Comparison of the behavior of soluble organic and inorganic nutrients in forest soils

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Abstract

The mechanisms by which potentially soluble inorganic nutrients are retained and eventually recycled within ecosystems have been characterized by many studies. Substantial amounts of potentially soluble organic nutrients are also released as plants grow, die, and decompose. In this study, a conceptual model was developed which shows the pools and significant processes generating and consuming dissolved organic matter and the associated nutrient elements. Experiments showed that the pool of potentially soluble organic matter in both mineral and organic horizons was much larger than the amount dissolved by any individual leaching event. Adsorption had the effect of buffering concentrations of dissolved organic matter in both mineral and organic horizons. The sorption equilibrium also slows the leaching rate of potentially soluble organic matter. By increasing the residence time of potentially soluble organic matter on solid surfaces, sorption results in a much greater time of exposure of soluble organic matter to decomposers while in the sorbed state. Literature sources indicate a bimodal distribution of decay coefficients of dissolved organic C and N with a refractory fraction dominating. A set of hypotheses comparing the factors controlling retention of inorganic vs. organic nutrients was developed. These hypotheses related to: sources of dissolved nutrients; properties of molecules controlling behavior; biological removal from solution; non-biological removal from solution and major factors allowing loss from the system. The major factor allowing loss of organic nutrients from the ecosystem is hydrologic short circuiting or absence of a mineral soil horizon rich in Fe and Al oxyhydroxides whereas, in the case of inorganic nutrients, it is hydrologic short circuiting or absence of a root network in addition to geochemical factors.

Keywords: Dissolved organic carbon; Dissolved organic nitrogen; Dissolved organic phosphorus; Adsorption; Decomposition; Nutrient cycling; Biogeochemistry

1. Introduction

Much of the emphasis on the cycling and leaching of nutrients in forests has been focused on inorganic nutrients. Essential limiting nutrients bound in organic forms are often not considered as being susceptible to leaching either because living cell membranes efficiently retain organic solutes or because many organic substances (e.g. lignin and cellulose) are virtually insoluble. Soluble organic nutrients are released, however, as vegetation grows, dies, and decomposes. For example, 22–41% of the C in freshly fallen autumn leaf litter in a deciduous forest was soluble in water (Qualls et al., 1991). Even such insoluble material as lignin in wood can generate substantial quantities of soluble organic matter as it is degraded by the white rot fungus Phanaerochaete chrysosporium (Reid et al., 1982).

This paper will emphasize the microbial nutrient carbon and the plant/microbial nutrient nitrogen carried by molecules of soluble organic matter. The scanty data which exists on dissolved organic P will...
also be discussed. While the emphasis of several experiments is on dissolved organic carbon, dissolved organic nitrogen is highly correlated with dissolved organic carbon and is found consistently among the major fractions of dissolved organic matter (Qualls and Haines, 1991). For example, in a biodegradation experiment (Qualls and Haines, 1992a), the C/N ratio changed little during biodegradation. The term dissolved will be used in an operational way with the understanding that colloidal forms may pass the filters used to separate forms (Thurman, 1985). However, most natural dissolved organic matter in soil solution and natural waters has a molecular weight below 2000 and is thus dissolved (Dawson et al., 1981; Thurman, 1985). Another convention used in this paper is that I will distinguish between “soluble” — including that which is dissolved and that which is potentially soluble but in the solid state at the time, and that which is actually dissolved.

Dissolved organic matter, and the nutrient elements bonded to it, is important in the following respects:

1. it is a major mode of export for N and P (Sollins and McCorison, 1981; Hedin et al., 1995) in many forest ecosystems;
2. it plays a major role in determining the balance and accumulation of N, P, and perhaps even C over the long period of soil development;
3. because natural DOM is acidic and is a powerful agent for complexing of metals, it plays an important role in the mineral weathering, metal toxicity, and metal export (Pohlman and McColl, 1988; Mierle and Ingram, 1991);
4. it provides a potential source of carbon for microbial growth (Meyer et al., 1987).

It is now realized that dissolved organic N is the major form of N in stream water draining from many mature forest watersheds (Sollins and McCorison, 1981; Hedin et al., 1995). In a study of 31 watersheds with unpolluted old-growth forests in Chile, representing an area without anthropogenic atmospheric N deposition, DON comprised about 95% of total N in stream water (Hedin et al., 1995). Relatively high concentrations of DON drain from the forest floor and this DON generally comprises most of the total N draining from the forest floor of intact forests (Fahey and Knight, 1986; Yavitt and Fahey, 1986; Qualls et al., 1991; Northup et al., 1995; Currie et al., 1996). The mechanisms by which inorganic nutrients are either retained or lost during succession or after disturbance of forest ecosystems are generally well known and illustrated in many studies. These include: loss of root uptake (Bormann and Likens, 1979); the rapid recovery of root uptake by stump sprouts (Boring et al., 1988); recovery of root uptake by seedling growth (Marks, 1974); delayed mineralization and subsequent nitrification due to a high C/N ratio in litter (Vitousek et al., 1979); temporary sorption on ion exchange sites (Vitousek et al., 1979); denitrification, and in the case of P, fixation or sorption on soil (Walker and Syers, 1976; Wood et al., 1984; Walbridge et al., 1991). The accumulation of large quantities of living biomass or dead organic matter is also a widely recognized means of storing essential nutrients in the ecosystem (Jordan, 1985). Increases in water flux from the root zone due to cutting and the concomitant reduction in evapotranspiration also play an important role in controlling the leaching of nutrients (Bormann and Likens, 1979). In the case of dissolved organic nutrients, however, the mechanisms controlling leaching from the ecosystem have not been clearly defined. Qualls et al. (1991) noted that the flux of DON from the forest floor was at least 50 times that lost from the watershed in stream water. Obviously, there are important mechanisms at work that prevent the leaching of soluble organic nutrients from ecosystems just as there are better known mechanisms preventing the loss of inorganic nutrients.

A conceptual diagram (Fig. 1) illustrates the significant processes generating and consuming dissolved organic matter and the associated nutrient elements. The primary objective of this paper will be to review and synthesize the literature. However, the results of several original experiments are presented to fill gaps in our knowledge of the important sorption interactions. More specifically the objectives of this study were to:

1. Propose a conceptual model for the factors controlling the leaching of soluble organic nutrients.
2. Present experimental evidence for adsorption/desorption interactions and review evidence for other processes such as decomposition, microbial dissolution (dissolution of solid organic matter by microbial activity), and exudation.
3. Compare the factors regulating the leaching of inorganic vs. organic nutrients in solution.

2. Materials and methods

2.1. Solubility desorption interactions in organic horizons

Two experiments were done to determine whether the leaching of soluble organic matter from organic horizons could be regulated by adsorption/desorption phenomena. The first experiment used a Lemneta peat (a dystic Pergelic Cryofibrast) sample from a drained black spruce forest soil in Alaska, and the second used a sample of forest floor on a soil of the Marla series, a sandy mixed Aquic Cryumbrept (Johnson et al., 1997), from a Pinus jeffreyi forest in the Whittell Forest on the eastern slope of the Sierra Nevada Mountains.

The first adsorption isotherm experiment was designed to show whether a sorption equilibrium might exist between DOC and solid organic matter in peat that might be capable of regulating concentration. Initial pore water from the Lemneta peat was extracted by 0.07 MPa vacuum on a membrane filter to
minimize the influence of the initial pore water on the subsequent sorption experiment. This extracted water was analyzed for DOC (using a Shimadzu 5050A TOC Analyzer). Peat soil samples (1.0 g dry weight equivalent) from the 20–25 cm depth were shaken for 5 days in 30 ml of water in five different concentrations of DOC. Preliminary experiments indicated that 5 days was sufficient for equilibration. The equilibrium DOC concentration was then measured. To make solutions in which the DOC varied, the natural soil pore water from the peat was diluted with an artificial solution which simulated the inorganic components of the water sample. Some DOC was also concentrated by ultrafiltration with a 500 MW cutoff membrane (YC-05 membrane, Amicon, Beverly, MA) which retained 93% of the DOC, and then the concentrated DOC was mixed with artificial inorganic solution. To suppress microbial activity, 5 mg/l HgCl₂ was added. Additional samples of each solution were shaken without any peat sample and later filtered to determine whether precipitation occurred in the absence of the solid phase. The solution pH of all samples was adjusted to the same value (6.5) as the pH of the solution initially extracted from the peat.

A similar adsorption experiment was performed on the pine forest floor sample to obtain the same information as described above for the peat sample, but using an adaptation of a method for obtaining adsorption isotherm data using continuous unsaturated flow-through intact soil cores (Qualls and Haines, 1992b). Circular cores of forest floor (Oa and Oi horizons) were placed in plastic rings with plastic mesh on the bottom. Large quantities of leachate were produced by leaching separate samples and the leachate was then concentrated about 5-fold by ultrafiltration. This concentrate was mixed with deionized water, again concentrated to remove salts (since salts passed through the ultrafiltration membrane), and then diluted with a simulated throughfall solution containing only inorganic salts to give three different DOC concentrations (0, 502, and 1005 mg/l). Then 5 mg/l HgCl₂ was added to suppress microbial activity during the experiment. This water was applied as artificial rainfall to the top of the cores at a rate of 3 cm for 4 h. The effluent was recycled once each day until the third day when the effluent DOC concentration appeared to be at equilibrium. Effluent from the second and third cycle was similar in concentration.

A set of methodological experiments were performed to determine whether the 5 mg/l HgCl₂ actually suppressed microbial activity without affecting sorption of DOC. Accumulation of CO₂ in the headspace was measured in an extra set of tubes (in the peat experiment) and in litter enclosed in a mason jar (in the forest floor experiment) with or without the HgCl₂ added to the solution. CO₂ evolution (measured using a LiCor 6250) in the HgCl₂ treatments was insignificant compared to replicate empty vessels. DOC adsorption was measured using the methods of the peat experiment with either 0, 5, 10, 20 or 40 mg/l HgCl₂ shaken with peat or ground forest floor material for only an hour (to minimize microbial changes in the control without HgCl₂). DOC adsorption isotherms did not differ with different concentrations of added HgCl₂, indicating no effect on DOC sorption.

2.2. Measurement of the pool of soluble organic carbon

The rationale for this experiment was that the cumulative amount of DOC in repeated extractions with water would approach an asymptote corresponding to the total pool of soluble organic matter. A sample of the Pinus jeffreyi forest floor material was ground (without drying) in a Wiley Mill. While grinding was meant to increase the surface area and speed the time to equilibrium, the physical grinding was not expected to increase the inherent chemical solubility of the organic compounds. Sets of three replicate tubes containing a 2 g dry mass equivalent of the ground litter were shaken with 20 ml of solution, with or without 5 mg/l HgCl₂. Each sample was shaken for 24 h, centrifuged, the supernatant poured off, a new solution added, and the process repeated for 18 days. Each supernatant solution was filtered through a 0.45 µm filter and analyzed for DOC. The cumulative mass of extracted organic carbon was plotted vs. the number of extractions. This curve was fitted to a model for the accumulation of the product of a first order reaction, which has also been used to determine potentially mineralizable nitrogen (Ellert and Bettany, 1988). As is commonly done with N mineralization potential data, the first extraction was omitted from the data when fitting the curve and this mass was later added to the calculated asymptote (Ellert and Bettany, 1988).
The difference between the sequentially extracted samples with and without HgCl$_2$ was also used to estimate the rate of microbial dissolution. The rationale for using sequential extractions was to remove as much of the pool of soluble carbon as possible, in order to observe the production of much smaller amounts by microbial dissolution over the time of incubation.

A separate experiment tested the time required to reach steady state concentration for ground forest floor samples during test tube experiments. Replicate samples were removed from the shaker after shaking for 1, 2, 3, 4, and 5 days. Samples were then centrifuged and the supernatant analyzed for DOC.

2.3. Evidence for mechanisms of adsorption

The mechanisms of adsorption of soluble organic matter were explored both on organic substrates (such as the forest floor material) and a mineral soil sample from the AB horizon of a Fannin soil, a fine-loamy, micaceous, mesic Typic Hapludult. The major interactions expected to be involved in sorption of soluble organic matter in mineral soils are listed in Table 1. In the mineral soil sample, the addition of various ions known to compete for ion exchange or ligand exchange sites was observed for its effect on suppressing or facilitating sorption (Table 1). Thirty milliliter solutions with no initial DOC were added to 3 g dry mass equivalent of soil to monitor facilitation or suppression of desorption. Also, solutions with 28 mg/l initial DOC were added to monitor the facilitation or suppression of adsorption. Solutions were not added sequentially but were added to separate samples. To keep ionic strength constant, a 0.1 M concentration of monovalent cations was compared to 0.05 M concentrations of divalent cations. Another strategy I adopted was to eliminate substances which are responsible for specific mechanisms of adsorption. To this end, I treated soil with ammonium oxalate and then citrate dithionite to remove amorphous iron and aluminum oxides (Jardine et al., 1989).

To investigate organic–organic sorption mechanisms, I adopted a modification of Leenheer’s (Leenheer et al., 1997; and J.A. Leenheer, personal communication) approach. The mechanisms hypothesized to be involved in the sorption of natural soluble organic matter to solid phase organic matter were: (1) simple electrostatic attraction to cation or anion exchange sites; (2) electrostatic cation bridging by divalent cations between adjacent carboxylic acid groups; (3) ligand exchange on iron or aluminum oxyhydroxides precipitated on organic surfaces; (4) the hydrophobic effect; (5) van der Waals forces; (6) hydrogen bonding. A 2 g dry mass sample of the Pinus jeffreyi forest floor was treated sequentially with 20 ml of several reagents and shaken for 24 h. Samples were centrifuged each time and the supernatant was removed. The extraction sequence began with acidic pyrophosphate to remove Ca and other complexable metals. Then the sample was extracted with acidic ammonium oxalate to remove Fe. Then the pH was adjusted to the original pH in water solution. Then it was extracted with acetone to remove water before adding hexane, a more hydrophobic immiscible reagent. Finally, dimethylsulfoxide (DMSO) was added, which is relatively polar solvent that suppresses hydrogen bonding (Hayes, 1985). Each supernatant was analyzed for concentration of DOC. To estimate the natural DOC concentration in the organic solvents, the general response observed is indicated by a 0 (no effect) or + (a large effect suppressing adsorption and facilitating desorption). The list of hypothetical mechanisms comes from the studies of Greenland (1971).

Table 1
Mechanisms of adsorption of DOC on a Typic Hapludult AB horizon mineral soil sample

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Ions added</th>
<th>Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td>K$^+$, NH$_4^+$, Na$^+$, Ca$^{2+}$</td>
<td>0</td>
</tr>
<tr>
<td>Cation exchange</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anion exchange</td>
<td>Cl$^-$, NO$_3^-$</td>
<td>0</td>
</tr>
<tr>
<td>Cation bridging</td>
<td>Ca$^{2+}$</td>
<td>0</td>
</tr>
<tr>
<td>Ligand exchange</td>
<td>SO$_4^{2-} &lt; $H$_2$PO$_4^-$ &lt; oxalate &lt; F$^-$</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Removal of Fe, Al oxyhydroxides by oxalate, dithionite</td>
<td>+</td>
</tr>
</tbody>
</table>

*a Effect of various ions and treatments meant to suppress or facilitate adsorption of DOC and the mechanisms involved is indicated. The general response observed is indicated by a 0 (no effect) or + (a large effect suppressing adsorption and facilitating desorption). The list of hypothetical mechanisms comes from the studies of Greenland (1971).
however, I prepared a set of standards by adding concentrated natural DOC extracted from the sample to the solvent and measured the absorbance at 420 nm. Then I compared the sample absorbance at 420 nm with these standards.

3. Results

3.1. Sorption–desorption equilibria for peat and forest floor material

The sorption experiment using a Lemneta peat sample demonstrated that the peat could either desorb or adsorb soluble organic matter on the solid organic surfaces. The peat released DOC when water with no DOC was initially added (Fig. 2). It also removed DOC from solution when concentrated dissolved organic matter was initially added. The initial concentration which corresponded to the porewater sucked from the original sample (45 mg/l) changed little after shaking (48.7 mg/l) suggesting that it was at equilibrium. The samples shaken without peat showed no change, indicating that DOC did not precipitate. The net effect of the sorption behavior was a buffering of concentration.

Cores of forest floor material subjected to artificial precipitation showed similar desorption and adsorption of dissolved organic matter (Fig. 3). When artificial precipitation with no DOC was applied and then recycled until steady state was reached, soluble organic matter was released into solution. However, when very high DOC concentrations were initially applied in the artificial precipitation, not only was further leaching of DOC from the litter suppressed, but a portion of the initial DOC was removed from solution. This behavior could not be explained by precipitation because controls containing the initial solutions incubated without the litter showed no changes in concentration. Final concentrations were buffered compared to the initial concentrations. On the first pass through the forest floor cores, the solution did not reach steady state. However, it appeared to reach steady state on the second cycle since the concentration did not change between the second and third cycle.

3.2. Size of the pool of soluble organic matter

In the forest floor there was evidence of a pool of potentially desorbable organic matter which is released more gradually that can be accounted for.

Fig. 2. Demonstration that DOC concentration in solution limits the desorption and adsorption of soluble organic matter on peat. The final equilibrium concentration is plotted vs. the concentration in the solution initially added to the soil (solid points) along with the solid regression line. Solutions shaken without peat exhibited no change, indicating no precipitation in the absence of the solid phase.
by dissolution of a very soluble substance. In the sequential extraction experiment, DOC continued to be leached after many cycles of extraction with water even while microbial activity was inhibited with HgCl$_2$ (Fig. 4). Even after 10 extractions, high concentrations of DOC were being leached. The pool of potentially soluble organic carbon was estimated at about 2.4% of the organic carbon of the litter. This estimate was dependent on the assumption that the desorption during the sequential extraction fit the model for the accumulation of product during a first order reaction, but the data fit this model well (Fig. 4).

The reason that leaching of DOC persisted over many sequential extractions was not simply that an individual extraction required a long period of time for equilibration. When samples of the ground material was shaken for varying times (Fig. 5) the concentration of DOC in the supernatant reached an approximate steady state within 1 day. Precipitation was not a factor since it did not precipitate even when it was concentrated 3-fold and shaken under conditions similar to the extractions. There was also no evidence of microbial dissolution since the extractions without HgCl$_2$ poison did not generate more DOC than the unpoisoned sample, despite the removal of a large portion of the pool of soluble DOC during the first few extractions. The HgCl$_2$ treatment suppressed respiration successfully and also did not affect sorption dynamics during the 1 h sorption isotherm experiment. Consequently, the most likely explanation for the persistence of the leaching of DOC was equilibrium desorption.

3.3. Mechanisms of sorption: inorganic–organic interactions

Response of DOC sorption and desorption to the addition of various ions and to the removal of iron and aluminum oxyhydroxides suggested that ligand exchange was the major adsorption mechanism in the Typic Hapludult sample (Figs. 1 and 2). The rationale for interpreting the evidence for adsorption mechanisms was to examine the effect of various ions
or reagents on two points of an adsorption curve, one point at which no DOC was added and in which desorption occurred, and one at which 28 mg/l DOC was added and most DOC was adsorbed. The ability of the various treatments to either facilitate or suppress adsorption or desorption was then examined. While none of the responses shown in Table 1 alone proves a particular mechanism, several of the most likely mechanisms can be eliminated as being the major contributors of adsorption in the Typic Hapludult sample with ligand exchange remaining as the most likely mechanism of adsorption.

If simple electrostatic attraction to anion or cation exchange sites were a mechanism of adsorption of the

Fig. 4. An estimate of the total pool of soluble organic matter in a pine forest floor sample by sequentially extracting 2 g of ground litter with 20 ml of water once each day for 21 days. The data points represent three samples with HgCl₂ added to suppress both decomposition and microbial dissolution and three samples without HgCl₂. The function shown on the figure was fit to the curve after the first data point was excluded. The data for the first day was then added to the function as an intercept (8.5). The calculated asymptote, an estimate of the total pool of soluble organic carbon, was 22.6 mg which was 2.37% of the total carbon.

Fig. 5. Rate of extraction of 2 g of ground forest floor material with 20 g of water.
dissolved organic matter, addition of high concentrations of monovalent cations or anions should result in desorption of DOC, or suppression of adsorption of added DOC (Greenland, 1971). High concentrations of monovalent cations with chloride as the counter-ion tended to increase adsorption instead of decreasing adsorption (Table 2). High concentrations of chloride and nitrate, added with potassium as the counter-ion, had either little effect or increased adsorption. Thus, simple electrostatic attraction to either anion or cation exchange sites in the mineral soil was unlikely to be a significant mechanism.

Another electrostatic mechanism which might result in adsorption of DOM is cation bridging, in which a divalent cation such as Ca$^{2+}$ lies between the negatively charged surface of a clay and the negatively charged carboxylic acid group of fulvic acid (Table 1). High concentrations of calcium nitrate failed to produce substantially different sorption compared to either KNO$_3$ or the deionized water control (Tables 1 and 2). Since this Typic Hapludult sample was low in base saturation, the addition of Ca$^{2+}$ would be expected to suppress desorption and facilitate adsorption if cation bridging by divalent cations was a significant mechanism. Cation bridging by trivalent cations such as Fe$^{3+}$ and Al$^{3+}$ was not investigated since precipitation of the metal hydroxides from solution would interfere with the detection of effects due to the soil itself.

Ligand exchange is another mechanism which has been proposed and investigated for the adsorption of fulvic acids, sulfate, phosphate, and fluoride, on iron and aluminum oxyhydroxides (Greenland, 1971; Parfitt et al., 1977). In this reaction, the hydroxyl group of the carboxylic acid, or phosphate, substitutes for the coordinated hydroxyl on the Fe or Al oxyhydroxide surface (Greenland, 1971). Consequently, it might be expected that competitors for ligand exchange sites would facilitate desorption and suppress adsorption. Indeed, sulfate, phosphate, oxalate, and fluoride all facilitated desorption and suppressed adsorption, and the order of their effect (Tables 1 and 2) corresponded to the affinity for ligand exchange sites (Greenland, 1971). At high concentrations, oxalate and fluoride can also destroy the oxyhydroxide surface (Greenland, 1971) so their effects cannot be absolutely attributed to competition for ligand exchange sites. However, the effect was seen at relatively low concentrations of these reagents.

Finally, a treatment of oxalate followed by citrate dithionite reagent to remove Fe and Al oxyhydroxides resulted in an 82% reduction in the DOC adsorbed (an equilibrium DOC concentration of 24.9 mg/l) when 28 mg/l DOC was added (not shown). This effect could also indicate the importance of ligand exchange (Parfitt et al., 1977).

### 3.4. Mechanisms of sorption: organic–organic interactions

Results of sequential extraction of forest floor material, particularly the response to DMSO, sug-
gested that hydrogen bonding was the most likely mechanism of sorption of the soluble organic matter to the solid organic matter. Extractions of the forest floor organic matter with acidic pyrophosphate and acidic oxalate to eliminate cation bridging by Ca$^{2+}$ and Fe$^{3+}$ failed to allow more release of DOC than during the sequential water extractions (Table 3). Extractions with acetone (to remove water) and then hexane actually suppressed leaching of colored DOC compared to the sequential water extractions. Consequently, the hydrophobic effect was eliminated as a major factor causing the desorption/adsorption behavior. However, the subsequent extraction with the relatively polar DMSO solvent, which suppresses hydrogen bonding, caused a large amount of DOC (20 mg) to be released into solution. Subsequent extractions with water yielded less DOC than would have been released in sequential extractions with water, suggesting that the DMSO treatment had depleted the pool of desorbable organic matter.

### 4. Discussion

The discussion will be organized around the model presented in Fig. 1, combining both original experiments and what is known from previous studies to present a comprehensive view of the interactions controlling the fate of soluble organic nutrients. Then the behavior of soluble organic nutrients will be compared with the behavior of soluble inorganic nutrients.

#### 4.1. Sorption in organic horizons

Soluble organic matter is leached only very gradually from litter. Qualls et al. (1991) noted that while flux of DOC from the forest floor was highest shortly after litterfall, the majority of the annual flux occurred at sustained rates which declined only gradually over the year. Such behavior could be explained by several alternative hypotheses:

1. solubility is regulated by simple dissolution of sparingly soluble substances;
2. diffusion limits dissolution from particle matrices;
3. microbial dissolution generates soluble organic matter gradually during decomposition;
4. a pool of potentially soluble organic matter exists as litter senesces and is released gradually because of sorption phenomena.

Our experimental results (Figs. 3 and 4) suggest that hypothesis (4) is the most likely explanation for this behavior.

Based on patterns of concentration in soil and stream water, Grieve (1991) speculated that there was a reservoir of partially soluble organic carbon in soil which could be dissolved in water percolating through the soil. He further speculated that decomposition processes could solubilize organic carbon. Christ and David (1996a) showed that leaching of forest floor samples with solution supported Grieve’s conclusion that there was soluble organic matter that could be dissolved in the leaching solution. They also concluded that change in leaching rate over time suggested microbial production of dissolved organic matter. In my study, direct comparison of poisoned vs. unpoisoned forest floor (Fig. 2) and peat did not indicate a significant role of microbial dissolution. In addition, this study has indicated that sorption, rather than solubility, regulated release of potentially soluble organic matter.

Temperature and antecedent moisture content are also important factors in controlling leaching of DOC. Based on seasonal patterns of concentration, Grieve (1991) proposed that production of dissolved organic matter increased exponentially with temperature. Christ and David (1996b) showed that DOC leaching increased exponentially with temperature between 3 and 28°C. These observed temperature effects could be due to the effect of temperature on microbial dissolution, solubility products, sorption equilibria, or even increases in diffusion out of particle matrices. Temperature effects deserve further attention to sort out the mechanisms. Christ and David also showed a
marked increase in DOC leached with increase in the antecedent moisture content of forest floor samples during prior incubation. The effects of antecedent water content could be due to kinetics, microbial dissolution during the antecedent time period, or dissolution or desorption of DOC in the entrained solution phase. The antecedent entrained solution has a longer time to come to adsorption equilibrium with the solid phase than with the water percolating through litter during a precipitation event. Indeed, the forest floor experiment shown in this paper demonstrated that equilibrium was not attained during the first artificial precipitation event even when microbial activity was suppressed.

4.2. Adsorption in mineral soils

Many studies have demonstrated adsorption of natural dissolved organic matter to specific clays, oxyhydroxides, or whole mineral soil samples. An adsorption isotherm done using continuous flow-through intact soil cores is shown in Fig. 6 (adapted from Qualls and Haines, 1992b). This example showed that the buffering of input concentrations ranging from 0.2 to 32 mg/l DOC resulted in equilibrium concentrations of a much narrower range of about 0.6–4. It also demonstrated that most of the DOC in solutions representative of that draining from the forest floor was adsorbed by the A horizon in this Typic Hapludult soil. Furthermore, the isotherm was linear within the range of naturally encountered input concentrations, suggesting that the adsorption sites were not near a point of saturation with adsorbed organic matter. Adsorption isotherm curves from other studies show only moderate curvature in the range of natural concentrations (McDowell and Wood, 1984; Nodvin et al., 1986). At least in the example of the A horizon, this observation is important because it suggests that the contribution of sorbed organic matter to organic matter content of the A horizon is partly regulated by equilibrium with the dissolved phase. Conversely, the reason that a portion of the DOM remains in solution is not simply that all available sorption sites are coated in a particular layer of the A horizon.

Protracted leaching during desorption experiments (Qualls and Haines, 1992b) also supported the notion that there was a large pool of potentially soluble organic matter in the mineral soil sample, which was only gradually released in accordance with sorption equilibria.


The study in this paper suggested that ligand exchange on iron and aluminum oxyhydroxides was the most likely mechanism accounting for most of the DOC adsorption in the Typic Hapludult sample. The suppression of DOC adsorption by citrate dithionite treatment was also documented by Jardine et al. (1989), although they did not interpret it as indicating the importance of ligand exchange because they noted no change in pH when DOC was added. Ligand exchange should release hydroxyl ion due to displacement of the hydroxyl group of the oxyhydroxide surface by the carboxylate group. The change in pH, however, may have been too small to measure in their experiment, compared to much larger amounts of fulvic acid added in the experiments of Parfitt et al. (1977) who did observe the release of hydroxyl ion. Parfitt et al. (1977) also found infrared spectroscopic evidence that ligand exchange was the major mechanism of adsorption of fulvic acid on goethite.
The large surface area of amorphous or short-range ordered oxyhydroxides and oxides of Fe and Al are likely to greatly enhance the adsorption capacity of soils in which these coatings occur on clays (Greenland, 1971). Kaolinite has a limited ability to adsorb fulvic acid and may have accounted for a small proportion of adsorption in the Typic Hapludult sample (Greenland, 1971). Certain clays also have the capacity to adsorb large amounts of fulvic acid. In volcanic soils, allophane and imogolite may adsorb large amounts of fulvic acid (Parfitt et al., 1977) and are likely to be responsible for retention of most dissolved organic matter on these soils.


While the adsorption/desorption of soluble organic matter to specific clays and oxides has been extensively investigated, the adsorption of soluble humic substances to solid soil organic matter has not. The solubility of soil humic substances as a function of pH is perhaps the best known phenomenon related to this problem, since it is the basis for the classical methods of extraction of soil humic substances. The mechanisms of interactions between xenobiotic pesticides and humic substances have also been extensively investigated (Leenheer, 1991). Methods such as infrared spectroscopy which have been important in investigating other organic sorption mechanisms probably have little potential where the functional group content of the sorbant and the sorbate are similar, as in the case of adsorption of soluble natural organic matter to solid natural organic matter.

The study of organic–organic sorption mechanisms in this study (Table 3) suggested that hydrogen bonding was important in controlling sorption of soluble organic matter in the forest floor. Failure of hydrophobic solvent and the removal of metals to result in desorption of large amounts of the pool of soluble organic matter seems to eliminate the hydrophobic effect, sorption to metal oxyhydroxide surfaces by ligand exchange, and cation bridging in explaining the dissolved organic matter sorption–desorption behavior in this forest floor material. However, hydrogen bonding seemed to be consistent with the effects of DMSO. Hydrogen bonding might occur between one protonated and one unprotonated functional groups, e.g.: two carboxylic acids, two phenolic hydroxyl, or a carboxylic acid and phenolic hydroxyl group. Van der Waals forces are also often implicated in organic–organic sorption behavior (Leenheer, 1991) and may also be involved in this sorption behavior.

4.5. Summary of sorption effects

The following is a summary of the importance of sorption in soluble organic matter interactions:

1. The pool of soluble organic matter is much larger than the amount dissolved by any one leaching event in both mineral and organic horizons.
2. Sorption has the effect of buffering concentration of dissolved organic matter both in mineral and organic horizons.
3. The leaching rate of potentially soluble organic matter is slowed by the sorption equilibrium.
4. By increasing the residence time of potentially soluble organic matter on surfaces, sorption is likely to increase the exposure of soluble organic matter to microbes while it is in the sorbed state.
5. The most likely mechanism for sorption in the mineral soil appears to be ligand exchange on iron or aluminum oxyhydroxides, while in the organic horizons it is likely H-bonding and perhaps van der Waals forces.

4.6. Dissolution of solid organic matter by microbial activity

Dissolution of insoluble organic matter might occur by the activities of microbial enzymes (pathway “c” in Fig. 1) to generate DOM. This DOM might be rapidly taken up (pathway “d”). Alternatively, the products might be refractory and persist, or the products of exoenzymatic dissolution could condense to form soluble humic substances. While the experiments in this study did not detect microbial dissolution, it is possible that the rate of microbial dissolution to form refractory DOM was too slow to be detected against the large pool of potentially soluble organic matter. There have been other two studies that suggest that microbial dissolution of insoluble organic matter may occur. Significant quantities of soluble organic matter can be generated from insoluble lignin as it is degraded by the white rot fungus P. chrysosporium.
(Reid et al., 1982). Bergbauer and Newell (1992) used labeled lignin from Spartina leaves in a pure culture with an ascomycete, and in 45 days of incubation 3.3% of the lignin was mineralized to CO₂ while 2.7% was solubilized to DOC. While 22% of the labeled polysaccharides was mineralized to CO₂, 4% was solubilized to DOC. Moran and Hodson (1989) however, used uniformly labeled lignocellulose isolated by the same extraction procedure and found that 2.1–4.7% of the original labeled lignocellulose was abiotically dissolved in poisoned controls, suggesting that not all of the dissolution observed in the experiment of Bergbauer and Newell was microbial dissolution. Moran and Hodson found that 10–40% of lignocellulose utilization by bacteria occurred via the generation of soluble decomposition products in aqueous incubations of the labeled and isolated lignocellulose. Soluble lignin-derived monomers and polymers have been found to accumulate in cultures of lignin-degrading actinomycetes (Crawford, 1981; Borgmeyer and Crawford, 1985). Thus, it appears that some amount of soluble organic matter can be generated from insoluble lignin and cellulose, although the only information on this process comes from pure cultures or aqueous incubations.

The amount of dissolved organic matter found in the general soil solution may disguise much greater rates of dissolution and turnover due to microbial decomposition. In order to be taken up by the cell membrane of microorganisms, virtually all polar macromolecules in plant detritus (e.g. cellulose, hemicellulose, lignin, and polyphenols) must be lysed and solubilized by exoenzymes either exuded outside the cell or held in the periplasmic space. Because this is the major process of decomposition, there is obviously a great deal more extracellular lysis, with rapid uptake of monomers and mineralization occurring near the cell surface, than is indicated by the fluxes of DOC from forest soil horizons. Most carbon and nitrogen released to the cycle through decomposition is broken down, dissolved, and taken up near the cell surface in a zone we might call the “microsphere” and is rarely distributed widely enough in the soil solution to lost by leaching. This contrasts with the bulk of the macromolecular DOC and DON found in soil solution whose turnover time is so long that it can be transported and leached. The movement of these dissolved products of exoenzymatic hydrolysis depends on the distance to which exoenzymes diffuse from the cell surface, the diffusion rate away and toward the cell surface, the swiftness of uptake at the cell membrane (presumably less for refractory monomers), and the velocity and content of pore water. Some monomers released by enzymatic hydrolysis may abiotically condense with other monomers outside cells (Martin and Haider, 1976), and this may be an important mode of humic substance synthesis. This abiotic condensation may generate some of the refractory dissolved humic substances or it may convert some compounds to insoluble humic acid (pathway “g” in Fig. 1).

There is some indirect evidence that microbial dissolution is important in producing DON. Using a budget of inputs and outputs from the forest floor, Qualls et al. (1991) found that more DON was leached from the forest floor than could be accounted for by the sum of water extractable organic N content of litterfall, DON in throughfall, plus inorganic N in throughfall. This implied that otherwise insoluble N containing compounds were incorporated into soluble organic acids during some biotic or chemical transformations. Indeed the Maillard reaction (Leenheer, 1991), in which amino acids (released during hydrolysis of proteins) and carbohydrates condense to form humic substances, could be responsible.

In summary, microbial dissolution is undoubtedly important in decomposition of cellulose, hemicellulose, proteins, and lignin in the sense that these macromolecules must be broken down into monomers which can enter the cell. However, the residence time of these enzymatic breakdown products outside the cell is so short that they only comprise a small percentage of the soil solution. The role of dissolution in formation of more refractory organic matter that appears to comprise the bulk of soil solution, however, has rarely been investigated and is likely difficult to detect against the background of a large pool of adsorbed soluble organic matter.

4.7. Decomposition of soluble organic matter

Limnologists have long realized that dissolved organic N and P were often the dominant forms of these nutrients in lakes (Wetzel, 1983). Consequently, most of the research on the decomposition of dissolved organic matter was done in lakes and streams.
and investigations of decomposition of soil dissolved organic matter are rare.

There is evidence that the majority of dissolved organic matter from terrestrial environments is refractory. Qualls and Haines (1992a) used incubations of dissolved organic matter from throughfall, forest floor water, soil water, and stream water to investigate biodegradability. While throughfall in one season and freshly fallen dead litter contained a large portion of rapidly biodegradable DOM, that draining from the forest floor and DOM in soil solution was largely refractory in winter, spring and summer samples (Table 4). Curves of DOC lost vs. time were distinctly biphasic, typically indicating a small proportion that decayed rapidly and a larger proportion that decayed much more slowly. Decay constants for this rapidly and slowly decaying fraction are listed in Table 4 (Qualls and Haines, 1992a). In freshly fallen leaf litter there is a large portion which is very biodegradable (McDowell and Fisher, 1976; Qualls and Haines, 1992a). In the study of Qualls and Haines (1992a), much of the labile soluble organic matter appeared to be decomposed before being leached from the litter since forest floor leachate collected shortly after litter fall contained far less of the labile fraction of soluble organic matter than did freshly fallen litter.

Yano et al. (1998) used a flow-through bioreactor, which had colonized by microbes, to measure a biodegradable fraction of forest floor solution from the Harvard Forest. In forest floor solutions from plots representing “average” biodegradability, about 12–15% of the DOC was designated biodegradable. This percentage is similar to the range 6–19% for the “rapidly decaying fraction” in Oa horizon solution listed in Table 4 (Qualls and Haines, 1992a). Two samples from plots subjected to long term N application, however, had a biodegradable fraction of about 40%.

Soluble organic matter exuded by roots comprised about 0.09% of the net primary production of a forest examined by Smith (1976). Other studies have found that root exudates are largely very labile substances with decay constants on the order of $50 \times 10^{-3}$ per day (Reid and Goss, 1983). Uselman et al. (2000) found that most of the exudate of tree seedlings of Robinia pseudoacacia was rapidly decomposed with a rate constant on the order of $500 \times 10^{-3}$ per day. Most analyses of exudates have found that they are predominantly simple carbohydrates, amino acids, and fatty acids (Smith, 1976; Krafczyk et al., 1984; Uselman et al., 2000). Given the production of exudates by the roots of forest trees, the question may arise why soil water does not contain a larger fraction of these labile substances. There are probably three reasons: (1) the production of root exudates is much smaller in quantity than production of litter; (2) the sugars and amino acids may be so labile that they are largely consumed in the rhizosphere; (3) given the great difference in decay between the large refractory fraction and the root exudates, the refractory substances dominate the composition after a long residence time.

There is little information on the decomposition of nitrogen in DOM from forest soils. Qualls and Haines (1992a), however, found that DOC and DON in soil

<table>
<thead>
<tr>
<th>Source of solution</th>
<th>Rapidly decaying</th>
<th>Slowly decaying</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial percentage</td>
<td>Decay constant ($d^{-1} \times 10^{-3}$)</td>
</tr>
<tr>
<td>Throughfall</td>
<td>18–49</td>
<td>70–40</td>
</tr>
<tr>
<td>Oa horizon</td>
<td>6–19</td>
<td>70–30</td>
</tr>
<tr>
<td>A horizon</td>
<td>5–8</td>
<td>80–30</td>
</tr>
<tr>
<td>B horizon</td>
<td>13–16</td>
<td>80–30</td>
</tr>
<tr>
<td>Stream water</td>
<td>7–15</td>
<td>$300^{b}$–50</td>
</tr>
</tbody>
</table>

a The initial percentage of the bulk solution DOC represented by each fraction was calculated by extrapolation of two exponential decay curves to time zero. The range represents samples collected in winter, spring, and summer (except for stream water).

b The small size of the fraction limited the reliability of this constant.
solution decomposed at roughly parallel rates. Amino acids released from macromolecular proteins or humic substances by exoenzymes might then be converted to NH$_4^+$ by deaminases outside the cell. The cell wall. However, the low concentrations maintained in soil solution, like those of glucose released by exoenzymes from cellulose, must mean that this component of the soil solution is both produced and efficiently absorbed from the immediate volume near the cell surface (the “microbosphere”).

In summary, the existing data on relative amounts and decomposition rates of different fractions of forest soluble organic matter suggests that there is a distinctly bimodal distribution in the decomposition constants of dissolved organic matter in forests. A substantial portion of the soluble organic matter is very labile (washed from leaves, in recently fallen litter, and in exudates) with a half life on the order of days. A large fraction, however, is very refractory and there is little in the intermediate category.

4.8. Plant uptake of dissolved organic nitrogen

The most important difference influencing the fate of dissolved inorganic vs. organic nitrogen is the capacity of plant roots to directly take up NH$_4^+$ and NO$_3^-$ ions. The influence of uptake by root networks in controlling the leaching of soluble inorganic nutrients is one of the basic tenets of biogeochemistry. Here we must make an important distinction between low molecular size amino acids which can pass through cell membranes, and nitrogen contained in macromolecules which cannot. It might be expected that very labile molecules containing limiting nutrients might be found only in low concentrations in soil solution. Indeed, dissolved free amino acids are found only in very low concentrations in soil solution, lake water, and stream water. Thurman (1985) summarized data showing that dissolved free amino acids only comprise about half of 1% of the DOC in natural waters and aquatic sediments. In a study of forest soil solution less than 7% of the DON was found in the base fraction, which would be expected to contain not only the free amino acids but also the free proteins (Qualls and Haines, 1991). Kielland (1994) found concentrations of three amino acids totaled 12–26 mM in soil extracts of tundra soils. Thus, I contrast the low molecular size amino acids, which are likely to turn over rapidly and are present in low concentrations, with the macromolecular organic N which is more refractory, present in higher concentration, and consequently more likely to be leached.

While the largest source of N taken up by roots had traditionally been regarded as NO$_3^-$ and NH$_4^+$ ions, plant roots can take up some low molecular size amino acids directly (Miettinen, 1959). It was generally considered that this uptake was minor compared with inorganic N until it was shown that it might account for 10–80% of the N uptake of several tundra plant species on organic soils (Chapin et al., 1993; Kielland, 1994). Subsequently, amino acids were shown to be a significant source of nitrogen for an alpine sedge (Raab et al., 1996). The significance of direct amino acid uptake in the nutrition of temperate forests remains to be tested.

Another way in which organic N can be taken up indirectly, bypassing the mineralization step, is via mycorrhizae. Mycorrhizal fungi not only take up amino acids directly, but can exude exoenzymes to break down macromolecules of organic matter and then either take up, or mineralize, amino acids that are released (Read, 1991). In terms of the diagram shown in Fig. 1, this portion of the process is identical to conventional microbial decomposition (processes “c” and “d”), except that in theory, the nitrogen can then be passed to the root.

Both the direct uptake of dissolved amino acids by roots and the utilization of organic N by mycorrhizal fungi prompted Chapin (1995) to refer to the bypassing of the mineralization step as “a new cog in the nitrogen cycle”. He postulated that this process would be important in infertile and acidic soils. Northup et al. (1995) found that an increase in polyphenol content of litter in a series of communities was correlated with an increase in the amount of DON leached from the forest floor and was negatively correlated with mineralization rate. They speculated that on the most infertile soils, high production of polyphenols might have an adaptive role in minimizing leaching of mineral N while facilitating the availability of soluble organic N.
4.9. Hydrologic factors

Inorganic nutrient forms, especially HPO$_4^{2-}$, H$_2$PO$_4^-$, and NH$_4^+$, are subject to sorption on soil surfaces (Brady, 1990). Likewise, several studies have shown that, at least in some ecosystems, most macro-molecular dissolved organic matter is adsorbed in some horizon of the mineral soil, especially horizons rich in iron or aluminum oxyhydroxides. The removal of this DOM by a solid surface somewhere in the ecosystem profile depends on sorption equilibrium, kinetics, and pathway. The capacity for the solution phase to come to equilibrium with adsorbing surfaces in some horizon is influenced by several hydrologic factors which are listed below in order of scale:

1. on the molecular scale, failure to reach equilibrium due to lack of time to equilibrate with surfaces, i.e., sorption kinetics are slow relative to hydrologic residence time;
2. diffusion through particles may limit the time to reach equilibrium;
3. preferential flow may “short circuit” exposure of entire soil surface;
4. on a larger scale, flow paths through a watershed may bypass the most strongly adsorbing horizons, e.g., surface flow, lateral flow, throughfall on stream channels, leaves falling into channel;
5. finally, the soil profile may simply lack a strongly adsorbing horizon.

There is evidence for the importance of these hydrologic factors that control the ability of the soil solution to equilibrate with the most strongly adsorbing horizon. In soil solution of the A horizon, Qualls and Haines (1992b) noted that DOC concentration varied little in lysimeter samples collected in the A horizon over short time periods as water flux varied greatly over a week of storms but they were much lower than concentrations draining from the forest floor. These results suggested that adsorption of the DOC equilibrated rapidly and in less time than the hydrologic residence time in the horizon. Furthermore, in continuous flow-through adsorption experiments using the same soil, the DOC concentration approached equilibrium after the first cycle of solution passed through the core. Other authors have used 24 h equilibration time for DOC batch sorption isotherms after preliminary tests of time to equilibrium. Thus, in the mineral soils tested, it appears that kinetics and diffusion into particles are fast relative to hydrologic residence times.

In the forest floor, the large and irregular size of particles, along with the remains of hydrophobic cuticles, may well be expected to increase the time necessary for diffusion out of particles and the tendency for preferential flow. During the batch sorption isotherm experiments in this study (Fig. 3), shaken and ground litter equilibrated by the second 24 h period. The same litter, when intact in cores, did not reach steady state until the second day of a 4 h per day simulated rain. Preferential flow has been demonstrated by the advection of dyes or other tracers including as artificial rain was applied to the forest floor (Burcar et al., 1994). The combination of the sorption equilibria, the slowness of diffusion from particles on the timescale of a rainstorm, and preferential flow may explain why soluble organic matter in the forest floor leaches gradually over the entire year rather than in one flush following litterfall as observed by Qualls and Haines (1991).

In watersheds with a highly adsorbing mineral horizon, there are several ways that hydrologic flow paths have been shown to bypass the mineral horizons during storms, resulting in increases in DOC concentration in first order forest streams: throughfall directly on the stream channel, stream water flowing over litter in the channel, throughfall on ephemeral channels where litter covers rocky colluvium, surface flow, and lateral flow (Dawson et al., 1981; Reeve and Fergus, 1982; Jardine et al., 1990). Qualls and Haines (1991) found that concentrations of DOC, DON, and DOP were all lower in B or C horizons or headwater seeps than in stream water and that stream water concentrations increased during the rising limb of the storm water hydrograph. This study suggested that a large portion of the dissolved organic nutrient output in stream water resulted from hydrologic bypassing of the predominant flowpath through the B and C horizon of the watershed. In an analogous sense, watersheds with wetlands, which are well known for their high DOC concentration, have surface flows which bypass the subsurface mineral horizons (Grieve, 1984). On a larger scale, watersheds with soils that lack strongly adsorbing mineral horizons also have been shown to have higher DOC concentrations in stream water (Klinge, 1967; Nelson et al., 1993).
4.10. Retention of dissolved organic nutrients during primary succession and soil development

The hypothetical relationship of hydrologic flow-path and soil weathering during primary succession to the tendency of dissolved organic nutrients to leach from the ecosystem is illustrated in Fig. 7. It depicts geochemical and hydrological controls dominating the tendency of an ecosystem to retain soluble organic nutrients produced by biological processes. Geochemical processes controlling retention are largely dependent on the presence or absence of Fe and Al oxyhydroxides or certain clays. One end member of this series along the geochemical axis is represented by sand dunes and other sandy soils such as the chronosequence examined by Walker et al. (1981) or the Indiana Dunes chronosequence (Olson, 1958). Another end member might be represented by volcanic soils such as those which occur at the Mt. Shasta mudflows chronosequence (Sollins et al., 1983) or other soils high in oxyhydroxides and allophane which strongly adsorb humic substances. Hydrologic short circuiting of B horizons high in metal oxyhydroxides can also bypass the adsorbing effects of soils, represented in the extreme by surface flow or surface flow wetlands. Streams may even be visualized within this framework as a case of surface flow. We can represent the changes during pedogenesis and succession as vectors within this triangle (e.g. as weathering produces metal oxyhydroxides or as podzolization progresses).

During ecosystem development on new substrates, various processes of pedogenesis and plant primary plant succession may occur at different rates. The accumulation of soil organic matter is determined by the balance between net primary production, mineralization of organic matter, and export of organic matter (including export of dissolved organic matter). The production of soluble organic matter is another factor determining export and may be represented along an axis perpendicular to the other two axes in Fig. 7. Processes such as podzolization, clay formation by weathering, and formation of metal oxyhydroxides occur over a much longer period but

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**GEOCHEMICAL FACTORS**

**INCREASING ADSORPTION OF SOLUBLE ORGANIC MATTER**

**LOSS**

**SANDY SOILS**

Clay Accumulation & Podzolization

SOILS HIGH IN OXYHYDROXIDES OR CERTAIN CLAYS

Fig. 7. Factors regulating the retention of soluble organic nutrients in ecosystems during primary succession and soil development. Geochemical factors are on the horizontal axis while hydrologic factors vary along the vertical axis. The graph is represented as a triangle because hydrologic short circuiting can render the geochemical composition of B horizon irrelevant. Changes occurring during pedogenesis can be represented by clay accumulation, development of oxyhydroxide coatings, or podzolization during weathering. Situations leading to hydrologic short circuiting include surface flow, perched water tables, channel throughfall, or paludification.
affect the accumulation and cycling of nutrients (Jenny, 1980).

A hypothesis outlining the changes in ecosystem stocks and forms of P during primary succession and soil development was advanced by Walker and Syers (1976) based on evidence from several chronosequences. They reasoned that there was a shift from dominance of primary mineral P (e.g., apatite) to organic P and later a dominance of secondary P minerals associated with extreme weathering and formation of Fe and Al oxides and oxyhydroxides. In later stages, they also reasoned that P would limit primary production as unavailable secondary mineral forms dominated the declining stocks of P. There are many analogies between the fate of P and that of soluble organic matter. The humic and fulvic acids which comprise most of the dissolved organic matter are negatively charged and adsorb to Fe and Al oxyhydroxides as does \( H_2PO_4^- \) (Greenland, 1971).

In fact, organic acids compete with \( H_2PO_4^- \) for the same ligand exchange reaction sites on Fe and Al oxyhydroxides. While behaving in many ways like \( H_2PO_4^- \), these organic acids often carry most of the N moving in solution (Qualls and Haines, 1991), thus linking the P and N cycles in an interesting way. Thus, much N, originally covalently bonded to DOC, can suffer much the same fate as the “occluded P” as proposed in the Walker and Syers hypothesis.

An extreme example of the effects of leaching of dissolved organic matter was documented by Walker et al. (1981). They analyzed a chronosequence formed on dunes whose ages stretch back hundreds of thousands of years. A metal–organic humic podzol layer formed and progressively moved down in the soil profile until it was below the root zone. Because the soil was sandy, this humic layer, and the biomass, comprised most of the nutrient stock. In the later stages, the migration of the nutrient-rich humic podzol layer below the rooting zone led to a sharp reduction in net primary production and a “retrogression” of succession. This situation represents one of the “end members” of the scheme shown in Fig. 7.

### 4.11. A comparison of factors controlling retention of soluble organic vs. inorganic nutrients: hypotheses

A set of hypotheses are outlined in Table 5 which compare soluble organic vs. inorganic nutrients with respect to the: (1) sources; (2) properties of the molecules which determine behavior; (3) major mechanisms by which the dissolved molecules are removed from solution; (4) major factors allowing loss from the ecosystem for soluble nutrients. The evidence for these generalizations about soluble organic nutrients has been presented through the preceding review and experimental results. Evidence for these generalizations about the cycling of inorganic nutrients are well known and a number of general reviews or ecosystem studies will be cited. As stated in Section 1, the nutrients considered are forms of nitrogen, phosphorus, and organic carbon only. In the case of soluble inorganic forms of nutrients, \( NO_3^- \), \( NH_4^+ \), and \( HPO_4^{2-} / H_2PO_4^- \) are the predominant molecules which might be in solution. However, in many cases the behavior of these may differ. In the case of the soluble organic nutrients, the generalizations are applied to macromolecules to exclude the free amino acids because they comprise a small percentage of the DON and because the importance of plant uptake of amino acids is unsettled.

The sources of soluble inorganic nutrients refer not to the sources of the elements to the ecosystem but the source of the soluble ion containing the element. Microbial mineralization is likely to be the predominant source of these soluble ions since annual plant uptake of these ions is generally supplied largely by mineralization in forest ecosystems. Other sources are atmospheric inputs in precipitation and dust (Schlesinger, 1991) and direct leaching from plants. Weathering is another source in the case of P, but it is likely to be small compared to the recycling by mineralization. In contrast, the major sources of soluble organic C, N, and P are leaching from detritus and direct leaching from live plants (McDowell and Likens, 1988; Qualls et al., 1991) and perhaps microbial dissolution.

Perhaps the most important property of inorganic N and P ions which govern their behavior is the small molecular size which allows transport through cell membranes by active transport. In contrast, the soluble macromolecules which carry most of the DOC, DON, and DOP do not pass through into cells without being hydrolyzed first, which in turn requires extracellular decomposition for assimilation of the nutrient element by microbes and roots. Consequently, root uptake which is so important in preventing loss of soluble
inorganic nutrients is not a factor for the macromolecular dissolved organic nutrients. This places further importance on geochemical factors in preventing leaching of macromolecular soluble organic nutrients. The predominant soluble inorganic forms of N and P are ionic, making them susceptible to sorption on cation or anion exchange sites. Many of the salts formed with counter-ions are soluble, but some such as the calcium salts of P at high pH are insoluble (Brady, 1990). In addition, the presence of hydroxyl group on the phosphate ions make them susceptible to other forms of sorption, which may be the most important factor in preventing leaching of phosphate ions.

Other properties of the soluble organic macromolecules which determine their behavior are that: (1) they are predominately negatively charged (although a significant fraction are neutral); (2) the presence of carboxyl and phenolic hydroxyl groups make interactions such as ligand exchange and hydrogen bonding important; (3) molecules are multidentate making bonds more stable (Table 5). In addition, the N atoms in the humic and hydrophilic acids do not contribute substantial positive charges in the macromolecules as they do in peptides. Instead, the carboxyl and phenolic hydroxyl groups largely determine the behavior of the nitrogen carried more or less “passively” by the humic and hydrophilic acids (Qualls and Haines, 1991). In the case of dissolved organic P, most macromolecules containing P behave as anions, but whether the negatively charged P ester groups or the carboxylic acids determine this behavior has not been determined (Qualls and Haines, 1991).

The major factors tending to remove the inorganic N and P ions from solution can be divided into biological and non-biological (Table 5). The inorganic ions are removed by root uptake and microbial uptake (immobilization) (Vitousek et al., 1979) while the

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Comparison of the factors controlling retention of soluble macromolecular organic nutrients vs. soluble inorganic nutrients in forest ecosystems: hypotheses</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inorganic</strong></td>
<td><strong>Organic</strong></td>
</tr>
<tr>
<td><strong>Sources</strong></td>
<td>Leaching from detritus</td>
</tr>
<tr>
<td>Microbial mineralization</td>
<td>Direct leaching from plants, exudation</td>
</tr>
<tr>
<td>Atmospheric input</td>
<td>Microbial dissolution</td>
</tr>
<tr>
<td>Direct leaching from plants</td>
<td></td>
</tr>
<tr>
<td><strong>Properties of molecules</strong></td>
<td>Mostly large molecules</td>
</tr>
<tr>
<td>Small + and −ions</td>
<td>Mostly charged</td>
</tr>
<tr>
<td>Many salts soluble</td>
<td>Some neutral</td>
</tr>
<tr>
<td>Some salts insoluble (e.g. salts of PO₄³⁻)</td>
<td>Carboxyl group interactions important</td>
</tr>
<tr>
<td></td>
<td>Multidentate</td>
</tr>
<tr>
<td></td>
<td>Most N does not act as cation</td>
</tr>
<tr>
<td>Electrostatic + Ligand exchange (H₂PO₄⁻)</td>
<td>Ligand exchange (regulating concentrations at a low level in mineral soil)</td>
</tr>
<tr>
<td>− Electrostatic (minor)</td>
<td>H-bonding or van der Waals forces (regulating concentrations at a high level in organic horizons)</td>
</tr>
<tr>
<td>Precipitation</td>
<td></td>
</tr>
<tr>
<td><strong>Major factors allowing loss from ecosystem</strong></td>
<td>Hydrologic short circuiting or absence of a horizon high in Fe and Al oxyhydroxides and certain clays</td>
</tr>
<tr>
<td>Hydrologic short circuiting of root network</td>
<td></td>
</tr>
<tr>
<td>Weak geochemical sorption/precipitation potential of soil</td>
<td></td>
</tr>
</tbody>
</table>
soluble organic macromolecules must be hydrolyzed by microbes. Inorganic ions are also removed from solution by sorption onto cation exchange sites or the less abundant anion exchange sites depending on charge. The PO4 ion is also removed by ligand exchange reactions or, at very acid or alkaline pH values, by precipitation (Brady, 1990). Like phosphate, ligand exchange is likely to be responsible for removal of a large portion of the macromolecular dissolved organic molecules in mineral soils. This mechanism is capable of maintaining relatively low levels in solution. Organic–organic mechanisms such as hydrogen bonding or van der Waals forces may also remove these macromolecules but these function to maintain concentrations at higher levels.

There are many processes which allow the loss of nutrients from forest ecosystems, either through disturbance, hydrology, or soil conditions. In the case of inorganic nutrients, disturbance or hydrologic short circuiting of an active root network has been demonstrated to be of importance, especially for nitrogen forms (Bormann and Likens, 1979; Vitousek et al., 1979; Parsons et al., 1994) but also for phosphorus (Stark and Jordan, 1978). In the case of phosphorus, presence or absence of geochemical controls over leaching, such as adsorption, are likely to be dominant in the lower mineral soil and during disturbance of root uptake (Walker et al., 1981; Wood et al., 1984; Walbridge et al., 1991). While erosion is very important, those losses are considered insoluble forms for purposes of this discussion. In the case of dissolved organic nutrients, hydrologic short circuiting or absence of a horizon rich in Fe and Al oxyhydroxides is hypothesized to be the major factor allowing loss from the system. Evidence for this hypothesis was presented in previous discussion of hydrologic factors and is illustrated by studies of Klinge (1967), Dawson et al. (1981), Walker et al. (1981), Reeve and Fergus (1982), McDowell and Wood (1984), Nelson et al. (1993).

5. Conclusions

Experiments showed that the pool of potentially soluble organic matter was much larger than the amount dissolved by any one leaching event in both mineral and organic horizons. Sorption of soluble organic matter to solid organic matter in organic horizon material regulated concentration at a relatively high level and was likely due to hydrogen bonding or van der Waals forces. Sorption of soluble organic matter to a Typic Hapludult AB horizon regulated concentration at a low level and appeared to be largely caused by ligand exchange on iron or aluminum oxyhydroxides. Adsorption/desorption had the effect of buffering concentrations of DOM in both mineral and organic horizons. The leaching rate of potentially soluble organic matter is slowed by the sorption equilibrium. By increasing the residence time of potentially soluble organic matter on surfaces, sorption results in a much greater time of exposure of soluble organic matter to decomposers while sorbed on surfaces.

Literature sources indicate a bimodal distribution of decay coefficients of dissolved organic C and N with a refractory fraction dominating. A set of hypotheses comparing the factors controlling retention of inorganic vs. organic nutrients was developed and classified as follows: sources of dissolved nutrients; properties of molecules controlling behavior; biological removal from solution; non-biological removal from solution; major factors allowing loss from the system. Perhaps the most important property of inorganic N and P ions that govern their behavior is the small molecular size that allows transport through cell membranes by active transport. In contrast, the soluble macromolecules which carry most of the DOC, DON, and DOP do not pass through into cells without being hydrolyzed first, which in turn requires extracellular decomposition for assimilation of the nutrient element by microbes and roots. The major factor allowing loss to the ecosystem for organic nutrients is hydrologic short circuiting or absence of a mineral soil horizon rich in Fe and Al oxyhydroxides whereas, in the case of inorganic nutrients, it is hydrologic short circuiting or absence of a root network in addition to geochemical factors.

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