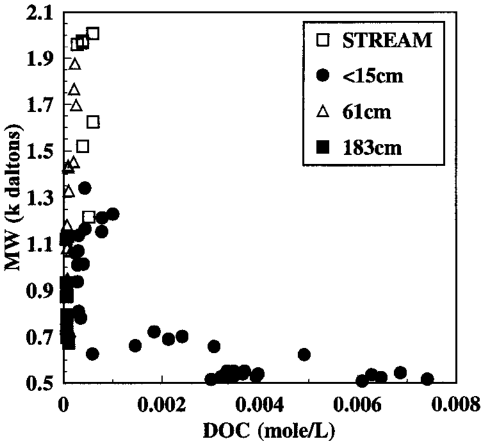

Figure 6. Relationship between DOC and M_W of samples taken at various depths in the hyporheic zone at the middle site. Higher M_W values indicate a greater aromatic fraction of the DOC in the sample. Analytical errors for each constituent are less than or equal to the symbol size plotted.

ing hydraulic gradient is always upward (i.e. groundwater discharge) through the hyporheic zone. The hydrology of the lower site is spatially and temporally more complicated due to its location lower in the catchment basin and the resulting longer flowpaths for groundwater discharging into the stream. Stream water flows downward and recharges the aquifer at the north edge of the stream; in the mid-stream area, the hydraulic gradient can either be upward or downward depending on the season, and upward groundwater flow into the stream has consistently been observed near the south edge of the stream. Therefore, to simplify comparison of data among the three sites, we have only used our sampling results from the south edge of the lower site where groundwater flows upward into the stream as it does at the other two sites.

Porewater pH profiles at both the upper and lower sites showed modest increases between 183 and 61 cm depth, decreased rapidly in the upper hyporheic zone, but were always about 0.5 pH units less than the observed stream values (figures 4 and 5). Both the upper and lower sites showed stable DOC concentrations in groundwater (between 183 and 61 cm depth), and about an order of magnitude increase in DOC in the hyporheic zone. At this point, however, the DOC profiles of these two sites diverge. Rapid decreases in DOC were evident at the upper site between 15 and 2 cm, whereas concentrations remained elevated in the shallow hyporheic zone at the other two sites. Like the middle site, the average stream DOC values (about 0.5 μmole L^{-1}) were substantially less than porewater concentrations at these two sites.

Profiles of CO_2 and CH_4 at the upper and lower sites differ in terms of both the shapes of the profiles and the observed concentrations. Hyporheic zone concentrations of CO_2 and CH_4 at the upper site were significantly less than the other sites, which is probably controlled by rapid groundwater discharge rates and elevated dissolved oxygen concentrations in groundwater at the upper site. The surface water at the upper site was supersaturated with CO_2 with respect to the atmosphere having concentrations of 1002 ppmv (36 μmole L $^{-1}$ aq) vs the measured atmospheric norm of 371 ppmv. The overall shape of the CO_2 profile is similar to both the other sites, however. Methane concentrations in the pond at the upper site is the only location where we observed higher concentrations in surface water (101 ppmv vs. $<$ 2 ppmv atmospheric) than porewater. This is probably a result of the generally quiescent conditions of the pond and the accumulation of organic sediments in the mid-region of the pond. Hyporheic-zone concentrations of CO_2 and CH_4 at the lower site (1426 ppmv and 481 ppmv, respectively) were similar to the middle site. In stark contrast, however, there was little or no apparent buildup over groundwater concentrations of either gas. This is consistent with the observation that groundwater is generally anoxic at the lower site.

Changes in the Quantity and Quality of DOC in the Hyporheic Zone. Given the significant differences in the physical and hydrological settings of the three study sites, the similarity of the DOC porewater profiles is somewhat surprising. At each site, groundwater DOC concentrations appeared stable as groundwater upwells through the bed, but a 7 to 50 fold increase in DOC occurred as groundwater enters the hyporheic zone. For all three sites the rise in DOC concentration, however, was coincident with rapidly decreasing M_W values over the same depth intervals (Figures 3, 4, and 5), indicating the “new” DOC produced in the hyporheic zone was largely comprised of aliphatic (lower molecular weight) compounds, and/or the less aliphatic fractions were being immobilized concurrent with the increase in the concentration of DOC. Previous studies of DOC transport through benthic sediments showed a preference for immobilization of high molecular weight DOC by heterotrophic bacteria in the hyporheic zone, while low molecular weight DOC was largely unaffected (Fiebig & Lock 1991). Adsorption to mineral grains or particulate organic carbon may also immobilize some high molecular weight DOC (Lock et al. 1984).

For each sampling period, profiles taken in the stream center and at each stream edge at the middle site showed a consistent buildup of DOC in the shallow hyporheic zone. A plot of M_W versus DOC for all stream, groundwater, and hyporheic samples taken at the middle site (Figure 6) segregates the samples from the hyporheic zone as having a more concentrated aqueous

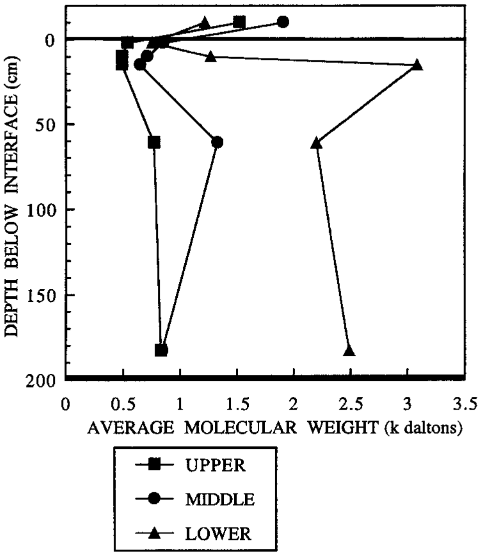

Figure 7. Calculated profiles of M_W of DOC in porewater and stream water from all three study sites. The zero cm depth marks the sediment-water interface, stream samples are plotted at –10 cm. Analytical errors for each constituent are less than or equal to the symbol size plotted.

carbon pool that was more aliphatic (lower M_W) in character. The considerable range in hyporheic-zone DOC buildup (Figure 6) is likely attributable to heterogeneities in streambed organic matter content, which have been shown to have a controlling influence on porewater DOC levels (Crocker & Meyer 1987). The clustering of data points from stream samples along the top left hand side of this figure indicates a less concentrated aqueous carbon pool that is probably more recalcitrant. However, the more aliphatic (lower M_W) DOC produced in the hyporheic zone would be more bioavailable to benthic heterotrophs and may therefore provide a significant trophic base for stream bioenergetics.

Calculated average molecular weights (M_W) of DOC from the three sites are shown in Figure 7. Groundwater at the lower site is more aromatic than the other sites, probably due to the longer groundwater flowpaths that would likely be discharging at this low point in the watershed. These longer flowpaths would result in a longer residence time in the groundwater aquifer, resulting in a “maturation” of the DOC as the more aliphatic DOC is preferentially consumed resulting in the remaining DOC having a more recalcitrant nature. Even though the source groundwater at the lower site had a higher M_W, the resulting shallow porewaters were similar in M_W to the other sites. The clustering of lower-site porewater M_W data with the other sites results from a 7-fold increase in DOC in the hyporheic zone, the bulk of which must have a similarly low M_W. Similarities among our hyporheic zone observations at all three sites suggests the same succession of DOC-controlling processes were operating along the entire stream length as groundwater discharged vertically to the stream.

Calculated Fluxes from the Hyporheic Zone to Allequash Creek. The hydraulic head differential (h) between the 61 cm sampling depth at the center sampling location and the stream surface at the middle site was measured on each sampling date and ranged from 8.1 cm to 6.2 cm during our study period, resulting in an estimated Darcy vertical velocity of 1.33×10^{-2} cm s^{-1} to 1.02×10^{-2} cm s^{-1}, respectively. On the date of the dye test, the head differential h was 7.5 cm, resulting in a Darcy velocity estimate of 1.23×10^{-2} cm s^{-1}. Dye injected at the 61 cm sampling point required 98 minutes to reach the sediment water interface, which gives an estimate of the groundwater flow velocity of 1.04×10^{-2} cm s^{-1}. While we recognize that diffusion and hydrodynamic dispersion result in an early arrival of the dye front (Freeze & Cherry 1979), the short travel distance of this test and the relatively high rates of flow should minimize these effects. Due to the somewhat greater than normal rainfall at the site prior to the dye test, our measured value may represent an upper bound on the vertical advective velocity. Using this measurement of flow velocity to the stream at the middle site, a low-range porosity of 26% for fine sand (Davis 1969), a 2 cm depth hyporheic porewater DOC average of 0.00267 mole L^{-1}, and ignoring biological uptake of DOC at the sediment-water interface itself, we estimate the efflux of DOC to the stream from a one meter wide cross-section of the streambed (stream width about 2 m) to be 6.2 moles m^2 d^{-1}. Using this same method, we calculate a discharge rate of CO_2 (330 μmole L^{-1} average at 2 cm) of 0.79 moles m^2 d^{-1}, and a delivery of 0.13 moles m^2 $d^{-1}$of CH_4(55 μmole L^{-1} average at 2 cm) to the sediment water interface at the middle site. Considering that the vast majority of this carbon load is added to groundwater as it passes through the hyporheic zone (Figure 3), these flux rates can also be considered hyporheic-zone production rates of dissolved carbon species.

To test whether the estimated groundwater delivery rates of DOC, CO_2, and CH_4 are reasonable, average daily fluxes of the carbon species in streamflow past the middle site were calculated. By multiplying the average streamflow (1.21×10^7 L d^{-1}) by the average stream concentration of DOC (0.00042 mole L^{-1}), we estimate 5,082 moles of DOC flow past the middle site daily. This daily flux is about 400 times greater than the groundwater flux of DOC from a 1 meter wide cross-section of the streambed. If we further calculate the length of the streambed necessary to account for all the DOC in the stream (assuming every square meter of the streambed has the same input rate, and assuming a uniform 2 meter wide streambed) a 0.4 km length of streambed would be necessary to account for the observed mass flux of DOC at the middle site, if it is derived from groundwater. The actual length of the stream from the middle site to the headwater basin is about 3.5 km, therefore assuming the observed flux of DOC from the streambed into the stream was constant between the middle and upper sites the stream DOC concentration would be approximately 0.0037 mole L^{-1} , more than eight times greater than what is actually observed. This indicates the more aliphatic DOC contributed by the hyporheic zone is probably being utilized by bacteria and algae at the sediment water interface, or in the stream itself, and thus, is not measurable in the stream. In addition, the discharge rate of groundwater to the stream is likely less in the area immediately upstream of the middle site, where substantial peat accumulations exist that would serve to retard the upward flow of water through the hyporheic and result in reduced delivery of carbon species to the stream. Similar estimated streamflow fluxes of CO_2 and CH_4past the middle site are 955 and 85 moles d^{-1}, respectively. Using the method outlined above, 0.6 km length of streambed would be required to account for all of the mass of CO_2, and 0.3 km to account for all the mass of CH_4 that flows past the middle site. These dissolved gases are continuously supersaturated with respect to the atmosphere and thus volatilizing from the stream, and/or being oxidized (CH_4) and biologically assimilated. Such a large disparity between estimated (0.6 and 0.3 km) and actual (3.5 km) stream lengths necessary to generate the observed stream mass fluxes of DOC, CO_2 and CH_4 emphasizes the labile nature of these dissolved species, and rapid rate by which stream ecosystems like Allequash Creek are capable of processing these important aqueous constituents.

Glacial outwash deposits in this region are dominated by quartz with minor amounts of other silicate minerals with a specific gravity of about 2.6 g cm^{-3} (Kenoyer 1992), annual sedimentation of organic debris and autochthonous carbon generation would have to account for about 2% (by weight) of the total mass of the hyporheic zone to support the observed DOC production and flux at this site. Given the observed high density of woody debris within the sediments, this small amount of carbon necessary to support the observed DOC production seems reasonable.

Summary

The hyporheic zone is an important interface hydrologically, chemically, and biologically for streams. The methods used to carry out an investigation of this biogeochemical environment, and the scale at which samples are collected can dictate the conclusions of the study. Based on our observations at Allequash Creek, we contend that investigations of the hyporheic zone in northern temperate streams, and likely elsewhere, require that investigators focus on the last few centimeters beneath the sediment/water interface. Using a device capable of sampling at the cm scale, we observed major changes in pH, DOC, DIC, CO_2 and CH_4 concentrations in groundwater as it flows into the hyporheic zone and then discharges to the stream. Between the 61 and 15 cm depth (10 cm at the lower site) we observed a large net production of DOC at all sites, but a net consumption of DOC in the last few centimeters below the sediment-water interface. Since we observed this net reduction of DOC across the sediment-water interface, the interface itself may be a DOC sink for discharging or recharging water.

The new DOC produced in the hyporheic zone is very different in character than ambient groundwater, as evidenced by substantial declines in M_W of the DOC-rich porewaters. This observation argues that the DOC enrichment processes in the hyporheic zone produce relatively simple, aliphatic carbon compounds (e.g. organic acids). These simple carbon compounds are a primary energy source for stream biota. Our simplified model would hold that the original source of the new DOC is likely organic material, such as stream deposited detritus that has been covered with sediments before it could decompose, along with autochthonous organic material generated by photosynthetic organisms. Aerobic and anaerobic heterotrophs oxidize some of this substrate and respire CO_2 and CH_4, respectively. Not all of this material is oxidized and partially oxidized compounds such as organic acids are formed and excreted. Under this model, CO_2, CH_4, and DIC should all increase as the sediment-water interface is approached, and pH should decrease, which is in fact what we observed. Although some of the CO_2 and CH_4 is most likely utilized by autotrophic bacteria and fungi at the sediment-water interface, the velocity of the water moving through the thin layer of benthic autotrophs would tend to lessen complete uptake of the carbon gases. Aliphatic/labile DOC, while being an active agent in only a small part of the basin spatially, is an important pathway for the flux of carbon and energy between primary and secondary production in stream sediments and subsequent availability to benthic organisms, or eventual removal from the watershed through release to the atmosphere, sequestration in sediments, or riverine transport out of the study area.

Our results indicate that shallow stream sediments with a renewable organic carbon source provide a source of DOC and carbon gases to the stream. Observed increases in DOC in the shallow hyporheic zone concurrent with a decrease in its average molecular weight suggests that the shallow hyporheic zone at this site is an area of intense biogeochemical change for through-flowing water. This transformation process thereby makes available many different carbon species that provide a significant trophic base for lotic bioenergetics.

Acknowledgements

The authors are grateful to Dave Niedermeier for help with field sampling, and Tim Kratz, Rob Striegl, and Jim Krohelski for critical comment on the manuscript.

References

Baertschi P (1976) Absolute ^{18}O content of standard mean ocean water. Earth Plante. Sci. Lett. 31: 341–344

Baker BL, Ladd TI, Telang SA, Costerton JW & Hodgson GW (1982) The Biogeochemistry of Streams: The Red Deer River. Alberta Research Management Division Report, RMD 82-154, 221 pp

Baker JH (1986) Relationship between microbial activity of stream sediments determined by the different methods, and abiotic variables. Microb. Ecol. 12: 193–203

Chin, Y, Aiken G & O'Loughlin E (1994) Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. Env. Sci. Technol. 28: 1853–1858

Crocker MT & Meyer JL (1987) Interstitial dissolved organic carbon in sediments of a southern appalachian headwater stream. J.N. Am. Benthol. Soc. 6: 159–167

Davis SN (1969) Porosity and Permeability of Natural Materials. Flow through Porous Materials. ed. R.J.M. DeWiest. Academic Press, New York, pp 54–89

Findlay S, Strayer D, Goumbala C & Gould K (1993) Metabolism of streamwater dissolved organic carbon in the shallow hyporheic zone. Limnology and Oceanography 38: 1493–1499

Findlay S (1995) Importance of surface-subsurface exchange in stream ecosystems: The hyporheic zone. Limnology and Oceanography 40: 159–164

Fiebig DM, Lock MA & Neal C (1990) Soil water in the Riparian zone as a source of carbon for a headwater stream. Journal of Hydrology 116: 217–237

Fiebig DM & Lock MA (1991) Immobilization of dissolved organic matter from groundwater discharging through the stream bed. Freshwater Biology 26: 45–55

Ford TE & Naiman RJ (1989) Groundwater-surface water relationships in Boreal forest watersheds: dissolved organic carbon and inorganic nutrient Dynamics. Can. J. Fish. Aquat. Sci. 46: 41–49

Freeze RA & Cherry JA (1979) Groundwater. Prentice-Hall, Inc.

Harvey JW & Bencala KE (1993) The effect of streambed topography on surface-subsurface water exchange in mountain catchments. Water Resources Research 29: 89–98

Hornberger GM, Bencala KE & McKnight DM (1994) Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. Biogeochemistry 25: 147–165

Kenoyer GJ & CJ Bowser (1992) Groundwater chemical evolution in a sandy silicate aquifer in northern Wisconsin, II Reaction modeling. Water Resources Research 28: 591–600

Krabbenhoft DP & KE Webster (1995) Transient hydrological controls on the chemistry of a seepage lake. Water Resources Research 31: 2295–2305

Krabbenhoft DP, Benoit JM, Gilmour C, Babiarz CL, Hurley JP & Andren AW (1997) Contributions of methylmercury from Littoral zone sediments to a Northern Wisconsin seepage lake. Can. J. Fish. Aquat. Sci. (in press)

Kratz TK, Schindler JE, Hope D, Riera JL & Bowser CJ (1996) Average annual carbon dioxide concentrations in eight neighboring lakes in Northern Wisconsin, USA. Verh. Internat. Verein. Limnol. (in press)

Lee DR & Cherry JA (1978) A field exercise on groundwater flow using seepage meters and mini-piezometers. J. Geol. Educ. 27: 6–10

Lock MA, Wallace RR, Costerton JW, Ventullo RM & Charlton SE (1984) River epilithon: Toward a structrual-functional model. Oikos 42: 10–22

McKnight DM, Smith RL, Harnish RA, Miller CL & Bencala KE (1993) Seasonal relationships between planktonic microorganisms and dissolved organic material in an alpine stream. Biogeochemistry 21: 39–59

Okweueze E (1983) Geophysical investigations of the bedrock and the groundwater-lake flow system in the Trout Lake Region of Vilas County, Northern Wisconsin. Ph.D. Thesis, University of Wisconsin

Palmer MA (1993) Experimentation in the hyporheic zone: Challenges and prospectus. J.N. Am. Benthol. Soc. 12(1): 84–93

Schiff SL, Aravena R, Trumbore SE & Dillon PJ (1990) Dissolved organic carbon cycling in forested watersheds: A carbon isotope approach. Water Resources Research 26: 2949–2957

Triska FJ, Kennedy VC, Avanzino RJ, Zellweger GW & Bencala KE (1989) Retention and transport of nutrients in a third-order stream in Northwestern California: Hyporheic processes. Ecology 70(6): 1893–1905

Vervier P, Dobson M & Pinay G (1993) Role of interaction zones between surface and groundwaters in DOC transport and processing: Considerations for river restoration. Freshwater Biology 29: 275–284

Walker JF, Krabbenhoft DP, Kendall C & Bullen TD (1993) Variability of isotopic composition and major-ion chemistry in near-stream groundwater and implications for evolution of streamflow chemistry in a small forested watershed, EOS, Transactions, American Geophysical Union, 1994 Spring Meeting, Program and Abstracts, May 23-27, Baltimore, MD, p. 135

White DS (1993) Perspectives on defining and delineating hyporheic zones. J.N. Am.Benthol. Soc. 12(1): 61–69