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# Variability in removal of dissolved organic carbon in hyporheic sediments

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*Abstract.* Dissolved organic carbon (DOC) is consumed by microbial metabolism as streamwater perfuses through a lateral gravel bar of the East Branch of the Wappinger Creek. The rate of DOC removal was estimated from the decline in DOC and travel time through the bar. Variability in DOC removal together with potential regulatory factors was determined for 14 dates spanning more than a 2-y period. DOC removal was not correlated with temperature, availability of oxygen, or residence time within hyporheic sediments. Hyporheic DOC could be predicted ($r^2 = 0.68$) from streamwater DOC concentrations, with a surprisingly constant 57% (±9% [1 SD]) removal of DOC. This pattern suggests an initial concentration-dependent adsorption of DOC onto surfaces. This mechanism allows for efficient retention of DOC within hyporheic sediments even under conditions (low temperature, high interstitial velocity) that might be expected to minimize biotic consumption of DOC.

*Key words:* dissolved organic carbon, hyporheic, sediment, microbes.

Since 1983 when Hynes pleaded for incorporation of groundwater ecology into stream ecology, there has been a tremendous proliferation of studies of invertebrates (Williams 1989), water chemistry (Triska et al. 1989) and microbial ecology (Hendricks 1992) of hyporheic zones. It is now clear that for many stream ecosystems, processes occurring in shallow subsurface sediments have a major impact on the biological, physical and chemical characteristics of a stream. Not surprisingly, most of these studies have been conducted in places, and at times, where the contribution of hyporheic processes to stream ecosystem budgets was expected to be high. No systematic assessment of the variability in importance of hyporheic metabolism has been attempted aside from general expectations based on stream morphology and hydrology (Boulton 1993, Findlay 1995). In this paper we attempt to predict variability in one hyporheic process, consumption of dissolved organic carbon (DOC), with the intent of providing a broader context for site-specific or single-time studies.

Variability in DOC has been shown to affect hyporheic respiration (Pusch and Schwoerbel 1994) and sediment bacterial activity (Findlay et al. 1993). Subsurface oxygen consumption can affect the ratio of production to respiration in stream systems and provide anoxic sites for denitrification (Duff and Triska 1990), methanogenesis (Dahm et al. 1991) or other $O_2$-sensitive processes such as nitrification (Jones et al. 1994).

Biotic consumption of organic carbon and oxygen within sediments may be affected by a wide variety of factors, including temperature, residence times, or carbon quality. Temperature is widely regarded as a master environmental control on biotic processes (White et al. 1991, Shiah and Ducklow 1994) with a general expectation of increases in DOC and $O_2$ consumption rates with warmer temperatures. Second, oxygen availability can limit organic matter degradation if alternative electron acceptors are not available and energetically feasible for coupling with organic carbon oxidation. Carbon consumption may be limited by the availability of oxygen and other electron acceptors while $O_2$ consumption may be affected by the availability of organic carbon. Lastly, the quality of DOC clearly varies among streams and temporally within single stream systems (Kaplan and Bott 1989, Kaplan and Newbold 1993), possibly leading to variability in rates of DOC uptake and oxygen depletion.

In this paper, we use a 2-y record of DOC concentrations within a gravel bar to assess variability in rates of DOC and $O_2$ removal and explore possible mechanisms affecting these rates. Previous work at this site showed that decreases in concentration of DOC as water moves through a lateral gravel bar are due to microbial uptake (Findlay et al. 1993).

## Study Site

The East Branch of the Wappinger Creek is a 3rd-order, hardwater, high-nutrient stream on the property of the Institute of Ecosystem Studies, Millbrook, New York. Annual average discharge

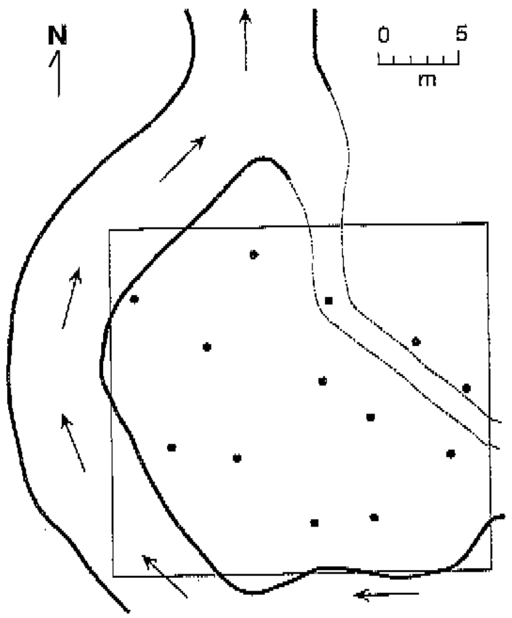

FIG. 1. Map of gravel bar in the East Branch of the Wappinger Creek showing the stream channel and locations of 13 sampling wells. The box outlined shows the area covered by the contour maps in Fig. 2.

is approximately 1 $m^3/s$, nitrate averages 3–4 mg $NO_3/L$, phosphate 100 μg $PO_4/L$. Streambed sediments in this reach range from cobbles to fine sand. The surrounding topography is very flat, consisting of glacial till. There are no hillslopes within ~400 m of the gravel-bar study site.

A hyporheic flowpath through a lateral gravel bar (Fig. 1) in the East Branch of the Wappinger Creek was sampled with a network of 13 wells over a period of more than 2 y (June 1992–November 1994). Wells were steel wellpoints, lined with PVC and screened for the lowest 20 cm. Water samples were collected approximately every 6 wk, excluding those months (typically January–March) when the wells were frozen. The depth to the water table under the gravel bar varies from 50 to 100 cm. Sediments are fairly coarse sand–pebble with a median particle diameter of ~5 mm and low organic content (1% of dry weight).

## Methods

Before collecting water samples, we measured the depth to water table in each well by lowering into the well a thin dowel with wires connected to a resistance meter. The distance from an arbitrary level line to the point where resistance dropped (i.e., the wires contacted the water surface) was measured for each well. Water samples for DOC and oxygen analyses were collected from each of the 13 wells with a peristaltic pump. The first 200 mL of water from each well were discarded. DOC samples (2 bottles per well) were filtered (combusted GF/F filters, 1.0-μm pore size) in the field. $O_2$ samples (2 per well) were collected in 60-mL BOD bottles and fixed upon return to the laboratory (<1 h later) where oxygen was assayed with Winkler titrations. DOC was measured following high-temperature catalytic oxidation in a Shimadzu 5000 TOC Analyzer.

The location of all wells was mapped using a tape and compass (Fig. 1). Data from the 13 wells were spatially interpolated (Kriged, SURFER, Golden Software Inc., Golden, Colorado) to convert 13 point estimates distributed over the gravel bar into a 25 × 25 array. Each cell in the array was about 90 cm × 60 cm. Well locations and corresponding data (water level, DOC, and $O_2$) were entered into a Geographic Information System (IDRISI) for calculation of mean concentrations of DOC and $O_2$. From these steps we derive an areally-weighted value for water chemistry variables in hyporheic sediments rather than using individual point estimates. All average values for hyporheic water referred to in this paper therefore represent areally-weighted means.

The depths to water table were entered to estimate the aspect and slope of the water table as a proxy for the direction and velocity of water flow. We estimated travel time for hyporheic water as the time required for a parcel of water to move from the head of the gravel bar to the mid-point of the bar (~10 m). Velocity was estimated from the slope of the water table times hydraulic conductivity for these sediments ($K_h$ = 0.7 cm/s). Hydraulic conductivity was estimated from particle size distribution using Equation 8.47 in Freeze and Cherry (1979). A set of 6 sediment samples from the top of the water table were collected from different locations on the gravel bar. The median particle size averaged (±1 SD) 5.3 mm (±3) and the average $d_{10}$ (10th percentile) was 0.86 mm (±0.6).

The rate of DOC removal was calculated as:

$$(\text{Streamwater DOC} - \text{hyporheic DOC})/\text{travel time}.$$

Streamwater DOC is the concentration measured in the stream channel immediately above the gravel bar ($n = 2$ for each sampling date), and hyporheic DOC is the areally-weighted average DOC concentration in the hyporheic zone.

Rates of oxygen consumption were calculated from the difference in concentration divided by travel time as for DOC removal. We have not corrected hyporheic $O_2$ concentrations for inward diffusion because we do not know oxygen concentrations in the subsurface airspace nor can we directly estimate the necessary diffusion constants. Therefore, our estimates of oxygen consumption are underestimates of in situ rates. The magnitude of the underestimation will be largest when subsurface water is farthest from saturation.

## Results

There were consistent southeast-to-northwest gradients of dissolved oxygen and DOC from the upstream end ("head") of the gravel bar with marked declines in hyporheic oxygen and DOC over a distance of approximately 10 m (e.g., Figs. 2A, B). The depth to water table (Fig. 2C) shows slopes from east to west, in the general direction expected if subsurface flow is "short-cutting" the gravel bar. Hyporheic water parcels with highest $O_2$ and DOC (bottom right of Figs. 2A, B) must represent water that has most recently left the open channel and entered the hyporheic flowpath.

Streamwater concentrations of DOC tended to show higher values in late spring and lower values in late summer but the seasonal pattern was by no means clear. Average hyporheic DOC concentrations were always less than streamwater concentrations (Fig. 3A). The magnitude of the difference between streamwater and hyporheic DOC showed no seasonal pattern (Fig. 3B) nor did the proportion of DOC removed (i.e., hyporheic DOC/stream DOC, Fig. 3C). The relationship between the rate of DOC removal and temperature was not significant ($p = 0.97$, Fig. 4) despite a fairly broad temperature range (~15°C) and samples spanning April through

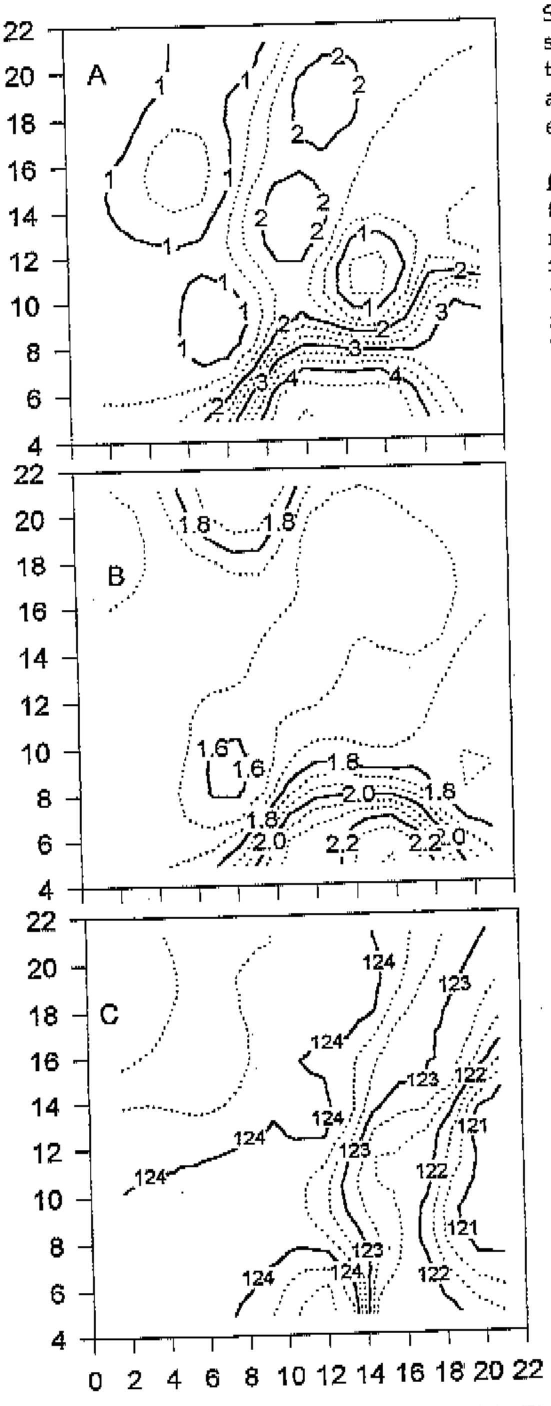

FIG. 2. Contour maps of (A) oxygen (mg/L), (B) dissolved organic carbon (mg C/L) and (C) depth to water table (cm below arbitrary datum). Contours ← were derived by kriging point observations from the 13 wells. Axes are m north or east of an arbitrary reference. Orientation is the same as box superimposed on map shown in Fig. 1.

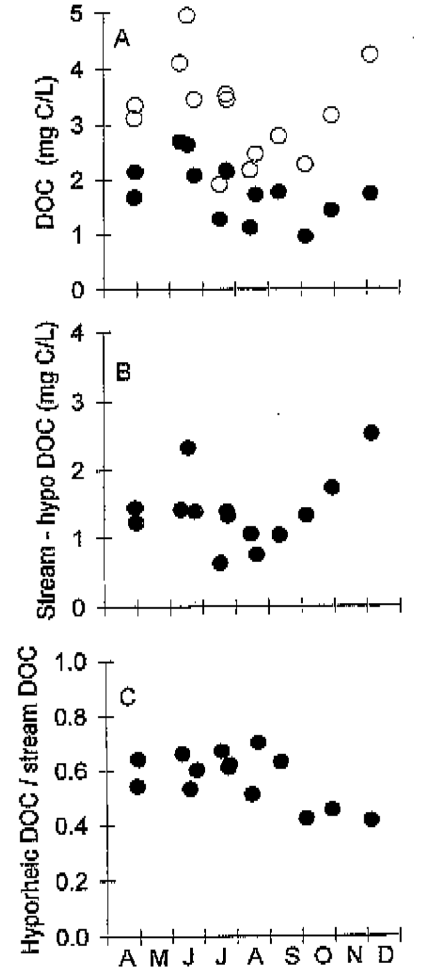

FIG. 3. Seasonal pattern of (A) streamwater (○) and hyporheic DOC (●); (B) the difference between streamwater and hyporheic DOC, and (C) the proportion of DOC removed.

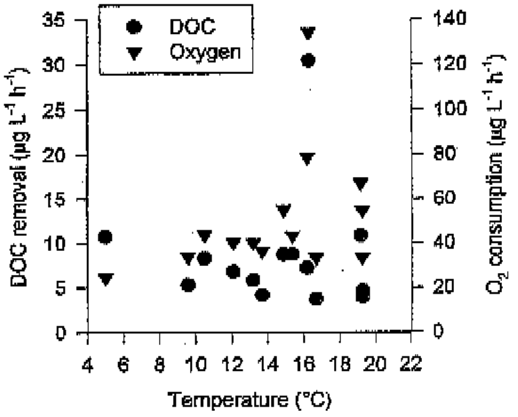

FIG. 4. Relationship between rates of hyporheic DOC removal or oxygen consumption and temperature.

December. The rate of $O_2$ consumption was not related to temperature ($p = 0.17$, Fig. 4), despite a 5-fold range in $O_2$ uptake rates. To examine possible temporal lags, we also regressed removal rates against the temperature in the previous month but found no improvement in relationships. Apparently, temperature does not strongly affect the rate of disappearance of DOC or oxygen from hyporheic water in this system.

To determine whether oxygen availability might be limiting DOC metabolism, we calculated for each date the difference in DOC (stream minus hyporheic) and the difference in oxygen (stream minus hyporheic). If we assume that metabolism of one mole of DOC requires one mole of oxygen (i.e., a molar respiratory quotient of 1:1), we would expect the points to fall on the 1:1 line shown in Figure 5. These points are actually minimal estimates of change in oxygen because we have not corrected for inward diffusion. All points except 1 (June 1993) fall well above the line, showing that the decline in oxygen is greater than would be expected based solely on the disappearance of DOC.

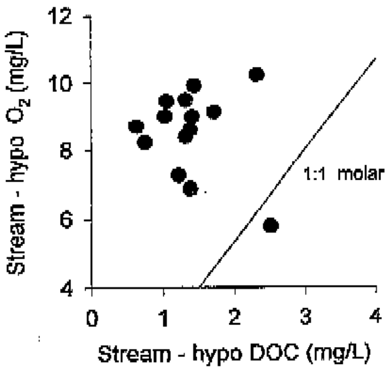

FIG. 5. Pattern of DOC and dissolved oxygen removal from hyporheic water. Values are differences between DOC (or oxygen) between streamwater and average hyporheic water. The 1:1 line represents a respiratory quotient of 1 mole oxygen consumed per mole of carbon respired.

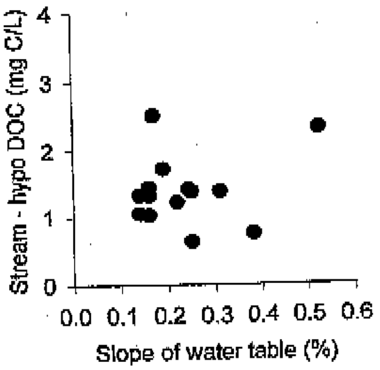

FIG. 6. Relationship between DOC difference (stream minus hyporheic) and slope of water table (surrogate for velocity) ($p = 0.5$).

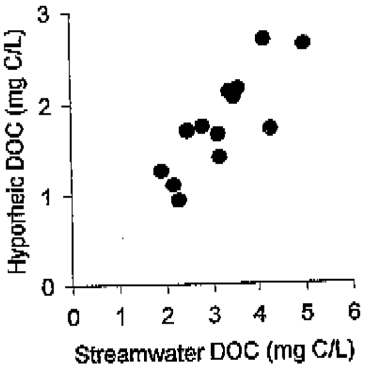

FIG. 7. Relationship between streamwater and average hyporheic DOC concentrations ($p < 0.01$, $r^2 = 0.68$).

Variability in hyporheic residence time might generate variability in observed declines in DOC and oxygen, with longer travel times allowing more metabolism, i.e., greater consumption of DOC or oxygen. No significant relationship was seen ($p = 0.5$, Fig. 6) between the difference in DOC (stream minus hyporheic) and the slope of the water table (proportional to velocity). Using observed differences in slope of the water table, and a hydraulic conductivity of 0.7 cm/s, the actual travel time to the mid-point of the bar would have ranged from 3 to 12 d over this 2-y period. As for DOC, there was no relationship between dissolved oxygen difference and the slope of the water table ($p = 0.56$). We used the simple difference between stream and hyporheic DOC (or $O_2$) in this regression rather than the rate of removal, because the rates are calculated based in part on the slope of the water table and would generate autocorrelation between the dependent and independent variables. Significant differences in residence time did not yield the anticipated differences in DOC or $O_2$ depletion. For dissolved oxygen, diffusion might partially explain the lack of a relationship, because longer travel times provide a longer period for inward diffusion of oxygen from unsaturated porespaces. Therefore, diffusion can counteract oxygen depletion, obscuring the effect of travel time.

The only significant predictor of hyporheic DOC we found in this study was the streamwater concentration of DOC (Fig. 7). The regression is significant ($p = 0.0003$, $r^2 = 0.68$) with a slope of 0.5 (±0.1 [1 SE]), showing a strikingly constant decline in concentration within hyporheic sediments.

## Discussion

The fact that streamwater DOC concentration was the best predictor of hyporheic DOC with a consistent removal strongly suggests physical adsorption as the predominant removal process. We have considered the possibility that dilution by low-oxygen, low-DOC groundwater could also generate the decreases in $O_2$ and DOC we have observed. The low relief of the surrounding land makes it very unlikely that near-surface lateral movement of groundwater is occurring. Moreover, we find no correlation between precipitation summed over the 7-d period prior to each sampling date and decline in DOC: $\Delta$ DOC $= 1.34 + 0.0025$ (±0.007 [1 SE]) × Precipitation; $r^2 = 0.01$. If dilution is driving the patterns we have observed over the past 3 y, we would expect to see a relationship with precipitation patterns. The low relief of the surrounding land surface and lack of relationship with rainfall leads us to discount the possibility of groundwater dilution of hyporheic water at this site.

Several studies have shown that DOC is immobilized by streambed sediments (McDowell 1985, Fiebig and Lock 1991) and appears to be a concentration-dependent process (Dahm 1981). At present, we can not separate adsorption to mineral surfaces from adsorption to biofilm extracellular material, but in neither case is DOC removed from biological activity. Respiration of carbon estimated from declines in oxygen is more than adequate to explain the eventual removal of adsorbed DOC from surfaces (Fig. 5). Respiration may lag adsorption by variable periods and so does not manifest itself as a simple relationship between decline in DOC and decline in dissolved oxygen. We have argued previously that drops in DOC were (ultimately) due to microbial catabolism (Findlay et al. 1993). Adsorption may be the first step in this process, with subsequent metabolism removing adsorbed carbon. Freeman and Lock (1995) have recently shown that the biofilm polysaccharide matrix can buffer sediment microbes against fluctuations in DOC supply. Thus, adsorption provides a mechanism for retention and metabolism of DOC passing through hyporheic sediments.

This mechanism allows for microbial removal of DOC even under physical conditions (low temperature, rapid flow) which would increase transport of DOC through the system with less opportunity for metabolism of DOC. Moreover, the stabilization of DOC on particle surfaces or biofilms permits induction and elaboration of extracellular enzymes capable of degrading large complex molecules (Lock 1993). If microbial uptake of compounds from solution were the only process, more refractory dissolved compounds might escape degradation as water moves through the sediment.

The lack of correlation between DOC or $O_2$ consumption and temperature was surprising given our expectation that low temperatures should limit biotic activity and therefore reduce rates of DOC consumption. Temperature control undoubtedly comes into play at extreme high or low temperatures but our results suggest that over a fairly broad range, temperature has only a secondary influence on sediment microbial communities.

Our finding that $O_2$ consumption exceeded the DOC depletion argues that a significant part of hyporheic metabolism is fueled by buried particulate organic carbon (POC). Using measures of $O_2$ consumption we can estimate the turnover of sediment POC due to respiratory demand. We have measured oxygen consumption by hyporheic sediments with re-circulating and static techniques. Re-circulating systems have an in-line dissolved oxygen probe to follow $O_2$ declines as water is pumped through a core. For static incubations a core is filled with air-saturated water, sealed for a 2-h period, and drained, and $O_2$ is then measured. We have found that the range of $O_2$ uptake rates expressed per dry weight of sediment is 0.1–1 $\mu$g $O_2$ $g^{-1}$ $h^{-1}$ (mean = 0.45, SD = 0.4, $n$ = 4). Sediment organic content ranges from 0.7 to 1.1% of dry weight (mean = 0.9, SD = 0.2, $n$ = 4). POC turnover times (standing stock of POC/carbon equivalent of respiration) range from 1.7 to 12 y, with a mean of 5.5 y. These long turnover times suggest that hyporheic respiration could be supported for a long time by the existing stock of organic matter. There is no obvious mechanism for re-supply of allochthonous POC to these sediments; the relatively slow interstitial velocities (range = 3–13 cm/h) and small pore spaces make it unlikely that infiltration could transport POC very far into these sediments. Flooding has not disturbed these sediments to more than a few cm depth for several years, so episodic burial of organic matter seems unlikely. Plant roots (primarily grasses and some annual weeds) occupy only the top 20 cm and so would not provide organic carbon to deeper, saturated sediments.

One alternative explanation for the patterns we have observed is that qualitative aspects of DOC composition are varying and influencing our observed rates of DOC removal. Whatever variations in quality might be driving variability in uptake, they are not tied to predictable seasonal events such as litterfall or spring blooms of benthic algae, or we would expect to see evidence of seasonal fluctuations in rates of DOC removal. At this stage in our understanding, we suggest that rapid, concentration-dependent adsorption is the mechanism controlling disappearance of DOC along these hyporheic flowpaths.

Our results show that temporal variability in DOC removal is, at least proximally, under the control of adsorptive processes. Description of other temporal and spatial scales of variability will enhance future research on hyporheic systems by providing a context for comparing disparate streams. For instance, in a very wide range of streams, hyporheic residence time was found to partially explain variability in oxygen distribution among streams (Findlay 1995). In that data set, residence time varied by more than 3 orders of magnitude, representing a very broad range of hydrodynamic conditions. Variability in residence time at the particular site used in the present study was only 4-fold, representing a much narrower band of the total range. Appreciation of multiple scales of variability provides the best context for site-specific studies of ecosystem function.

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