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Kinetics and mechanisms of dissolved organic carbon retention in a headwater stream

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Abstract. Freeze-dried aqueous extracts of autumn-shed maple leaves, birch leaves, and spruce needles were added to a third-order reach of Bear Brook, New Hampshire at concentrations similar to those predicted to occur during peak leaf fall. Leachate from each species was rapidly removed from solution. With initial concentrations of added leachate of approximately 5 mg l^{-1}, dissolved organics (DOC) uptake ranged from 73 to 130 mg m^{-2} h^{-1} for the first five hours of travel downstream from the point of addition. There was no preferential removal of DOC of low molecular weight, or of monomeric carbohydrates relative to phenolics or unidentified DOC.

Stream sediments and organic debris rapidly removed DOC from solution in laboratory experiments. No significant flocculation or microbial assimilation of sugar maple leachate occurred in stream water alone. Stream sediments showed small increases in respiration with addition of leaf leachate, but no increase in respiration occurred upon addition of leachate to organic debris. Abiotic adsorption due to the high concentrations of exchangeable iron and aluminium in stream sediments may be responsible for much of the rapid removal of leaf leachate observed in field experiments. Abiotic processes appear to retain DOC within the stream, thereby allowing subsequent metabolism of dissolved organic carbon by stream microflora.

Introduction

In forested regions, leaf litter is an important energy input to headwater stream ecosystems (Fisher and Likens 1973; Cummins 1974). Bacteria, fungi, and various functional groups of aquatic invertebrates (e.g. Suberkropp and Klug 1976; Cummins and Klug 1979) all colonize leaf surfaces, using the leaf as both food and physical substrate. Leaf litter also produces large amounts of dissolved organic matter. Up to 30% of a leaf's dry weight can be lost within twenty-four hours of submersion (Petersen and Cummins 1974; McDowell and Fisher 1976). Using a mass balance approach, McDowell and Fisher (1976) showed that dissolved organic matter produced by autumn-shed leaves in a small Massachusetts stream could represent a significant source of energy for the stream, as much as 11% of total annual respiration.

Numerous experiments with laboratory microcosms (Lock and Hynes 1976; Rounick and Winterbourn 1983), experimental stream chambers (Bott et al. 1978; Dahm 1981; Kaplan and Bott 1983; Kuserk et al. 1984) and articifical stream channels (Cummins et al. 1972) have demonstrated that leaf leachate can be metabolized by stream microorganisms. Microorganisms of the stream bottom, rather than the water column, appear to dominate the metabolism of organic compounds in leaf leachate (e.g. Lock and Hynes 1976; Dahm 1981).

Most research on leaf leachate metabolism in stream microcosms shows that metabolism is relatively slow, generally taking many hours or days (e.g. Cummins et al. 1972; Dahm 1981; Rounick and Winterbourn 1983). Yet field experiments (Lush and Hynes 1978) demonstrate that leachate uptake can be extraordinarily rapid, on the order of 1–2 hours, under natural conditions. In addition, DOC concentrations in many small headwater streams are relatively constant over time, and never reach those predicted to occur due to leaf leaching (McDowell and Fisher 1976). These observations suggest that rapid abiotic adsorption may be partially responsible for damping fluctuations in DOC concentrations in natural streams.

In this paper, I describe the results of a study designed to assess the kinetics and relative importance of biotic and abiotic mechanisms in the retention of dissolved organic carbon by a small headwater stream in New Hampshire, U.S.A. I used field experiments to establish rates of leachate disappearance in the stream, and then examined the nature of the removal mechanism using laboratory experiments. I hypothesized that if biotic processes were responsible for DOC disappearance, I would observe preferential removal of low-molecular-weight compounds as found by Kaplan and Bott (1983). In addition, I hypothesized that a previously adapted microflora (McArthur et al. 1985) would result in more complete uptake of leachate from tree species common in the Bear Brook watershed than from trees not commonly found in the watershed.

Methods and materials

Description of study site

Bear Brook is a third order stream draining the reference watershed (W6) of the Hubbard Brook Experimental Forest, West Thornton, New Hampshire. Vegetation in the watershed is dominated by beech (*Fagus grandifolia*), yellow birch (*Betula alleghaniensis*) and sugar maple (*Acer saccharum*). Soils are well-drained Spodosols (Haplorthods) with pH less than 4.5. Precipitation averages 130 cm yr^{-1}, and is uniformly distributed throughout the year. A detailed description of the watershed is given by Likens et al. (1977).

Bear Brook is strongly heterotrophic, with large allochthonous inputs of organic matter (Fisher and Likens 1973). Leaf litter is a major input of organic matter, as the stream has a closed forest canopy overhead. Primary production within the stream is negligible (Fisher and Likens 1973). Bacterial concentrations are low and range from 10^4 to 10^5 per ml using acridine orange direct counting (McDowell 1984). Dissolved organic carbon concentrations range from 1 to 5 $mg\,l^{-1}$, with lowest concentrations found during periods of low flow (summer and winter), and highest concentrations found during autumn storms (McDowell 1982; McDowell and Likens, in prep.). During 1978–1979, DOC concentration in Bear Brook averaged 2.26 $mg\,l^{-1}$ with a standard deviation of 0.93 $mg\,l^{-1}$ (McDowell 1982).

Organic debris dams are an important component of the stream, and are the site of large accumulations of sediments and organic debris (Bilby and Likens 1980). Substrate in the stream bed consists of cobbles, boulders, and bedrock, with localized accumulations of fine sediments and organic debris. Sediments are loosely packed, often poorly sorted, and are not cohesive; they appear to be well oxygenated to a depth of at least several centimeters. Iron, aluminum, and organic matter content of stream sediments varies inversely with particle diameter. The finest sediments contain as much as 20% organic matter, 16 $mg\,g^{-1}$ acid-soluble Al, and 14 $mg\,g^{-1}$ acid-soluble Fe (Meyer 1979).

The concentrations of most dissolved substances in Bear Brook vary within a narrow range (less than a factor of three), and can be predicted from stream flow (Johnson et al. 1969). Concentrations of both DOC and phosphorus in stream water are determined in large part by reactions occurring in mineral soil of the watershed (McDowell and Wood 1984; Wood et al. 1984). Abiotic adsorption of dissolved phosphorus occurs in the channel of Bear Brook as well as the watershed (Meyer 1979).

Field experiments

My basic approach was to add previously prepared leaf leachate to Bear Brook at concentrations similar to those predicted to occur from leaf leaching during autumn. I determined the removal of DOC in the experimental reach by monitoring the decrease in DOC concentration as the leachate traveled downstream. Some decrease in DOC concentration at downstream stations might be expected as a result of the dilution of DOC-enriched stream water with ground water; to correct for this, I measured the rate of ground water infiltration by adding a relatively inert tracer (NaCl) to the leachate solution.

Leachate preparation. Leaves used in the production of leachate were collected shortly after abscission from the branches of sugar maple and yellow birch trees. Leaves were dried at 35°C, fragmented by hand to facilitate wetting, and soaked for 24 h at 2°C in distilled water (40 g leaf per litre). Branches from a red spruce tree were collected from a felled tree and dried at 35°C. After one week of drying, needles were removed from the branches and ground in a hammer mill with a 1-mm screen. The ground spruce needles were leached for 24 h at 2°C in distilled water (90 g needles per litre). The needle or leaf leachate then was decanted, poured through 100- and 50 μm Nitex netting, and filtered through a glass fiber prefilter (Millipore AP 20) and filter

(Gelman A-E) using a large-volume Millipore pressure filtration apparatus operated at 2.7 atmospheres. No attempt was made to produce leachate under sterile conditions. Leachate was frozen in plastic-lined stainless steel pans (1 × 1 m) and lyophilized in a Stokes freeze dryer, yielding a crystalline, readily soluble product; solubility was greater than 95%. Although freeze drying had some effect on the organic chemistry of leaf leachate (Table 1), it did not result in the large changes in the average molecular weight of DOC which Giesey and Briese (1978) observed upon freezing pond water samples containing high concentrations of humic substances.

Experimental procedures. During field experiments, a solution of leachate and NaCl was siphoned into the stream continuously for 7–10 h at a rate sufficient to raise the DOC concentration approximately 5 mg l^{-1} above background. Leachate solution was added at a turbulent, well-mixed spot above a small pool; the completeness of mixing was monitored by measuring conductivity (Beckman Model RC 16C) in the pool. Sodium concentration increased to levels approximately 4 mg l^{-1} above background. Experimental conditions during each enrichment experiment are given in Table 2. The concentrated leachate solution was sampled four times over the course of each experiment. Stream water samples were collected above the point of leachate addition ('background' samples) and at five or six downstream stations. Samples were taken from well-mixed reaches in the center of the channel. Downstream stations were sampled prior to the start of the experiment to determine whether background samples were representative of the entire experimental reach. Although the concentrations of both Na and DOC increase with distance downstream in the adjacent Falls Brook watershed (Johnson et al. 1981), I observed no differences in Na or DOC concentrations within the experimental reach of Bear Brook.

Experiments were generally conducted on an undisturbed third-order reach of Bear Brook below the confluence of tributary streams draining watersheds 5 and 6 (W5 and W6) of the Hubbard Brook Experimental Forest. In one experiment (July 1979) leachate was added to a tributary stream (W5) free of any sizeable accumulations of organic debris. All organic debris dams had been experimentally removed from a 500-metre reach of this stream in 1977, resulting in the scouring of most organic matter from the stream channel (Bilby and Likens 1980). One week prior to the leachate enrichment experiment I removed all visible accumulations of organic matter from a section of the stream lacking debris dams.

Samples for organic analysis were filtered in the field within one hour after collection (Whatman GF/C) and stored on ice prior to return to the laboratory. Dissolved organic carbon was analyzed using a modified version of the persulfate digestion method (Menzel and Vaccaro, 1964). Modifications included sparging of the sample with O_2 rather than N_2 and sealing the ampoules under a continuous stream of oxygen, as originally suggested by

Table 1. Organic composition of three freshly prepared and subsequently freeze-dried and resolubilized leachates of sugar maple leaves. NMW = nominal molecular weight of DOC in thousands of daltons. All values % of total DOC unless noted otherwise; phenolics and carbohydrates assumed to contain 40% C.

Constituent	Avg. fresh (Stan. Dev.)	Avg. freeze dried (Stan. Dev.)
Total DOC (mg l^{-1})	4.35 (0.16)	5.63 (0.16)
< 1 NMW	16.9 (1.6)	11.9 (1.3)
1–10 NMW	63.6 (6.3)	62.9 (5.7)
10–100 NMW	11.8 (6.3)	9.6 (3.3)
> 100 NMW	7.6 (0.9)	14.6 (5.1)
Monomeric carbohydrates	12.7 (0.5)	14.3 (0.4)
Polymeric carbohydrates	10.2 (0.9)	9.8 (0.4)
Phenolics	31.5 (1.4)	33.9 (0.4)

Baldwin and McAtee (1974). Carbon dioxide produced by the persulfate oxidation was stripped into carrier gas (Stainton 1973) and analyzed on a gas partitioner (Fisher-Hamilton Model 29) or infrared analyzer (Beckman Model 865).

The molecular weight distribution of DOC was determined using ultrafiltration. Dissolved organic carbon was separated into fractions of less than 1,000, 1,000–10,000, 10,000–100,000 and greater than 100,000 daltons nominal molecular weight (NMW) with UM-2, PM-10, and XM-100 ultrafilters (Amicon Corp.). Details of the operation of the ultrafilters are given in Cole et al. (1984).

Phenolics (total hydroxylated aromatics, often referred to as 'lignin and tannin') were measured using a modified Folin–Ciocalteau reagent (Kloster 1974) and a tannic acid standard. Monomeric and polymeric carbohydrates were determined using the periodate oxidation method (Johnson and Sieburth 1977, Burney and Sieburth 1977, Johnson et al. 1981) and glucose standards. Samples for carbohydrate analysis were frozen in 30 ml polyethylene bottles prior to analysis. A comparison of frozen and freshly analyzed samples showed that freezing had no effect on measured carbohydrate concentrations. Residual, or 'unidentified' DOC was calculated as the difference between total DOC and the sum of phenolic and carbohydrate carbon (assuming 40% C content in phenolics and carbohydrates).

I estimated the travel time between sampling stations by following the increase in conductivity at each station following the additon of the concentrated leachate/NaCl solution. Discharge at each station was determined using sodium concentrations and the dilution gauging method (reviewed by John 1978). The sodium concentration of unfiltered samples was measured using atomic absorption spectrophotometry (Perkin-Elmer Model 403).

Calculation of DOC removal. I used Na concentration to differentiate between removal of leachate DOC by biotic and/or abiotic processes and dilution of leachate DOC by ground water. For each sample, I first subtracted the background DOC and Na concentrations to determine the concentrations of DOC and Na present due to leachate addition. The concentration of leachate DOC which should be present (if no removal or addition occurred) was calculated by multiplying Na concentration in the sample by the ratio DOC:Na in the concentrated leachate solution. Observed values of DOC higher than the expected value reflected production of DOC in the reach; observed values of DOC lower than the expected value indicated that DOC had been removed from solution. Similar calculations were used to determine the expected values of other organics. The removal of DOC was expressed two ways – as the % of the expected DOC remaining in solution, or $mg\,m^{-2}\,h^{-1}$ (removal in a reach, $mg\,l^{-1}$, multiplied by the flow, $l\,h^{-1}$, divided by the area of the reach).

Laboratory experiments

Site of DOC removal. To identify the site of DOC removal, I studied three components of the stream – water, organic debris, and sediments. Organic debris was collected from distinct aggregations of detrital leaf particles, which had an average diameter of approximately 5 mm. Unsorted sediments were collected from the stream bottom; rocks over 2 cm in diameter were excluded. Stream water, autoclaved stream water plus organic debris (26 g dry weight in 1.75 l), or autoclaved stream water plus sediments (1400 g dry weight in 1.75 l) were placed in polypropylene containers aerated with compressed air, and held at 15 ± 1°C. A solution of leaf leachate (sugar maple) and NaCl was added to each of three experimental containers (final concentration 5 mg leachate DOC l^{-1} and 3 mg Na l^{-1}) and the concentrations of DOC were determined over a 9 h sampling period.

I varied the ratio of sediment: water in another series of microcosms in order to quantify the effects of experimental conditions on leachate removal. Sediments and autoclaved stream water were placed in 250-ml Erlenmeyer flasks. Sediment concentration varied from 0.02 to 0.90 $g\,ml^{-1}$. The concentration of added leachate was 9.5 $mg\,l^{-1}$; the amount of DOC remaining in solution was measured after 6 h incubation at 15°C with intermittant shaking.

Nature of removal mechanism. Two experiments were conducted in an attempt to discriminate between biotic and abiotic removal of leachate by stream sediments and organic debris. They were measurement of respiration in the presence and absence of leaf leachate, and measurement of DOC adsorption following sterilization of sediments by autoclaving. In the following experiments, I used sieved sediments 1 to 5 mm in diameter. Sediments of this size are abundant, readily collected, and show low variability in DOC removal (McDowell 1982).

Respiration of leaf leachate was measured by monitoring the change in CO_2 concentration in a sealed 550 ml bottle containing sediments or organic debris with and without leaf leachate (10 mg DOC l^{-1}). Bottles were shaken 5 min prior to sampling and at hourly intervals. Water samples (5 ml) were drawn from one port in the stopper and replaced with autoclaved stream water dispensed through a second port. Carbon dioxide was measured using a modified version of the syringe stripping method of Stainton (1973) in which sample size and He volume were reduced to 5 and 10 ml, respectively. The difference between two replicates was less than 5%. Sterile controls showed no change in CO_2 concentration during 9 h.

Removal of DOC by autoclaved and untreated sediments was calculated from the results of experiments similar to those used to determine the equilibrium DOC concentration of soil samples (McDowell and Wood 1984). Sediments were autoclaved for two hours at 121°C, cooled to room temperature, and autoclaved a second time. Because autoclaving caused DOC to be released from the sediments, I rinsed them several times with autoclaved stream water using sterile technique. Sediments (70 g dry wt) and 90 mls autoclaved stream water were placed in a 250 ml Erlenmeyer flask. Leaf leachate was added at 5, 10, 15, and 25 mg DOC l^{-1} with two replicate flasks for each concentration. Dissolved organic carbon was measured after 6 hours of incubation at 15°C with intermittant shaking.

Because increased release of DOC from stream sediments is often the byproduct of various sterilization procedures (Lock and Hynes 1976; Dahm 1981), I determined the effect of the DOC produced by autoclaving of sediments on the removal and respiration of ^{14}C-glucose. I chose to use glucose because it is present in significant quantities (approximately 7–11% of leachate) in freeze-dried sugar maple, spruce, and yellow birch leachate (J. Segal, pers comm.). Flasks containing 75 g of sediment and 100 ml of autoclaved stream water were inoculated with 53,700 dpm uniformly labeled ^{14}C-glucose, stoppered tightly, and incubated for 6 h at 15°C. Concentrations of DOC in the stream water ranged from 1.5 to 89 mg l^{-1}. Stream water with 89 mg DOC l^{-1} was produced by autoclaving in the presence of stream sediments (700 g l^{-1}); concentrations less than 89 mg l^{-1} were obtained by diluting with autoclaved stream water of ambient DOC concentration (1.5 mg l^{-1}). The method described by Cole and Likens (1979) was used to strip $^{14}CO_2$ from solution and trap it for scintillation counting. The $^{14}CO_2$ and ^{14}C-DOC remaining in solution were counted on a Beckman LS 330 liquid scintillation counter using the channels-ratio method and the method of external standards.

Results

Field experiments

Disappearance of DOC from various leachates. Dissolved organic carbon from sugar maple, yellow birch, and red spruce leachate was rapidly removed from solution in Bear Brook (Figure 1). Dissolved organic carbon from various

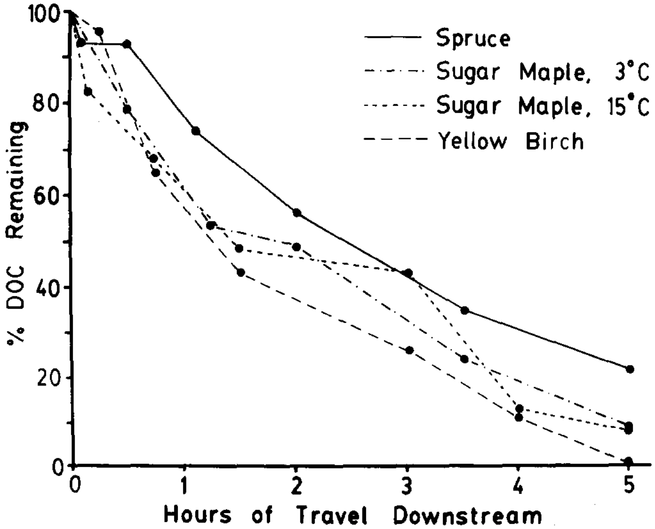

Figure 1. Removal of spruce, yellow birch, and sugar maple leachate in Bear Brook. Each point represents the mean of three samples taken at hourly intervals. Average standard deviation of these means is 3.7%.

leachates had an average 'half-life' of 2 h in the stream, and approximately 10% of the leachate remained in solution after 5 h (110 to 140 m) of travel downstream (Figure 1). Disappearance of sugar maple leachate was rapid during both summer and autumn, despite a difference of 12°C in the temperature of stream water (Figure 1; Table 2). DOC removal at a given point in the stream was relatively constant during an experiment (Figure 2). Over the study reach of 120–140 m, inputs of ground water approximately doubled stream flow, resulting in dilution of leachate DOC to 2.5 mg l^{-1} above background at the last station. There were no significant changes in concentrations of DOC or Na in the concentrated leachate solutions during any enrichment experiments. This suggests that both flocculation and microbial uptake of DOC were minimal in the stock solution.

An analysis of covariance (% remaining by leachate type covarying with travel time downstream) was used to test the hypothesis that uptake of sugar maple, yellow birch and spruce leachates (Figure 1, sugar maple 15°C) varied with leachate type. Results of the ANCOVA showed significant differences between the leachate types. A t-test (one tailed) comparing the amount of DOC remaining in solution at the end of 5 h was used to test the hypothesis that uptake of sugar maple and yellow birch was more complete than uptake of spruce leachate. There was no significant difference ($p < 0.05$) between the amounts of spruce and maple DOC remaining after 5 h of travel downstream, but the difference between yellow birch and spruce was significant.

Table 2. Experimental conditions and DOC removal during stream enrichment experiments. Values of DOC removal are means (standard deviation) of three samples taken at hourly intervals at stations corresponding to the indicated hours of travel downstream from the point of addition. Travel times are equivalent to approximately 15, 60, and 120 m downstream.

Leachate	Date	Temp. (°C)	Flow ($l\ sec^{-1}$)	Leachate DOC ($mg\ l^{-1}$)	DOC Removal ($mg\ m^{-2}\ hr^{-1}$) 0–0.8 Hours	0.8–2.7 Hours	2.7–5.0 Hours	0–5.0 Hours
Sugar maple	7 Aug. 1979	14–15	1.3	4.7	311(25)	91(16)	97(8)	113(13)
Sugar maple	18 Oct. 1978	2–3	1.4	3.7	230(35)	68(9)	60(24)	73(12)
Yellow birch	25 Aug. 1980	14–15	1.1	5.0	291(46)	130(6)	75(4)	125(6)
Spruce	2 Sept. 1979	13–14	1.0	5.5	180(160)	143(3)	115(13)	130(8)
Sugar[a] maple	4 July 1979	11–12	0.9	5.6	326(38)	52(60)	0(30)	78(18)

[a] This experiment conducted on W5 (a tributary of Bear Brook) in a section free of any sizeable accumulations of organic matter (see text).

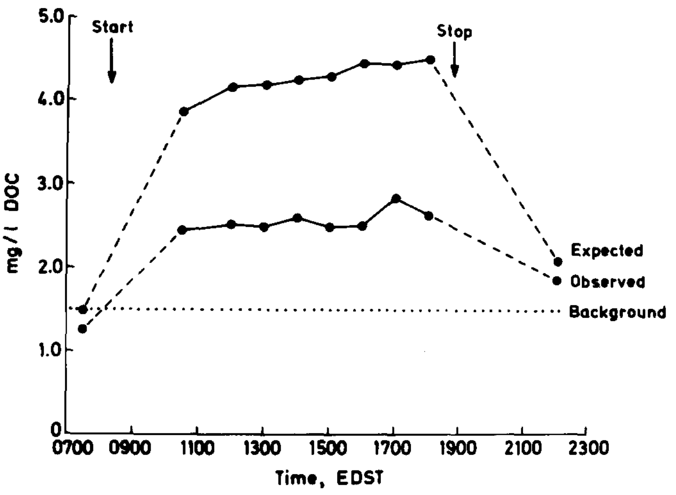

Figure 2. Observed and expected concentrations of DOC during sugar maple leachate addition. All samples taken 40 m below the point of leachate addition. Observed – actual DOC concentration; expected – concentration expected if no removal of DOC occurred. Average removal – 60%, standard deviation 3%. 'Start' indicates the beginning of leachate addition; 'stop' indicates the cessation of leachate addition.

Disappearance of various functional groups in leaf leachate. Monomeric carbohydrates, polymeric carbohydrates, phenolics, and unidentified DOC in sugar maple leachate were all rapidly removed from solution in Bear Brook (Figure 3). Discontinuities in removal rate with distance downstream appeared to be basically similar for each functional group (Figure 3). Two-way analysis of variance (% remaining by the factors travel time and functional group) showed that there was a significant interaction effect between travel time and functional group, making it difficult to assess the importance of functional group alone. A series of paired t-tests (one-tailed) was used to test the specific hypothesis that selective uptake by microorganisms would result in more complete removal of monomeric and polymeric carbohydrates than phenolics or unidentified DOC. Data were included from samples collected at 0.25, 0.75, 1.5, 3.0, 4.0 and 5.0 h of travel downstream. There were no significant differences ($p < 0.05$) between monomeric carbohydrates and either phenolics or unidentified DOC, indicating that selective uptake of monomeric carbohydrates did not occur. There was a significant difference ($0.01 < p < 0.05$) in the retention of polymeric carbohydrates and unidentified DOC, but no significant difference between polymeric carbohydrates and phenolics. The freeze-dried sugar maple leachate used in field experiments had an average soluble carbon content of 39%. Assuming that phenolics and carbohydrates contained 40% C, phenolics, carbohydrates, and unidentified DOC comprised 32, 24 and 44% of total DOC, respectively. Dissolved organic carbon of three

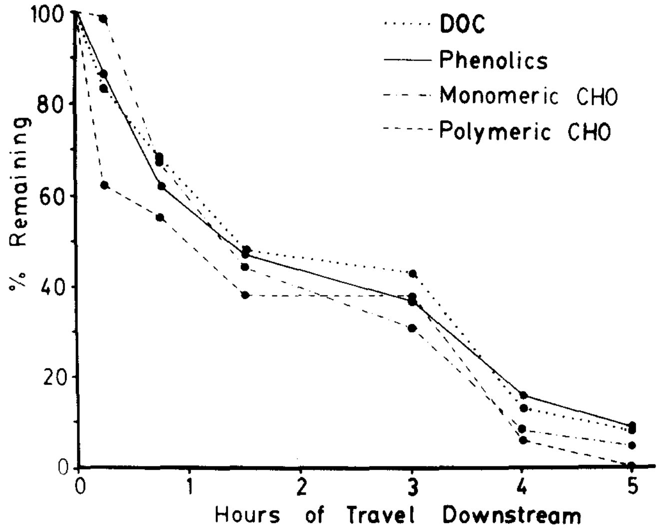

Figure 3. Removal of phenolics, carbohydrates, and DOC (sugar maple leachate) in Bear Brook. 'CHO' refers to carbohydrates; 'DOC' refers to unidentified DOC, i.e. total DOC minus DOC in carbohydrates and phenolics.

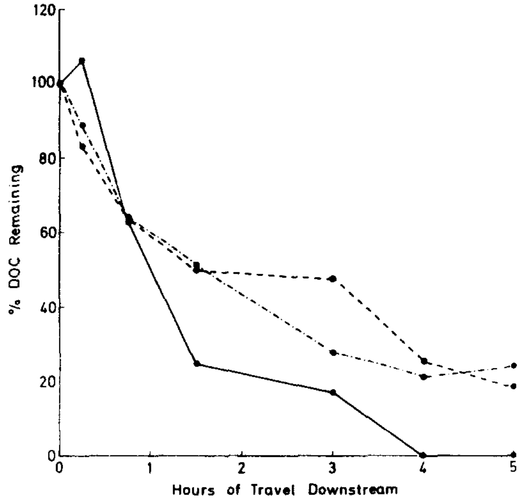

Figure 4. Removal of DOC (yellow birch leachate) according to molecular weight. Each point represents a single sample. < 1 – DOC of nominal molecular weight (NMW) less than 1,000 daltons; 1–100 – DOC of NMW between 1,000 and 100,000 daltons; > 100 – DOC of NMW greater than 100,000 daltons.

molecular weight classes was rapidly removed from the water column of Bear Brook (Figure 4). Only one sample was taken at each station, precluding statistical analysis of the data.

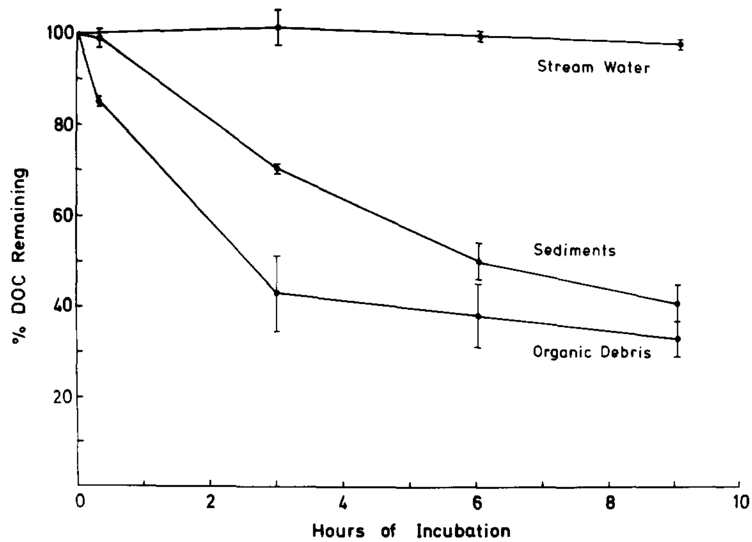

Figure 5. Removal of leaf leachate (sugar maple) in laboratory experiments with stream water, sediments, and organic debris. Bars represent mean plus and minus one standard deviation; $n = 3$.

Laboratory experiments

Site of DOC removal. The site of DOC removal in Bear Brook was the stream bottom. Both sediments and organic debris rapidly removed DOC (Figure 5). In constrast, when sugar maple leachate was added to stream water alone, DOC concentration remained unchanged for 9 h (Figure 5). The fraction of total DOC removed from solution in laboratory experiments was not as high as that observed in field experiments, although the kinetics of DOC removal were similar. The fraction of added DOC removed from solution increased as a function of sediment: water ratio (Figure 6). Maximum removal of 45% of added DOC was obtained with 0.9 g sediment ml^{-1}; further increases in the sediment: water ratio were not practical.

Mechanism of DOC removal. No removal of DOC occurred in stream water alone (Figure 5), suggesting that neither flocculation of DOC nor uptake of DOC by bacteria in the stream's water column was a significant pathway for DOC removal. Abiotic processes appeared to be responsible for much of the removal of leaf leachate by stream sediments. There was no detectable increase in respiration associated with the addition of leaf leachate to organic debris, and a small but statistically significant ($p < 0.05$, two-way ANOVA) increase in respiration when leachate was added to sediments (Figure 7).

Sediments sterilized by autoclaving removed DOC from solution (Figure 8). The slope of DOC uptake vs initial DOC concentration is a measure of the

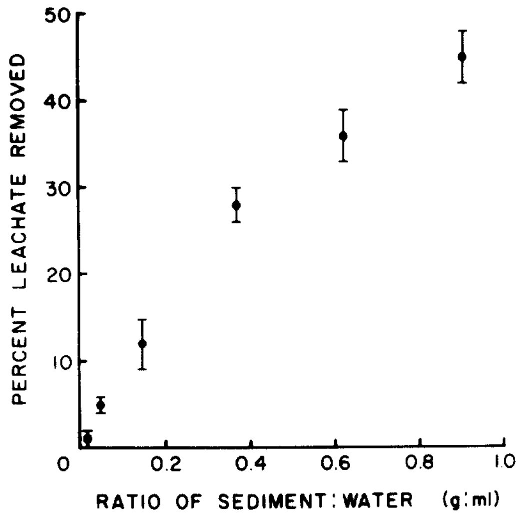

Figure 6. The effects of sediment: water ratio on removal of DOC (sugar maple leachate). Bars represent the range of two experimental replicates.

partitioning of DOC between sediments and stream water, while the concentration at which DOC is neither taken up nor released is an estimate of equilibrium DOC concentration for the sediment (Taylor and Kunishi 1971; McDowell and Wood 1984). The partition coefficient of autoclaved sediments was half that of untreated sediments, and significantly greater than zero ($p < 0.05$, t-test), indicating that leachate DOC was removed by autoclaved sediments at a rate half that of untreated sediments. Autoclaving caused substantial production of DOC (or death of microbes that normally keep DOC concentrations low), resulting in much higher equilibrium DOC concentration for autoclaved than untreated sediments (28 vs 0.6 $mg\,l^{-1}$; Figure 8). Autoclaving organic debris was not practical. Despite repeated rinsing background concentrations of greater than 100 $mg\,l^{-1}$ were observed in the experimental microcosms. I attempted to sterilize organic debris using $HgCl_2$ (15 $mg\,l^{-1}$), but found that this also resulted in large and variable production of DOC.

Removal of ^{14}C-glucose by stream sediments was inversely related to DOC concentration in the overlying water column (Figure 9). Because $^{14}CO_2$ production (and presumably biological uptake of ^{14}C-glucose) were unaffected by DOC concentration, the 50% decrease in ^{14}C-glucose removal between 1.5 and 89 mg $DOC\,l^{-1}$ was probably due to competition between glucose and DOC for adsorption sites on the sediments. Thus, I estimate that at least 50% of ^{14}C-glucose uptake by untreated sediments was abiotic. Further increases in the concentration of added DOC might have resulted in additional reductions in ^{14}C-glucose removal (Figure 9), and hence higher estimates of the fraction of abiotic uptake. Isotopic dilution due to addition of unlabeled

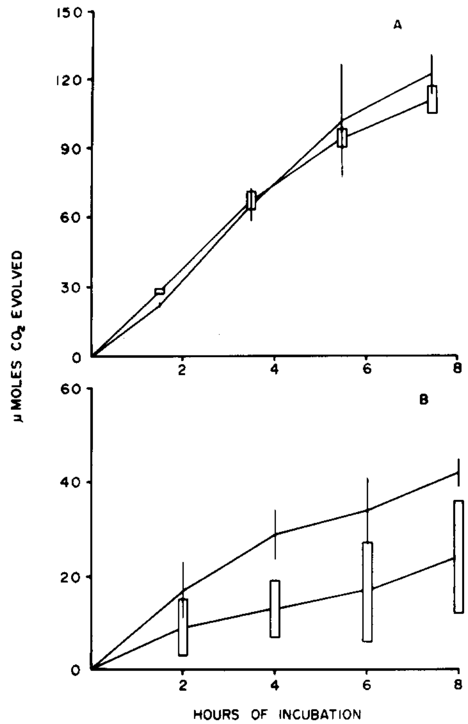

Figure 7. Respiration of microorganisms associated with a) organic debris and b) stream sediments in the presence and absence of leaf leachate. Bars indicate mean plus and minus standard deviation of 3 samples incubated in the presence of leaf leachate (sugar maple). Boxes indicate mean plus and minus standard deviation of 3 samples incubated in the absence of leaf leachate.

glucose in the DOC produced by autoclaving may have resulted in decreasing specific activity of the radiolabeled glucose. I have no direct measure of glucose concentrations which would detect such substrate dilution. However, decreases in the specific activity of glucose should have resulted in decreases in both total glucose removed and total $^{14}CO_2$ produced if the observed glucose uptake were biotic. No decrease in $^{14}CO_2$ production was observed (Figure 9).

Discussion

Rate of DOC removal

The rate of DOC removal in Bear Brook during the first hour after experimental addition of leaf leachate (200–300 mg m^{-2} h^{-1}, Table 2) is equal to or higher than that reported in most other studies. In field experiments similar

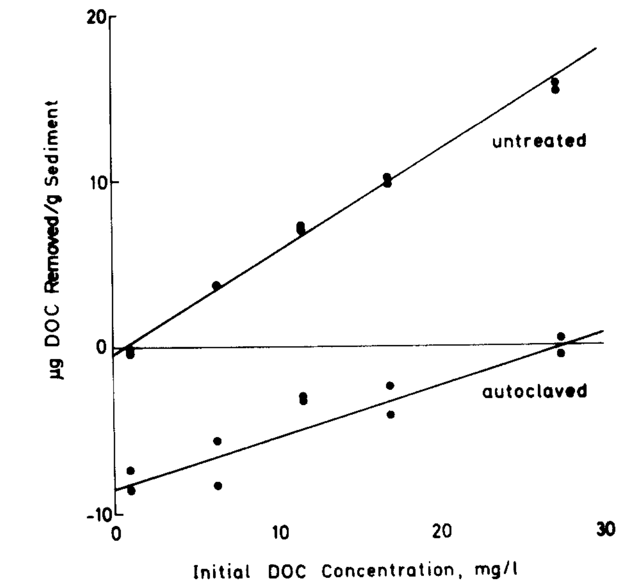

Figure 8. Removal of DOC (sugar maple leachate) by autoclaved and untreated sediments. Points below the zero line indicate a net release of DOC.

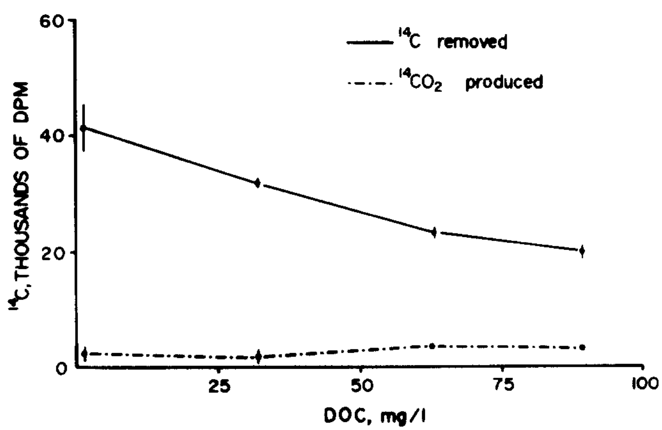

Figure 9. ^{14}C-glucose removal and $^{14}CO_2$ production by sediments as a function of DOC concentration in overlying stream water. Bars represent the range of two experimental replicates. Mean (standard deviation) of four autoclaved controls – 156(42) dpm respired; there was no detectable removal of glucose by autoclaved controls. Initial amount added was 54,000 dpm radiolabeled glucose.

to my own, Lush and Hynes (1978) found that dissolved organic matter leached from sugar maple leaves was removed from the water column of a small spring brook at the rate of 200–440 mg DOC m^{-2} h^{-1}. Wallis et al.

(1979) found that uptake of glucose by a small stream in the Marmot Creek Basin, Canada, ranged from 86 to 182 mg C m^{-2} h^{-1}, and Kuserk et al. (1984) observed uptake of DOC from bovine manure extract at a rate of 50 to 200 mg C m^{-2} h^{-1} in field experiments. Uptake of leaf leachate DOC in small experimental streams or microcosms has ranged from 10 to 400 mg m^{-2} h^{-1} (Cummins et al. 1972; Lock and Hynes 1975, 1976; Dahm 1981; Kaplan 1983; Kuserk et al. 1984).

The removal of DOC in my experiments was extremely rapid, given the relatively low initial concentrations of leachate DOC. In many of the experiments cited above, the initial concentration of added DOC (10–35 mg l^{-1}) was much higher than that which I used in field experiments. Use of a lower concentration of DOC is more representative of the average input of DOC during peak litter fall, approximately 3–6 mg DOC l^{-1} (McDowell and Fisher 1976).

Rates of DOC removal decreased with distance downstream (Table 2). This is not surprising, given that the added leachate DOC was almost entirely gone at the last sampling station (Figure 1). Removal rate is presumably some function of DOC concentration, and hence one would expect some decrease as substrate concentrations decrease (Dahm et al. in press). Although Newbold et al. (1983) have use reaction kinetics to try to differentiate between biotic and abiotic mechanisms of NH_4 removal in whole-stream enrichment experiments, I do not feel that this approach is practical for Bear Brook. The heterogeneous nature of the sand, silt, cobbles, and boulders which comprise the stream channel make accurate estimation of actual surface area exceedingly difficult (Kuserk et al. 1984). I have calculated removal rates on the basis of surface area of the channel, without regard to morphometry of the stream bottom. A second important consideration in determining the total area of reactive surfaces in the stream channel is the depth of hyporheic flow. In Bear Brook, this varies considerably from none (exposed bedrock) to perhaps a meter or more. The sometimes erratic changes in DOC removal rate with distance downstream (Figure 1; Table 2) are presumably due to variability in the total surface area of stream sediments to which the leachate solution is exposed.

The design of an enrichment experiment (pulsed or continuous addition) can also affect DOC removal rates in field experiments (Kuserk et al. 1984). I used continuous enrichment in the studies described here, because I felt that continuous enrichment at modest concentrations best simulated the release of leachate following autumn leaf fall. A second advantage of continuous enrichment experiments is the opportunity to obtain replicate samples over time at a given point in the stream.

During autumn, when Bear Brook receives large natural inputs of DOC from leaf leachate, DOC concentrations are held near background levels by the rapid removal of leaf leachate by stream sediments. I conducted one enrichment experiment shortly after peak litter fall (Table 2) to determine experimentally whether saturation with leachate occurs during autumn. Despite the low temperature of stream water (3°C) and an abundance of freshly fallen leaves in the stream channel, DOC concentrations rapidly returned to background levels after addition of sugar maple leachate. Thus, there was no apparent saturation of the DOC removal mechanism during autumn.

Use of Na as an inert tracer may have slightly underestimated DOC removal. Some adsorption of sodium by stream sediments does occur in laboratory experiments (McDowell 1982), especially at concentrations greater than 5 mg l^{-1}. If adsorption of Na occurred in the field experiments, I may have underestimated DOC removal by as much as 5–10% (McDowell 1982). Increased concentrations of Na during field experiments probably had little effect on DOC removal, as DOC removal in laboratory experiments is independent of Na concentration (McDowell 1982).

Removal of leachate from various species

My initial hypothesis that removal of leachate from sugar maple and yellow birch leaves would be more complete than removal of spruce needle leachate due to the presence of a pre-adapted microflora was only partially supported by the results of my field experiments. Uptake of yellow birch leachate was more rapid than uptake of spruce, but there were no differences in the removal of spruce and sugar maple leachate. Lock and Hynes (1975) also found that removal of conifer leachate in stream microcosms was often slower than that of deciduous leachates. In streams similar to Bear Brook ('soft water'), they observed that the fraction of leachate remaining in solution after 9 hours varied from 23% (aspen) to 85% (pine). Similar results were obtained by Wallis et al. (1979) in field experiments. They found significant removal of glucose and glutamic acid in Middle Creek Tributary, but observed no removal of spruce leachate. Dahm et al. (in press) also found that removal of Douglas fir leachate was significantly slower than removal of alder leachate in experimental stream chambers.

Litter fall in the Bear Brook watershed is composed primarily of beech, yellow birch, and sugar maple leaves (Gosz et al. 1973). Because beech leaves leach quite slowly (e.g. McDowell and Fisher 1976), sugar maple and yellow birch are probably the dominant natural inputs of leaf leachate to Bear Brook. Both of these naturally important leachates were rapidly removed from Bear Brook's water column in field experiments (Figure 1).

Removal of DOC by sediments and organic debris

The relative importance of sediments and organic debris in the removal of DOC is difficult to assess without accurate estimates of the total quantity of each in Bear Brook. Data on organic debris in Bear Brook are available, but there are no data on organic matter associated with the surface of clays and other fine particles in stream sediments. Meyer (1978) estimated that the standing stock of particulate organic matter (excluding logs) was 700 g m^{-2} in Bear Brook. Using the rate of DOC sorption which I observed in my laboratory experiments (0.055 mg DOC g organic $matter^{-1}$ h^{-1} over the first three hours; Figure 5), I estimate that organic debris could be responsible for removal of 38.5 mg DOC m^{-2} h^{-1}, which is less than 25% of the rate which I observed in field experiments (Table 2). On the basis of this crude calculation, it appears that organic debris is relatively unimportant in the removal of DOC. Further evidence in support of this conclusion was obtained in an enrichment experiment in which I added sugar maple leachate to a tributary of Bear Brook free of any sizeable accumulations of organic debris. Removal of DOC was quite rapid in this experiment (Table 2) despite the lack of organic debris in the stream channel. Mickleburgh et al. (1984) also found that stone surfaces and gravel were significant sites for DOC removal, but that organic floc was quantitatively unimportant.

Mechanism of DOC removal

My experiments do not provide unequivocal proof that either abiotic or biotic mechanisms dominate the removal of DOC in field enrichment experiments. Although I have interpreted my results to mean that abiotic retention of DOC was more important than biotic uptake in removal of DOC in Bear Brook, alternate explanations are possible.

The lack of any preferential removal of monomeric or polymeric carbohydrates relative to phenolics (Figure 3) suggests that the mechanism of initial DOC removal may be primarily abiotic in Bear Brook. Laboratory experiments (Kaplan and Bott 1983) show that microorganisms in White Clay Creek metabolize leaf leachates, and preferentially remove carbohydrates rather than phenolics from stream water enriched with jewel weed leachate. The preferential removal of polymeric carbohydrates relative to unidentified DOC (Figure 3) may be the result of microbial uptake; there was no selective removal of monomeric carbohydrates, however. Kaplan and Bott (1983) also found that the uptake of DOC predominantly less than 10,000 NMW occurred at a rate almost five times that of high nominal molecular weight DOC (227 vs 48 mg C m^{-2} h^{-1}). Thus, if microbial uptake were important in Bear Brook, one would expect to see highly selective removal of low molecular weight compounds. This was not the case (Figure 4), suggesting that abiotic mechanisms dominate the leachate removal process in field experiments.

Additional evidence that abiotic processes probably play a significant part in leachate removal in Bear Brook was obtained in laboratory experiments. The results of my sterilization experiments (Figures 8 and 9) suggest that at least half of DOC removal was due to abiotic processes. No increase in respiration was observed when leachate was added to organic debris (Figure 7a), and an increase in total respiration equivalent to only 12% of the leachate DOC removed by stream sediments was observed during 8 hours (Figure 7b).

If all DOC removal in these experiments were due to microbial assimilation with an efficiency of 50%, total respiration would have doubled in these experiments.

Use of respiration data to discriminate betweeen biotic and abiotic removal of DOC depends to a large extent on the value used for microbial assimilation efficiency. Although approximately 50% is commonly accepted as the norm, significant variation does occur (Payne 1970). Values as low as 4–10% respiration of radiolabelled glucose absorbed by sediment bacteria (i.e. 90–96% apparent assimilation efficiency) have been reported (e.g. Meyer-Reil 1978; Toerien and Cavari 1982). King and Klug (1982), however, indicate that actual respiration values may be considerably higher than those reported in the literature because of isotopic dilution. Potential changes in microbial assimilation efficiency over the course of an experiment (Ishida et al. 1982) further complicate interpretation of respiration data.

Many studies of DOC uptake by lake and stream sediments may have overestimated biotic uptake at the expense of abiotic adsorption due to the methods employed to produce sterile ‘controls’. Sterilization often alters the chemical environment in sediment samples much more so than in water samples. The increases in DOC associated with sterilization by autoclaving dramatically reduce the total uptake (biotic and/or abiotic) of ^{14}C-glucose by stream sediments (Figure 9). Sterilization with relatively high concentrations of organic compounds such as formalin or TCA (e.g. Toerien and Cavari 1982) may completely block any adsorption of a labelled compound of interest due to competition for adsorption sites. Smaller increases in ambient DOC concentrations such as those produced by addition of $HgCl_2$ (e.g. Dahm 1981) may partially block the adsorption of radiolabelled organic compounds and hence underestimate rates of abiotic adsorption.

In contrast to my interpretation of the results for Bear Brook, the removal of leaf leachate from other streams is generally thought to be due to microbial uptake of DOC (e.g. Cummins et al. 1972; Lock and Hynes 1976; Dahm 1981; Kaplan and Bott 1983; Kuserk et al. 1984; Dahm et al. in press). Dahm (1981) provides strong evidence for the importance of both biotic and abiotic uptake of leachate DOC in experimental stream chambers. To extrapolate his results to the field, however, requires knowledge of the kinetics of leachate removal. My results and those of Lush and Hynes (1978) suggest that to adequately mimic natural streams, DOC removal in the laboratory must be nearly complete after three to five hours. Because the design of stream microcosms can determine the total amount of DOC removed in short-term experiments (Figure 6), alteration of the proportions of stream water and sediment might well have altered the relative importance of the abiotic adsorption of DOC observed by Dahm (1981). The only study reporting rapid (1–4 h), nearly complete removal of leaf leachate DOC due to microbial uptake is Lock and Hynes (1976). Differences in mineralogy or microbial numbers between Bear Brook and the Speed River might be responsible for the apparent differences in DOC uptake mechanisms.

I hypothesize that abiotic retention of DOC in Bear Brook is the result of adsorption by amorphous iron and aluminum oxides on the surface of stream sediments, similar to the adsorption of phosphorus by stream sediments (Meyer 1979). In soils of the Bear Brook watershed, abiotic adsorption of DOC by iron and aluminum sesquioxides is an important reaction regulating the flux of organic matter through the soil profile (McDowell and Wood 1984). Concentrations of acid-soluble Fe and Al in fine stream sediments are equivalent to those of the highly reactive B horizon soil (Meyer 1979; McDowell and Wood 1984). Addition of ferric chloride to stream microcosms (McDowell 1982) results in increased removal of DOC by Bear Brook sediments. In Norris Brook, another stream in the Hubbard Brook drainage, addition of aluminum chloride to the stream in field experiments resulted in decreased DOC concentrations in stream water (Hall et al. 1985). Dahm (1981) showed that in the Cascade Mountains of Oregon, significant abiotic adsorption of DOC by stream sediments occurs due to complexation by amorphous iron and aluminum oxides. Davis (1982) has also shown that significant amounts (up to 60%) of naturally occurring dissolved organic carbon can be removed from solution due to adsorption by alumina ($\gamma - Al_2O_3$). Thus, it seems likely that any abiotic retention of DOC by Bear Brook sediments is due to reaction with iron and aluminum oxides present in stream sediments.

Magnitude and fate of DOC removed during autumn

The amount of DOC removed from the water column during autumn leaf fall is small relative to the pool of organic matter in stream sediments. Total leaf input during autumn (direct fall and wind transport) is 411 $g\,m^{-2}$ (Fisher and Likens 1973). Assuming that average leaching of this litter is 15%, I estimate that the DOC input from autumn leaf fall is approximately 25 $g\,m^{-2}$ in Bear Brook. The organic carbon content of Bear Brook sediments (1 to 5 mm in diameter) is approximately 0.4%, and the bulk density is 1.4 $g\,cm^{-3}$. Assuming an average sediment depth of 10 cm, the organic carbon content of Bear Brook sediments is approximately 560 $g\,m^{-2}$. As the standing stock of organic debris in the stream channel is 350–540 $g\,C\,m^{-2}$ (Fisher and Likens 1973, Meyer 1978, Likens and Bormann 1979), the total standing stock of organic carbon in Bear Brook is approximately 1 $kg\,m^{-2}$. Despite the fact that leaf leachate is a significant fraction of total DOC inputs during autumn, leachate sorbed by stream sediments is equivalent to only 2% of total organic carbon in the stream bed, and thus could not be measured directly. Despite its apparent quantitative insignificance relative to total organic C in the stream channel, leachate DOC removed from the water column by biotic or abiotic means could be of significance in the establishment and maintenance of epilithic communities (Rounick and Winterbourne 1983).

If abiotic adsorption of DOC is in fact occurring in Bear Brook, the ultimate fate of this organic carbon becomes an intriguing question. Although in any given year adsorption of leaf leachate DOC represents a negligible fraction of total organic C in the ecosystem (2% as calculated above), over decades significant amounts of carbon would accumulate in the absence of removal mechanisms. Export of stream sediments during periods of high flow and replenishment of sediments by freshly eroded soil is one mechanism by which the stream could retain the capacity to adsorb DOC. Less than 12% of the DOC which is removed by stream sediments and organic debris is respired during the first 8 hours after leachate addition (Figure 7). Over a longer time period, however, much of this DOC may be metabolized by microorganisms. Adsorption of organic compounds on particulates in aquatic systems does not preclude their metabolism by microorganisms (Larson and Vashon 1983; Subba-Rao and Alexander 1982). Adsorption on particulate surfaces also can make dissolved organic matter available to invertebrates which are unable to assimilate the dissolved compounds directly (Arruda et al. 1983; Rounick and Winterbourne 1983).

Abiotic adsorption of DOC in Bear Brook appears to dampen temporal fluctuations in resource (carbon) availability. Much of the large pulse of DOC produced by the leaching of autumn-shed leaves is apparently retained within the ecosystem by abiotic mechanisms, thereby allowing the subsequent metabolism of this carbon by micro- and macroflora associated with the epilithon (Rounick and Winterbourn 1983; Lock et al. 1984). The extent to which biotic and abiotic coupling of DOC cycles occurs in other streams is not known at present, but the work of Dahm (1981) suggests that it may be considerable.

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References

Arruda, J.A., G.R. Marzolf, and R.T. Faulk. 1983. The role of suspended sediments in the nutrition of zooplankton in turbid reservoirs. Ecology 64:1225–1235.

Bilby, R.E. and G.E. Likens. 1979. Effect of hydrologic fluctuations on the transport of fine particulate organic carbon in a small stream. Limnology and Oceanography 24:69–75.

Bilby, R.E. and G.E. Likens. 1980. Importance of organic debris dams in the structure and function of stream ecosystems. Ecology 61:1107–1113.

Baldwin, J.M. and R.E. McAtee. 1974. Determination of organic carbon in water with a silver-catalyzed peroxydisulphate wet-chemical oxidation technique. Microchemical Journal 19:179–190.

Bott, T.J., J. Preslan, F. Finlay, and R. Brunker. 1977. The use of flowing-water microcosms and ecosystem streams to study microbial degradation of leaf litter and nitrilotriacetic acid (NTA). pp. 171–184 in Developments in Industrial Microbiology, Society for Industrial Microbiology.

Burney, C.M. and J. McN. Sieburth. 1977. Dissolved carbohydrates in seawater. II, A spectrophotometric procedure for total carbohydrate analysis and polysaccharide estimation. Marine Chemistry 5:15–28.

Cole, J.J. and G.E. Likens. 1979 Measurements of mineralization of phytoplankton detritus in an oligotrophic lake. Limnology and Oceanography 24:541–547.

Cole, J.J., W.H. McDowell, and G.E. Likens. 1984. Sources and molecular weight of 'dissolved' organic carbon in an oligotrophic lake. Oikos 42:1–9.

Cummins, K.W. 1974. Structure and function of stream ecosystems. Bioscience 24:631–641.

Cummins, K.W., and M.J. Klug. 1979. Feeding ecology of stream invertebrates. Annual Review of Ecology and Systematics 10:147–172.

Cummins, K.W., M.J. Klug, R.G. Wetzel, R.C. Petersen, K.F. Suberkropp, B.A. Manny, J.C. Wuycheck, and F.O. Howard. 1972. Organic enrichment with leaf leachate in experimental lotic ecosystems. Bioscience 22:719–722.

Dahm, C.N. 1981. Pathways and mechanisms for removal of dissolved organic carbon from leaf leachate in streams. Canadian Journal of Fisheries and Aquatic Sciences 38:68–76.

Dahm, C.N., A.K. Ward, and K.W. Cummins. 1985. Uptake of dissolved organic carbon in streams: effects of source and concentration. Canadian Journal of Fisheries and Aquatic Sciences (In press).

Davis, J.A. 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. Geochimica Cosmochimica Acta 46:2381–2393.

Fisher, S.G. and G.E. Likens. 1973. Energy flow in Bear Brook, New Hampshire: an integrative approach to stream ecosystem metabolism. Ecological Monographs 43:421–439.

Giesey, J.P. and L.A. Briese. 1978. Particulate formation due to freezing humic waters. Water Resources Research 14:542–544.

Gosz, J.R., G.E. Likens, and F.H. Bormann. 1973. Nutrient release from decomposing leaf and branch litter in the Hubbard Brook Forest, New Hampshire. Ecological Monographs 43:173–191.

Hall, R.J., C.T. Discoll, G.E. Likens and J.M. Pratt. 1985. Physical, chemical, and biological consequences of episodic aluminum additions to a stream ecosystem. Limnology and Oceanography 30:212–220.

Ishida, Y., I. Imai, T. Miyagaki, and H. Kadota. 1982. Growth and uptake kinetics of a facultatively oligotrophic bacterium at low nutrient concentrations. Microbial Ecology 8:23–32.

John, P.H. 1978. Discharge measurements in lower order streams. Internationale Revue der Gesamten Hydrobiologie 63:731–755.

Johnson, K.M., C.M. Burney, and J. McN. Sieburth. 1981. Doubling the production and precision of the MBTH spectrophotometric assay for dissolved carbohydrates in seawater. Marine Chemistry 10:467–473.

Johnson, K.M. and J. McN. Sieburth. 1977. Dissolved carbohydrates in seawater. I, A precise spectrophotometric analysis for monosaccharides. Marine Chemistry 5:1–14.

Johnson, N.M., G.E. Likens, F.H. Bormann, D.W. Fisher, and R.S. Pierce. 1969. A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New Hampshire. Water Resources Research 5:1353–1363.

Johnson, N.M., C.T. Driscoll, J.S. Eaton, G.E. Likens, and W.H. McDowell. 1981. 'Acid rain', dissolved aluminum and chemical weathering at the Hubbard Brook

Experimental Forest, New Hampshire. Geochimica Cosmochimica Acta 45:1421–1437.
Kaplan, L.A. and T.L. Bott. 1983. Microbial heterotrophic utilization of dissolved organic matter in a piedmont stream. Freshwater Biology 13:363–377.
King, G.M. and M.J. Klug. 1982. Glucose metabolism in sediments of a eutrophic lake: tracer analysis of uptake and product formation. Applied and Environmental Microbiology 44:1308–1317.
Kloster, M.B. 1974. Determination of tannin and lignin. Journal of the American Water Works Association 66:44–46.
Kuserk, F.T., L.A. Kaplan, and T.L. Bott. 1984. In situ measures of dissolved organic carbon flux in a rural stream. Canadian Journal of Fisheries and Aquatic Sciences 41:964–973.
Larson, R.J. and R.D. Vashon. 1983. Adsorption and biodegradation of cationic surfactants in laboratory and environmental systems. pp. 425–434 in Developments in Industrial Microbiology. Society for Industrial Microbiology.
Likens, G.E., F.H. Bormann, R.S. Pierce, J.S. Eaton, and N.M. Johnson. 1977. Biogeochemistry of a forested ecosystem. Springer-Verlag, New York.
Likens, G.E. and F.H. Bormann. 1979. The role of watershed and airshed in lake metabolism. Arch. Hydrobiol. Beih. 13:195–211.
Lock, M.A. and H.B.N. Hynes. 1975. The disappearance of four leaf leachates in a hard and soft water stream in south western Ontario, Canada. International, Revue der Gesamten Hydrobiologie 60:847–855.
Lock, M.A. and H.B.N. Hynes. 1976. The fate of 'dissolved' organic carbon derived from autumn-shed maple leaves (*Acer saccharum*) in a temperate hard-water stream. Limnology Oceanography 21:436–443.
Lock, M.A., R.R. Wallace, J.W. Costerton, R.M. Ventullo, and S.E. Charlton. 1984. River epilithon: toward a structural-functional model. Oikos 42:10–22.
Lush, D.L. and H.B.N. Hynes. 1978. The uptake of dissolved organic matter by a small spring stream. Hydrobiologia 60:271–275.
McArthur, J.V., G.R. Marzolf, and J.E. Urban. 1985. Response of bacteria isolated from a pristine prairie stream to concentration and source of soluble organic carbon. Applied and Environmental Microbiology 49:238–241.
McDowell, W.H. 1982. Mechanisms controlling the organic chemistry of Bear Brook, New Hampshire. Ph.D. thesis, Cornell University. 152 pp.
McDowell, W.H. 1984. Temporal changes in numbers of suspended bacteria in a small woodland stream. Verhandlugen Internationale vereinigung for theoretische and Angewandte Limnologie 22:1920–1925.
McDowell, W.H. and S.G. Fisher. 1976. Autumnal processing of dissolved organic matter in a small woodland stream ecosystem. Ecology 57:561–569.
McDowell, W.H. and T. Wood. 1984. Podzolization: Soil processes control dissolved organic carbon concentrations in stream water. Soil Science 137:23–32.
Menzel, D.W. and R.F. Vaccaro. 1964. The measurement of dissolved organic and particulate carbon in sea water. Limnology and Oceanography 9:138–142.
Meyer, J.L. 1978. Transport and transformation of phosphorus in a forest stream ecosystem. Ph.D. thesis, Cornell University.
Meyer, J.L. 1979. The role of sediments and bryophytes in phosphorus dynamics in a headwater stream ecosystem. Limnology and Oceanography 24:365–375.
Mickelburgh, S., M.A. Lock, and T.E. Ford. 1984. Spatial uptake of dissolved organic carbon in river beds. Hydrobiologia 108:115–119.
Newbold, J.D., J.W. Elwood, M.S. Shulze, R.W. Stark, and J.C. Barmeier. 1983. Continuous ammonium enrichment of a woodland stream: uptake kinetics, leaf decomposition, and nitrification. Freshwater Biology 13:193–204.
Payne, W.J. 1970. Energy yields and growth of heterotrophs. Annual Review of Microbiology 24:17–52.
Petersen, R.C. and K.W. Cummins. 1974. Leaf processing in a woodland stream. Freshwater Biology 4:343–368.
Rounick, J.S. and M.J. Winterbourn. 1983. The formation, structure, and utilization of

stone surface organic layers in two New Zealand streams. Freshwater Biology 13:57–72.

Stainton, M.P. 1973. A syringe gas-stripping procedure for gas chromatographic determination of dissolved inorganic and organic carbon in fresh water and carbonates in sediments. Journal of the Fisheries Research Board of Canada 30:1441–1445.

Subba-Rao, R.V. and M. Alexander. 1982. Effect of sorption on mineralization of low concentrations of aromatic compounds in lake water samples. Applied and Environmental Microbiology 44:659–668.

Suberkropp, K. and M.J. Klug. 1976. Fungi and bacteria associated with leaves during processing in a woodland stream. Ecology 57:707–719.

Taylor, A.W. and H.M. Kunishi. 1971. Phosphate equilibria on stream sediment and soil in a watershed draining an agricultural region. J. of Agricultural and Food Chemistry 19:827–831.

Toerien, D. and B. Cavari. 1982. Effect of temperature on heterotrophic glucose uptake, mineralization, and turnover rates in lake sediments. Applied and Environmental Microbiology 43:1–5.

Wallis, P.M., H.B.N. Hynes, and P. Fritz. 1979. Sources, transportation, and utilization of dissolved organic matter in groundwater and streams. Scientific Series No. 100. Inland Waters Directorate, Water Quality Branch, Ottawa, Canada.

Wood, T., F.H. Bormann, and G.K. Voigt. 1984. Phosphorus cycling in a northeastern hardwood forest: biological and chemical control. Science 223:391–393.