

Pathways and Mechanisms for Removal of Dissolved Organic Carbon from Leaf Leachate in Streams

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Removal of dissolved organic carbon (DOC) from water resulting from adsorption and microbial uptake was examined to determine the importance of biotic and abiotic pathways. Physical-chemical adsorption to components of the stream sediment or water and biotic assimilation associated with the microbial population was determined in recirculating chambers utilizing leachate from alder (*Alnus rubra*). Adsorptive mechanisms were further separated into interactions involving (1) specific clay minerals, (2) amorphous solid phases of hydrous aluminum and iron oxides, and (3) fine particulate organic matter. Physical-chemical adsorptive mechanisms for alder leachate removal exhibited rapid kinetic equilibration between the DOC and solid phases, but only a specific fraction of the DOC, likely containing certain chemical functional groups, was adsorbed. The amorphous aluminum and iron oxides possessed a much higher potential capacity than the clay minerals or fine particulate organics for DOC adsorption. Microbial uptake of DOC from the alder leachate was kinetically slower than adsorptive uptake. However, microbial activity was overall much more effective in the removal and degradation of the total DOC pool leached from alder leaves. Over a 48-h period, 97% of added ¹⁴C labeled leachate was removed from solution by adsorption (~20%) and microbial utilization (~77%). The rate of microbial uptake was 45 µg C/g sediment C·h⁻¹ or 14 mg C·m⁻²·h⁻¹.

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Afin d'évaluer l'importance des voies métaboliques biotiques et abiotiques, nous avons étudié l'enlèvement du carbone organique dissous (COD) de l'eau, résultant de l'adsorption et de l'assimilation microbienne. Un extrait par lessivage d'aulne (*Alnus rubra*) a été utilisé pour déterminer, dans des chambres de recirculation, l'adsorption physico-chimique aux composants du sédiment du cours d'eau ou l'assimilation aqueuse ou biotique associée avec la population microbienne. Les mécanismes d'adsorption ont été de plus subdivisés en interactions comportant (1) des minéraux spécifiques de l'argile, (2) des phases solides amorphes d'aluminium hydrique et d'oxydes de fer et (3) des matériaux organiques particuliers fins. Il y a équilibre cinétique rapide des mécanismes d'adsorption physico-chimique d'enlèvement de l'extrait d'aulne entre les phases COD et solides. Toutefois, seulement une fraction spécifique de COD, contenant probablement certains groupes fonctionnels chimiques, est adsorbée. L'aluminium amorphe et les oxydes de fer possèdent une capacité potentielle de beaucoup supérieure à celles des minéraux argileux ou des matériaux organiques particuliers fins pour l'adsorption du COD. L'assimilation microbienne du COD de l'extrait d'aulne est cinétiquement plus lente que l'assimilation par adsorption. Cependant, l'activité microbienne est dans l'ensemble beaucoup plus efficace dans l'enlèvement et la dégradation de la masse totale de COD extraite par lessivage des feuilles d'aulne. Sur une période de 48 h, 97% de l'extrait marqué au ¹⁴C ajouté avait été enlevé de la solution par adsorption (approximativement 20%) et utilisation microbienne (approximativement 77%). Le taux d'assimilation microbienne est de 45 µg C/g de sédiment C·h⁻¹ ou 14 mg C·m⁻²·h⁻¹.

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THE importance of dissolved organic carbon (DOC) in aquatic ecosystems is becoming increasingly apparent. Quantitatively, DOC is by far the most abundant form of reduced carbon in streams (Hobbie and Likens 1973; Wetzel and Manny 1977; Lush and Hynes 1978a; Moeller et al. 1979; Triska et al. 1980), rivers (Williams 1968; Malcolm and Durum 1976; Klotz and Matson 1978; Naiman and Sibert 1978), lakes (Wetzel and Rich 1973; Rich and Wetzel 1978), estuaries (Stephens 1967; Head 1976; Happ et al. 1977), and oceans (Williams 1975). The pathways and mechanisms for cycling these large pools of DOC represent critical transfers in the energetics of all aquatic ecosystems. In particular, processes which incorporate DOC into particulate form where either mineralization or further transfer up the food chain can occur are important steps in the transformation of DOC in these aquatic environments. Information which can differentiate physical-chemical processes of adsorption, flocculation, and aggregation of DOC from microbial uptake for a variety of heterogeneous natural inputs is needed. Knowledge of the mechanisms and factors controlling the uptake and degradation of the DOC load is essential.

For small headwater streams in relatively undisturbed localities, DOC plays an important role in stream budgets. Hobbie and Likens (1973) estimated 79 and 88% of the organic carbon export in two small northeastern U.S. watersheds to be in the dissolved state. Fisher and Likens (1973) calculated an annual energy budget for a second-order northeastern stream in which export was 70% dissolved organic matter (DOM). In Augusta Creek of southwestern Michigan, 75% of the carbon in transport was DOC (Wetzel and Manny 1977). Triska et al. (1980) presented data for two years from a high-gradient first-order stream in the Oregon Cascades which showed DOM to comprise 72 and 56% of total carbon export. DOC exceeds POC transport for streams throughout a wide geographical range and generally includes between 60 and 90% of the total carbon.

The chemical nature of the DOC in aquatic ecosystems is still largely unknown, primarily because the heterogeneous mixture composing DOM defies separation and identification. Larson (1978) was able to classify only about 20% of the DOM as lipids, carbohydrates, phenols, proteins, or amino acids, after extensive effort on samples from a small Pennsylvania stream. Although potential sources for this DOM are numerous, soil eluates, leaf leachates, decomposing wood, aquatic plant material (algal and macrophytic), and decomposing forest litter likely provide major inputs for undisturbed streams. The degree of contribution from each of these sources will vary with the season and between systems. For example, McDowell and Fisher (1976) estimated that 42% of the total DOM in autumn for a small New England stream in a deciduous forest was derived from leaf litter. In streams where primary production exceeds respiration (Min-

shall 1978), the proportion of DOM derived from algal and macrophytic plants would likely be increased.

Studies involving leaf leachate utilization have included both chamber and field estimates. Cummins et al. (1972) and Wetzel and Manny (1972) followed a number of chemical and biological variables in a large artificial stream following a 30-h exposure to hickory (*Carya glabra*) and maple (*Acer saccharinum*) leaves. Lock and Hynes (1975, 1976) studied the disappearance of DOC from four leaf species in small circulating bowls with and without sediment, under sterile and unsterilized conditions, and with soft and hard water. Bott et al. (1977) studied microbial uptake of DO^{14}C from white oak (*Quercus alba*) leaves in a small recirculating chamber. A field study using a mass balance approach (McDowell and Fisher 1976) calculated that 77% of autumnal leaf leachate was taken up during a 77-d period. Another field experiment in a small spring stream, utilizing eastern white cedar (*Thuja occidentalis*) and sugar maple (*Acer saccharinum*) leachate calibrated against a conservative tracer (Na), measured 36–86% leachate uptake in about 1 h (Lush and Hynes 1978b). In all studies, a major fraction of the entering leaf leachate was removed from solution during the first few hours after addition.

Exact mechanisms, rates, and pathways of DOC removal for various compounds extracted from the leaf matrix remain obscure. Microbial uptake undoubtedly accounts for a significant fraction of the disappearance (Lock and Hynes 1975, 1976; Bott et al. 1977). However, Lush and Hynes (1973) demonstrated that abiotic reactions affected by pH, water chemistry, leaf species, and temperature could cause a DOC drop of as much as 50% over 2.5 d. Lock and Hynes (1976) found that precipitation of maple leaf leachate in distilled water is negligible, but amounted to 20–25% in well water. When sediment was added, removal of maple leaf DOC increased dramatically with 85% removal in 24 h, and 98% in 48 h. The locus for sediment uptake was suggested to be at least 40%, and possibly up to 100% microbial. However, their experiment utilizing Tyndallized sediment suggested 30–40% abiotic uptake. Like biotic processes, abiotic uptake of DOC by stream sediment is expected to show a wide variation in efficiency dependent on numerous variables. Factors affecting abiotic uptake may include clay types, sediment size distribution, pH, redox potential, water hardness, and organic content.

In the Pacific Northwest, particularly in the coastal streams and rivers and in the riparian zones of clear-cut forests, red alder (*Alnus rubra*) frequently dominates streamside vegetation. Therefore, leachate from alder was chosen as the DOC source in experiments designed to assay microbial and physical-chemical processes of DOC removal from the water column. Estimates for both the quantity of DOC removed and the relative rate of removal by abiotic and biotic pathways was sought. The physical-chemical mechanisms for uptake were further separated into interactions involving (1) specific

clay minerals, (2) amorphous solid phases of hydrous aluminum and iron oxides, and (3) fine detrital particulate organic matter. These phases, in association with the microbial population, were considered to be the most important pathways for DOC uptake in streams of low dissolved solids and near neutral pH, characteristic of western Oregon. Therefore, the purpose of the study was to differentiate between abiotic and biotic uptake of DOC in streams and to provide rate information for these removal mechanisms for a common DOC source.

Materials and Methods

Red alder leaves were collected just before abscission. The leaves were dried 48 h at 50°C and then stored in a desiccator until use. The DOC solution was produced by 12 h of leaching at room temperature in filtered distilled water with constant agitation. Some microbial activity in the leachate solution involving primarily the more labile fractions surely occurred (e.g. Cummins et al. 1972; Wetzel and Manny 1972), but with uniform techniques, time, and temperature, these problems were minimized. The resultant DOC must, though, be considered to be partially depleted in the most labile compounds initially leached from the leaves. High-temperature extraction techniques were avoided, both to duplicate as closely as possible stream leaching conditions and to avoid enhanced denaturation and solubilization brought on by elevated temperature. Alder leaves labeled with ^{14}C were grown from seedlings in a $^{14}\text{CO}_2$ enriched atmosphere and leached in the same manner.

The secondary clay minerals used in adsorption studies were pure X-ray diffraction standards from Ward's Natural Sciences. Chlorite, kaolinite, and montmorillonite clays saturated with sodium were tested. Sufficient clay was used in the adsorptive experiments to preclude saturation of available uptake sites at the clay surface. Semiquantitative information on the clay mineralogy of Cascade stream sediments was obtained, after density separation and saturation with K and Mg, by X-ray diffraction from a $\text{CuK}\alpha$ radiation source (Harward et al. 1969).

The removal capacity of amorphous hydrous aluminum and iron was tested using pure electrolytically plated iron and high purity aluminum wire dissolved in redistilled 5 mol/L HCl. Small aliquots of concentrated aluminum or iron standards were added to known amounts of alder leachate and adjusted to pH 7 with 0.1 mol/L NaOH. The samples were agitated for 3 min, filtered, and Al, Fe, and DOC in the precipitate and solution were measured. A modified ferrozine method was used for Fe determinations (Stookey 1970; Murray and Gill 1978), a catechol violet method for Al (Dougan and Wilson 1974), and wet oxidation by potassium persulfate to CO_2 with subsequent determination by infrared analyzer for DOC (Menzel and Vaccaro 1964).

The definition used in this paper for DOC is the organic carbon passing through a 0.4- μm Nucleopore[®] filter. This is an arbitrary definition with many colloidal size particles, not truly dissolved organic molecules, smaller than this cutoff (Lock et al. 1977). Use of this traditional demarcation allows comparison with previous work. In a few cases, where leachate uptake was being tested in solutions containing high concentrations of clay particles, centrifugation

at 3000 rpm for 5 min was used in lieu of filtration, since clogging was unavoidable.

Mercuric chloride (HgCl_2) was added at a concentration of 100 mg/L in all experiments where microbial processes were to be inhibited. An occasional plate count was performed to verify the lack of bacterial activity.

The determination of the amount of amorphous solid in 12 first-order stream sediment samples and one seep, located in coniferous forests on the west slope on the central Cascade Mountains of Oregon (Dahm 1980) utilized successive extraction with an oxalate buffer of pH 3 for 2 h in the dark, followed by 3 min of boiling in 1 mol/L KOH solution (Dudas and Harward 1971). Only the finer particles of sediment, consisting of material passing through a 75- μm sieve, were analyzed. The oxalate buffer preferentially removes amorphous Fe, while the KOH solution extracts uncrystallized Al phases. The difference in sample weight before and after treatment, adjusted for the loss of organic material, estimates the amorphous inorganic sediment content.

Field studies investigating the uptake of DO^{14}C by stream sediment were performed in Oak Creek, a third-order stream. Stream sediment was carefully extracted from the upper 5 cm of a pool and sieved through a 4-mm sieve. One portion of the sediment was cleaned of organic material by repeated application of 35% hydrogen peroxide (H_2O_2). The cleaning process lowered the organic content from 2.6 to 0.6%. The sediment with low organic content from H_2O_2 oxidation and a second untreated aliquot of sediment were poisoned with HgCl_2 . About 1.4 kg of sediment including (1) freshly sieved unpoisoned sediment, (2) the HgCl_2 poisoned sediment, and (3) the H_2O_2 organic cleaned and HgCl_2 poisoned sediment were added to Plexiglas[®] chambers with a recirculating pump (Bott et al. 1978). Ten litres of low organic carbon water was added to each chamber and the alkalinity adjusted to 30 mg CaCO_3/L , resulting in a pH between 7.1 and 7.4 for each chamber. These values for pH and alkalinity are within the range of measured values for streams in western Oregon. The chambers measure 38 cm long, 31 cm wide, and 10 cm high with a bottom surface area of 0.12 m^2 .

After 24 h of instream equilibration, 500 mL of ^{14}C labeled alder DOC, leached 12 h at room temperature, was added to each chamber. The alder leachate increased the DOC concentration 9.8 mg C/L. Samples were drawn every 5 min initially, with progressively longer sampling intervals during the first 24 h, and then every 4 h on the 2nd day. Samples were filtered on pre-rinsed 0.4- μm Nucleopore[®] filters and analyzed for total ^{14}C activity, DO^{14}C , and DOC. The DO^{14}C was determined by acidifying the sample with 0.4 mL of 3% H_3PO_4 and purging with O_2 for 5 min to remove $^{14}\text{CO}_2$. The $^{14}\text{CO}_2$ was determined by difference. The cocktail consisted of a 10-mL water sample and 10 mL of New England Nuclear Aquasol II[®]. Samples were radioassayed by liquid scintillation techniques (Beckman LS-150) and corrections for background radioactivity and differences in counting efficiency were made.

Results and Discussion

The clay minerals to be tested for their capacity to adsorb dissolved organic carbon from alder leachate were determined by X-ray diffraction of sediment from four Cascade Mountain streams. The predominant

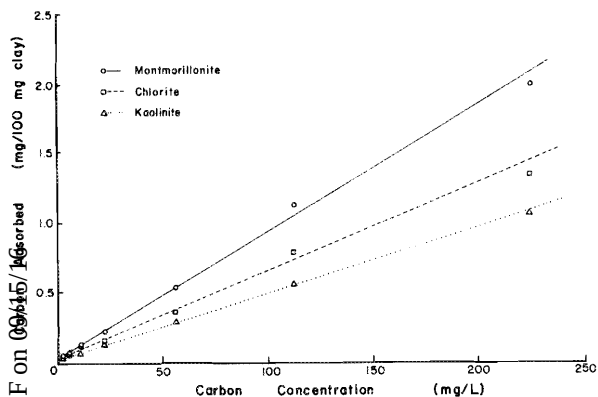


Fig. 1. Adsorption of DOC from alder leachate by montmorillonitic, chloritic, and kaolinitic clays. Exchange positions on the clays were saturated with sodium.

Crystalline clay found in all sites was an intergraded chlorite (Singleton and Harward 1971). Secondary peaks for montmorillonite clay also were seen at each site. At two sites, traces of kaolinite also were present. Therefore, the crystalline clays chlorite, montmorillonite, and kaolinite were examined for their capacity to adsorb DOC leached from alder leaves.

Montmorillonite was most efficient in removing DOC from solution at pH 7 (Fig. 1), followed by chlorite then kaolinite. The adsorptive capacity of montmorillonite accounted for about 0.8% of the available DOC leached from alder leaves over a concentration range of 2–224 mg C/L. The adsorptive uptake of DOC by chlorite was about 0.6%, and for kaolinite 0.5%. The vast majority of the DOC resulting from the leaching of a nitrogen-rich deciduous leaf was not susceptible to physical-chemical bonding to solid clay surfaces of montmorillonite, chlorite, and kaolinite. Adsorption to crystalline clay minerals by only a small fraction of the organic compounds released by leaching of leaf material is indicated. If significant displacement of DOC from solution to the sediment is the result of abiotic processes, sediment components in addition to crystalline clays must be participating.

Studies with soil solutions (Inoue and Wada 1968; Wada 1977) have documented the high adsorptive capacity of uncrystalline amorphous clays and crystalline clays coated with amorphous inorganic material for dissolved organic matter, particularly humic and fulvic acids. The reduced resolution and peak heights of the X-ray diffraction patterns for the clay samples extracted from the four Cascade streams indicated a high percentage of poorly crystallized amorphous material. This observation was quantified by measuring the weight loss from fine detritus, collected from 12 first-order streams and one seep, after successive acidic and alkaline dissolution treatments (Dudas and Harward 1971). The resulting weight loss, corrected for the loss of particulate organic matter, ranged from 7.9 to

TABLE 1. Distribution of amorphous material in the sediment fraction passing through a 75- μ m sieve and collected on a 0.4- μ m filter paper for 12 first-order streams and one seep, with the percentage of Fe plus Al in the amorphous phase. The sites are all first-order streams in coniferous forests on the west slope of the central Oregon Cascades about 70 km east of Eugene, Oregon.

Site	Amorphous content (%)	Fe + Al in amorphous material (%)
Elk Meadow seep	9.8	23.1
Elk Meadow	11.8	13.0
WS 10	7.9	14.6
Q101A	14.8	8.3
WS1	27.4	4.2
Ennis	22.8	4.5
B301	17.4	6.3
Doe	24.4	4.2
Quartz	9.6	12.1
Behms	12.1	12.3
Burwell	18.1	9.1
WS 2	10.2	9.7
WS 9	12.0	12.2

27.4% (Table 1). Much of this amorphous material was thought to consist of uncrystallized aluminosilicate clays and hydrous oxides of iron and aluminum. Subsequent analysis of the extracted phase showed iron plus aluminum to constitute from 4.2 to 23.1% of the amorphous fraction (Table 1). The Elk Meadow seep sample was the most enriched in percentage amorphous iron and aluminum. The high percentage of amorphous material in the fine sediment is potentially a significant adsorbent of DOC, either by coprecipitation when dissolved metals enter oxygenated and neutral pH water or through adsorption to the amorphous material coating sediment surfaces.

Laboratory studies to assess the maximum potential for alder leachate uptake associated with the hydrous oxides of aluminum and iron and a montmorillonite clay saturated with iron in the cation-exchange positions at pH 7 (Scharpenseel 1968; Theng and Scharpenseel 1975) were carried out in DOC solutions from 2 to 232 mg C/L. The carbon adsorbed (in milligrams per 100 milligrams of clay or metal) in the presence of excess metal or clay increased markedly over the crystalline clay uptake for both hydrous aluminum and iron oxides and montmorillonite pretreated with the amorphous iron coating (Fig. 2). Hydrous aluminum oxide was most effective as an adsorbent, removing ~33% of the carbon in solution. The hydrous iron oxide and montmorillonite clay perfused with amorphous iron were not significantly different, with a removal capacity of 26% of available DOC. This percentage was much greater than the 0.8% removal by sodium-saturated montmorillonite alone. The amorphous phases of hydrous aluminum and iron oxide, either precipitating from the water column, where significant inputs occur, or associated with the sediment

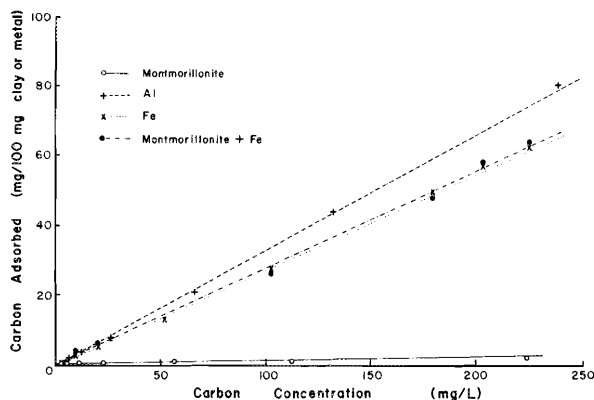


FIG. 2. Adsorption of DOC from alder leachate by amorphous precipitates of Fe and Al and a montmorillonitic clay saturated with Fe. The adsorption by montmorillonitic clay saturated with sodium from the previous figure is shown for reference.

are potential sites for abiotic physical-chemical adsorption of one-quarter to one-third of the DOC released from alder leaves.

In assessing the capability for adsorption by the crystalline clays and amorphous hydrous metal oxides, an apparent linear relationship between the adsorption by weight as a function of DOC concentration resulted (Fig. 1 and 2). The form of these lines is strongly influenced by measurements made at DOC concentrations in excess of 10 mg C/L. In undisturbed streams and rivers, DOC concentration is rarely above 10 mg C/L (Moeller et al. 1979) and increases in DOC concentration measured following leaf abscission in autumn is unlikely to exceed 1–2 mg C/L (McDowell and Fisher 1976). Therefore, the accuracy of DOC uptake curves at low DOC concentration is critical for estimating potential abiotic uptake by the sediment. For low concentrations of DOC, the maximum precision of the wet oxidation method (Menzel and Vaccaro 1964) of analysis is approached. Use of uniformly labeled ^{14}C substrates may provide the necessary sensitivity to overcome the analytical problems and assess the linearity of abiotic DOC uptake at low concentrations.

An additional potential site for abiotic uptake of DOC is the particulate organic detritus of the sediment. Stevenson (1972) and Jackson et al. (1978) reviewed the capacity of humic acids to absorb hydrophobic organic compounds, especially toxic pesticides and herbicides. Khan and Schnitzer (1972) concluded that humic acid can firmly bind 2% or more by weight of hydrophobic organic compounds. For specific types of organic compounds, adsorption by humic colloids and particles may be a key factor in transport and breakdown.

Although abiotic uptake of alder leachate, primarily associated with amorphous components of the sediment, can potentially remove a significant fraction of the released DOC, a large percentage remains in solu-

tion. This fraction is either degraded by the microbial community in solution or at the sediment-water interface, or exported from the ecosystem. Utilizing a radioactively labeled ^{14}C alder leaf leachate, the rates and efficiency of DOC uptake with both an untreated sediment and the same sediment poisoned by HgCl_2 were measured. In addition, a third chamber was tested in which the sediment was pretreated with H_2O_2 to oxidize the particulate detrital organic material, and also poisoned with HgCl_2 . Any increased DOC uptake by the poisoned chamber with particulate organic material over the chamber cleaned of organic material with H_2O_2 is attributable to particulate organic-dissolved organic interaction.

The initial response in each chamber, following the introduction of the labeled alder leachate, was a rapid decrease in DO^{14}C activity occurring predominantly in the first 10 min (Fig. 3). The decrease in the first 10 min removed between 18 and 23% of the DO^{14}C in each chamber, and represents abiotic displacement of one fraction of the alder leachate to sedimented or suspended particles larger than $0.4\ \mu\text{m}$. The sediment in the poisoned chambers displayed no further DO^{14}C uptake over the 48 h of the experiment. Water in the unpoisoned chamber, after about 1 h, began a steady decrease in DO^{14}C activity. Fifty percent of the labeled organic fraction had been removed by 9.3 h after addition and 90% uptake was measured at 31.1 h. Within 48 h, 97% of the initial DO^{14}C activity was taken up by the sediment.

Radiocarbon removed from solution as DO^{14}C by the microbial population can either be incorporated into microbial biomass or metabolized and respired as $^{14}\text{CO}_2$. A measurable respiration response from the unpoisoned sediment appeared about 6 h after the leachate addition (Fig. 3). No measurable $^{14}\text{CO}_2$ was detected in either of the poisoned chambers. Metabolic $^{14}\text{CO}_2$ in the unpoisoned system increased steadily, after the 6-h lag period, until 22% of the labeled carbon was present in the inorganic carbon fraction. The fraction of DO^{14}C incorporated into microbial biomass is 57% over 48 h, assuming all of the rapid initial abiotic uptake of DO^{14}C is held unavailable to the microbial flora. Abiotic adsorption of DO^{14}C does not necessarily preclude eventual microbial uptake or mineralization, so the estimate of 57% for DO^{14}C incorporation into microbial tissue may be underestimated.

Abiotic decrease of the radiocarbon label from solution could result either through an actual decrease in the DOC concentration or through exchange reactions between labeled compounds in solution and unlabeled adsorbed particulate organic carbon. If the adsorptive uptake of the DOC is dominated by (1) exchange reactions on the surfaces of the sediment with inorganic cations or anions, (2) formation of stable insoluble complexes with dissolved species in solution, or (3) bonding at the interface of solution and solid surfaces, total DOC concentration in solution will show a concomitant drop. However, if the DO^{14}C uptake is

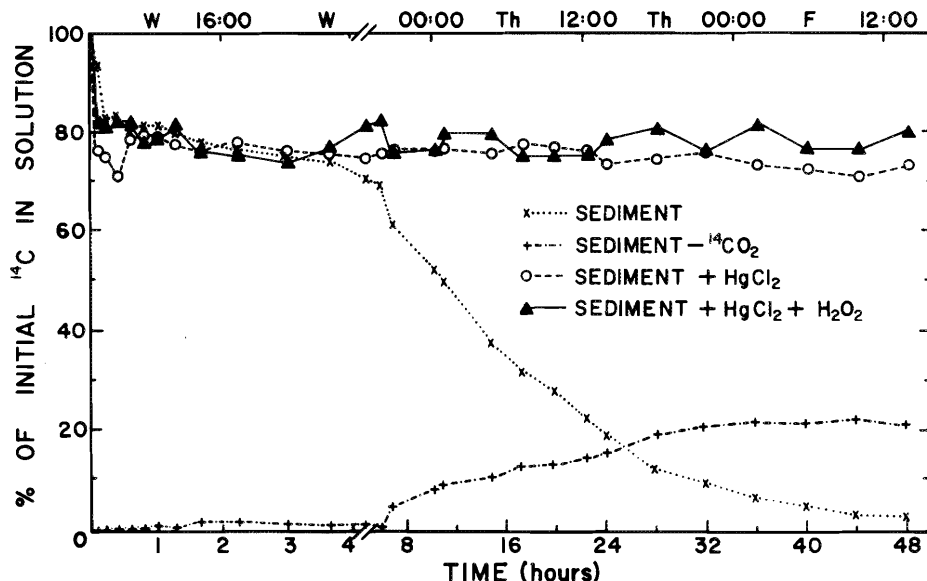


FIG. 3. Uptake of radiocarbon from leachate derived from labeled alder leaves in three recirculating chambers filled with stream sediment and water. Two chambers were poisoned, one with particulate organic matter present and the other with it removed. One chamber was left untreated. In addition, the concentration of $^{14}\text{CO}_2$ from microbial respiration in the untreated chamber is shown.

the result of exchange reactions with adsorbed organic material, total DOC concentration will be reduced less than DO^{14}C activity. In all three recirculating chambers, a definite drop in DOC concentration occurred over the first 2 h (Fig. 4). Leachate concentration was calculated to increase the DOC concentration in each chamber by 9.8 mg C/L. The equilibrium DOC concentration before leachate addition for the sediment, sediment plus HgCl_2 , and sediment plus HgCl_2 and H_2O_2 treatments was 1.4, 3.6, and 5.8 mg C/L, respectively. Two hours following addition of the DOC, there was a 34, 25, and 21% removal of total DOC from the unpoisoned, poisoned, and poisoned plus H_2O_2 oxidized treatments, respectively. In each treatment, decreases in total DOC concentration approximated DO^{14}C uptake closely enough to indicate primarily DOC uptake, and not predominantly exchange of the radioactive compounds with unlabeled sediment organic matter. The small total DOC increase during times of peak sunlight intensity in the unpoisoned chamber may be a result of algal excretion (Jackson and Volk 1970), although algal biomass was small. Previous work on the capacity of crystalline clays to adsorb DOC affirms the generally low affinity measured between alder leachate and kaolinite, chlorite, and montmorillonite. Evans and Russell (1959) studied the adsorptive capacity of bentonite and kaolinite saturated with various cations for soil fulvic and humic acids. Kodama and Schnitzer (1974) reported adsorption of fulvic acid on kaolinite at pH 6.5 ranging from 2.2 to

3.4% by weight with increased adsorption on smaller clay particles. Rashid et al. (1972) measured adsorption of a marine humic acid on chlorite and kaolinite and in no cases did adsorption exceed 0.4% by weight. Theng and Scharpenseel (1975) measured 2% adsorp-

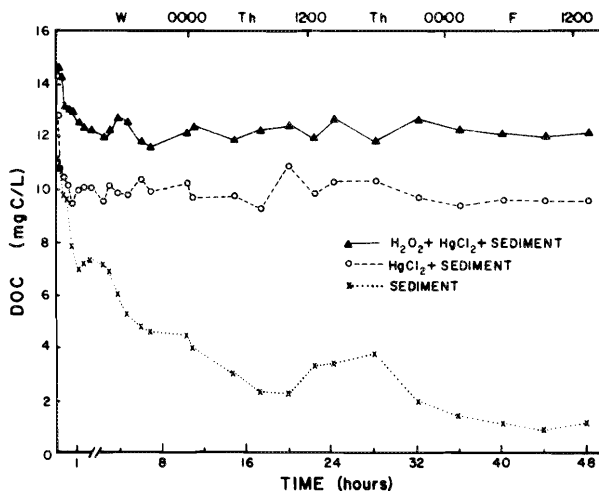


FIG. 4. Concentration of DOC in each recirculating chamber throughout period when radiocarbon uptake was measured. A concentration increase in DOC of 9.8 mg C/L was initially added to each chamber by the alder leachate. Differences in initial concentration of DOC in each chamber resulted from unequal background levels of DOC.

tion of soil humic acid on sodium-saturated montmorillonite. Hedges (1977) tested the uptake capacity of the organic compounds glucose, valine, and stearic acid on kaolinite and montmorillonite. Glucose and valine were not appreciably removed by either clay, but stearic acid was removed from 13 to 46% by weight over a concentration range of 0.1 to 1.0 mg/L. Alder leachate removal by the crystalline clays chlorite, kaolinite, and montmorillonite was uniformly low, below values reported for soil fulvic and humic acids (Fig. 1). The heterogeneous mixture of organic compounds released during leaching of alder leaves contained few compounds structurally susceptible to adsorption by the crystalline clays tested.

Rather than adsorption to crystalline clays, abiotic uptake of alder leachate was focused in the amorphous solids of the sediment and water column, which are largely composed of hydrous aluminum and iron oxides (Table 1). Greenland (1971) argued that humic and fulvic acid association with clay minerals in soils is governed by polyvalent metals at the clay surface, particularly iron and aluminum hydroxides. These bridging cations of hydrous aluminum and iron can adsorb certain defined organic structures. Levashkevich (1966) demonstrated this adsorptive capacity between freshly precipitated iron and aluminum hydroxides and soil fulvic acids. Iron and aluminum hydroxide adsorbed 20–32 mg and 47–59 mg per 100 milligrams, respectively, at pH 5.0–5.5. Theng and Scharpenseel (1975) have documented the efficiency of ^{14}C labeled humic acid adsorption on montmorillonite with various bridging cations at the saturation sites. Fe^{+3} and Al^{+3} produce the greatest increase in uptake capacity. These results are in agreement with the measured alder leachate uptake by freshly precipitated iron and aluminum hydroxide and iron-saturated montmorillonite (Fig. 2).

In the field tests utilizing recirculating chambers, most of the alder leachate loss was from microbial uptake (Fig. 3). A significant and kinetically rapid abiotic removal occurred within minutes of the introduction of alder leachate, but overall disappearance over 48 h was primarily microbial. Cummins et al. (1972) and Lock and Hynes (1975, 1976) also attributed leaf leachate uptake in microcosm experiments to be primarily microbial. In addition, Sepers (1977) concluded that the utilization of dissolved organic compounds in aquatic environments is primarily attributable to the bacterial portion of the microbial community. For alder leachate, only 3% remained in solution after 2 d. The capacity of the microbial population for processing a diverse variety of organic structures from solution is clear. Rapid equilibration of the leachate with particular phases resulted in abiotic displacement to the sediment of one organic fraction released by the leaching process, where accumulation or microbial processing can proceed. However, direct uptake from solution by the microbial community removed the greatest

proportion of leached alder under the experimental conditions.

The biotic and abiotic rate and efficiencies of uptake of DOC are linked to numerous physical, chemical, and biological factors. Temperature, organic substrate concentration and structure, concentration of inorganic compounds such as nitrogen and phosphorus, grazing impacts from invertebrates and protozoans, pH, E_h , sediment type, and sediment size are examples of parameters potentially exerting an important influence on bacterial activity. Abiotic mechanisms of uptake are also influenced by pH, E_h , ionic strength of the solution, cation-exchange capacity and saturating cations in the sediment, concentration of amorphous phases, temperature, sediment and clay types, DOC concentration and structure, and the concentration of divalent and trivalent cations such as Al, Fe, Ca, and Mg, both in solution and in the sediment. Attempts to compare results obtained under widely varying physical and chemical environments, both in the sediment and the water, should not lose sight of the inherent problems these variables can present.

Reported rates of leaf leachate DOC uptake both in microcosms and field experiments range over almost two orders of magnitude (Table 2). The rate of alder leachate removal in this study was $18 \text{ mg C} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, and is at the lower end of uptake rates reported. If abiotic adsorption is subtracted from the total, microbial uptake is $14 \text{ mg C} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. A second method for expressing DOC uptake is based on the organic fraction as the center of biotic removal. Uptake of DOC then is calculated at $45 \mu\text{g C/g sediment C} \cdot \text{h}^{-1}$. Alternately, if the total uptake rate is calculated over the first 9 h of the experiment (corresponding to the time length used by Lock and Hynes 1975), the rate becomes $43 \text{ mg C} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. Clearly, the degree of initial DOC enrichment and the length of the experiment are important variables in a rate calculation, particularly where rapid abiotic uptake is coupled with microbial uptake, or where the organic substrate is markedly diminished during the early phases of the experiment. A removal rate calculated over the first 20 min following the alder leachate addition, when maximum abiotic removal occurred, is $442 \text{ mg C} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, similar to the rates determined by Lush and Hynes (1978b) in their field experiment. Although uptake rates of DOC vary widely depending upon ambient physical and chemical conditions, rapid and efficient removal of the majority of the DOC was observed in all cases. Inputs of DOC to streams from allochthonous riparian vegetation are removed and processed such that only a small fraction of this DOC is transported from the ecosystem. The focus for this uptake and processing is centered in the stream sediment and is largely microbial.

The rate and efficiency with which DOC is converted to bacterial biomass or adsorbed to particles control where in the stream system the DOC becomes available as potential food. Conversion to bacterial

TABLE 2. Calculated rates of leaf leachate uptake per unit area per hour for reported microcosm and field experiments.

DOC source	Time, h	Uptake rate, mg C·m ⁻² ·h ⁻¹	Reference	Comments
Hickory (<i>Carya glabra</i>) and maple (<i>Acer saccharum</i>)	48	220	Cummins et al. (1972) and Wetzel and Manny (1972)	178-209 mg CaCO ₃ /L pH = 8.0-8.4 Large, recirculating stream
Aspen (<i>Populus tremuloides</i>)	9	120	Lock and Hynes (1975)	225 mg CaCO ₃ /L
Aspen (<i>Populus tremuloides</i>)	9	110	" " " "	5 mg CaCO ₃ /L
Maple (<i>Acer saccharum</i>)	9	73	" " " "	225 mg CaCO ₃ /L
Maple (<i>Acer saccharum</i>)	9	50	" " " "	5 mg CaCO ₃ /L
Pine (<i>Pinus resinosa</i>)	9	40	" " " "	225 mg CaCO ₃ /L
Pine (<i>Pinus resinosa</i>)	9	10	" " " "	5 mg CaCO ₃ /L
Cedar (<i>Thuja occidentalis</i>)	9	28	" " " "	225 mg CaCO ₃ /L
Cedar (<i>Thuja occidentalis</i>)	9	23	" " " "	5 mg CaCO ₃ /L
Cedar (<i>Thuja occidentalis</i>)	0.5	270	Lush and Hynes (1978)	Recirculating chamber 200 mg CaCO ₃ /L
Maple (<i>Acer saccharum</i>)	0.5	250-550	Lush and Hynes (1978)	pH = 7.8 Field experiment
Alder (<i>Alnus rubra</i>)	48	18	This paper	30 mg CaCO ₃ /L
Alder (<i>Alnus rubra</i>)	9	43	This paper	pH = 7.4 Temp. = 15°C
Alder (<i>Alnus rubra</i>)	0.3	442	This paper	Recirculating chamber

biomass and particles efficiently retains most of the potential energy from alder leachate in a utilizable form for organisms otherwise unable to assimilate directly DOC. The efficiency and rate at which retention mechanisms operate upon other likely sources of DOC, such as aquatic plant lysates, soil eluates, conifer leachate, products of wood decomposition, and root exudates, need to be measured. If most DOC entering streams is normally susceptible to efficient and rapid biotic or abiotic uptake, the biological significance of total DOC analysis is questionable. Instantaneous measurements of DOC concentrations are probably often dominated by refractory compounds which are less readily utilized than the quantitatively less-abundant labile fraction. Compounds not adsorbed to soil or sediment and resistant to microbial degradation may constitute much of the total analyzed DOC, while the tightly cycled and strongly retained subfraction comprises the portion of biological import. Future research should consider not merely the total DOC in solution, but concentrate on the quantity, quality, retention, and turnover of the biotically active fraction in stream ecosystems.

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