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Soluble Organic Nutrient Fluxes

Robert G. Qualls*
Bruce L. Haines
Wayne T. Swank

Introduction

Inorganic nutrients have been the focus of most studies of the cycling and leaching of elements after disturbance. However, soluble organic nutrients, such as the forms of C, N, and P that are bound in organic matter, are also released from living and dead organic matter. The mechanisms by which inorganic nutrients are retained or lost after clearcutting are generally well known and illustrated in many studies. These include loss of root uptake (Likens and Bormann 1995), 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), and in the case of P, fixation or sorption on soil (Wood et al. 1984; Walbridge et al. 1991). The increase in water flux from the root zone due to cutting and the concomitant reduction in evapotranspiration also plays an important role in controlling the leaching of nutrients (Likens and Bormann 1995). The factors that control the leaching of *organic* nutrients after clearcutting or other disturbances, however, have not been extensively investigated.

Dissolved organic nitrogen (DON) is the major form of N in the streamwater draining many mature forest watersheds (Lewis 2002; Perakis and Hedin 2007). Relatively high concentrations of DON drain from the forest floor, and this DON also generally makes up most of the total N draining from the forest floor of intact forests (Qualls et al. 1991; Michalzik et al. 2001).The importance of DON in solution transport in intact forests and the sudden inputs of potentially soluble nutrients in logging slash suggest that the transport of soluble organic nutrients may be important in the retention or loss of nutrients after clearcutting.

Our objectives in this study were to (i) compare fluxes of the dissolved organic nutrients dissolved organic carbon (DOC), DON, and dissolved organic phosphorus

* Corresponding author: Department of Natural Resources and Environmental Science, University of Nevada, M.S. 370, Reno, NV 89557 USA

(DOP) in a clearcut area and an adjacent mature reference area, (ii) determine whether concentrations of dissolved organic nutrients or inorganic nutrients were greater in clearcut areas than in reference areas, and (iii) identify the strata where the greatest net leaching and deposition occur.

Site and Methods

The study site was on, or adjacent to, Watershed 2 (WS 2) at the Coweeta Hydrologic Laboratory in the Nantahala Range of the Southern Appalachian Mountains of North Carolina (83°26'W, 35°04'N) at an elevation of 840 m. Annual precipitation was 127.6 and 153.4 cm during the first and second years of the study, respectively. Snow comprises only 2% to 10% of precipitation.

The area was covered by a deciduous forest dominated by several species of *Quercus*, *Carya* spp., *Acer rubrum*, and *Cornus florida*. The forest had been undisturbed for at least 62 years except for mortality due to the chestnut blight (Monk and Day 1988). Thickets of *Kalmia latifolia* and *Rhododendron maximum* cover portions of the study area. Soil in the study area is Chandler loam, a coarse-loamy, micaceous, mesic, Typic Dystrochrept. The dry mass of the forest floor on WS 2 averaged 1145 g/m^2 (Ragsdale and Berish 1988). Annual litterfall was 498 g/m^2 (dry mass) and had a C/N mass ratio of 60 (W. T. Swank, unpublished data, 1991).

An experimental clearcutting was combined with the installation of a weather station in an area on the perimeter of WS 2 to simulate the clearcutting experiment on the adjacent WS 7. An area of 890 m^2 was cut in November 1985, after leaf fall. Four 5 m x 5 m plots were randomly located within the area, excluding the weather station. The perimeter of the clearcut area was trenched to about a 60 cm depth, and the trench was lined with plastic to prevent root growth from the surrounding forest. We uniformly redistributed woody debris over the plots so that the dry-weight equivalent of approximately 120 Mg/ha lay on each plot to mimic the experimental clearcut on WS 7 in 1977 (Boring et al. 1988). Then, an uncut reference plot was randomly located in the area, or areas, matching all criteria for slope, aspect, soil series, and depth of the A horizon for a given cut plot. Thus, each cut plot was paired with an uncut plot and treated as a block, as in a case-control experimental design (Breslow 1996).

Solution was collected above the forest floor (throughfall or slash leachate), below the Oa horizon, in the mid-A horizon, the mid-AB horizon, the mid-B, and 20 cm below the upper boundary of the C horizon. In the cut plots, slash leachate collectors were placed *above* the litter but beneath all woody logging debris. Sampling and the measurement of water fluxes were described by Qualls et al. (2000). Water fluxes in throughfall and from the bottom of the Oa horizon were measured as by Qualls et al. (1991). Interception by forest floor litter in the clearcut was assumed to be the same as in the reference plots. Annual water fluxes from the bottom of the rooting zone of the uncut plots were assumed to be equal to the annual streamflow on the gauged watershed (WS 2). Using this flux as a reference, annual fluxes from the rooting zone of the cut plots were based on an empirical model that predicts the increase in streamflow due to cutting over that of a reference watershed at Coweeta (Douglass and Swank 1975). Water fluxes from each depth increment between the bottom of the Oa horizon and the bottom of the root zone were interpolated by distributing total transpiration among soil increments in proportion to the distribution of fine roots (McGinty 1976). Fluxes for each form of nutrient were then calculated by multiplying the water flux by the concentration of the each nutrient form.

Concurrent with the clearcutting study, a larger study involving an additional eight plots on the reference WS 2 was done that also measured fluxes in streamwater and a more detailed examination of mechanisms. Other aspects of this study that have been presented include: annual fluxes of C, N, and P from throughfall and from the forest floor of the uncut area of WS 2 (Qualls et al. 1991), potential rates of biodegradation of DOC and DON from all strata (Qualls and Haines 1992b), chemical fractionation of DOC and DON from all strata (Qualls and Haines 1991), measurement of adsorption of DOC (Qualls and Haines 1992a), determination of the mechanisms of adsorption of DOC (Qualls 2000), effects of clearcutting on DOC, DON, and DOP concentrations (Qualls et al. 2000), and an analysis of the factors controlling fluxes through the soil and from streamwater on the uncut watershed (Qualls et al. 2002).

Results and Discussion

Over a two-year period the estimated water flux from the bottom of the rooting zone was 1.47 times higher in the cut plots, or 26 cm (table 5.1). This increase in water flux is very similar to streamflow increases measured on adjacent WS7 (23 cm yr^{-1}) the first two years following clearcutting (Swank et al. 2001; see also Swank et al., chapter 3, this volume).

Concentrations and fluxes of DOC, N forms, and P forms in the cut versus uncut plots (figures 5.1–3) demonstrated three major points: First, dissolved organic C and N concentrations were higher in the cut plots in slash leachate (vs. throughfall), forest floor leachate, A horizon soil solution, and B horizon soil solution (figures 5.1–2). In the case of DOP, concentrations were much higher in the cut

Table 5.1 Average hydrologic fluxes over the two-year sampling period (in annual units).

Stratum or horizon	Water fluxes (m/yr)	
	Uncut	Cut
Precipitation	1.42	1.42
Throughfall or slash	1.25	1.36
Oa	1.22	1.32
A	0.89	1.07
AB	0.74	0.95
B	0.58	0.83
C	0.55	0.81

Source: Qualls et al. (2000).

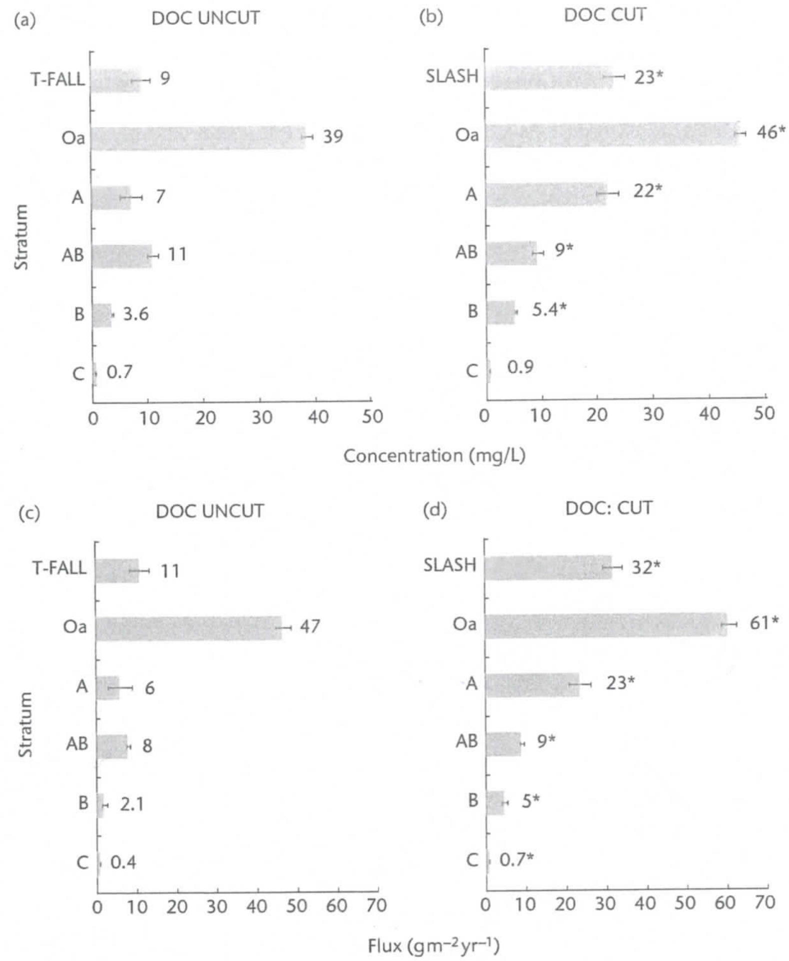

Figure 5.1 Flux weighted average concentrations (**a** and **b**) and fluxes (**c** and **d**) of DOC for the uncut and cut plots. Strata or soil horizons are indicated on the vertical axis. Asterisks indicate significant ($P < 0.05$) differences (a significant main effect of cutting treatment in the ANOVA) between cut vs. uncut plots and are placed on the bar that was greater in magnitude. Error bars are standard error of the mean, indicated only for the organic form, and reflect variability among plots, not temporal variability. Numbers beside the bars indicate values. From Qualls et al. (2000).

plots in the slash leachate (vs. throughfall) and forest floor but not in the mineral soil (figure 5.3). Second, greater water fluxes through the soil horizons of the cut plots (table 5.1) combined with greater concentrations in some horizons to give greater fluxes of DOC, DON, and DOP in all strata (figures 5.1–3). Third, fluxes of DON were greater than those of dissolved inorganic N, even in the cut plots (figure 5.2). However in the case of P, fluxes of inorganic P exceeded those of DOP in the cut plots in slash and forest floor leachate (figure 5.3).

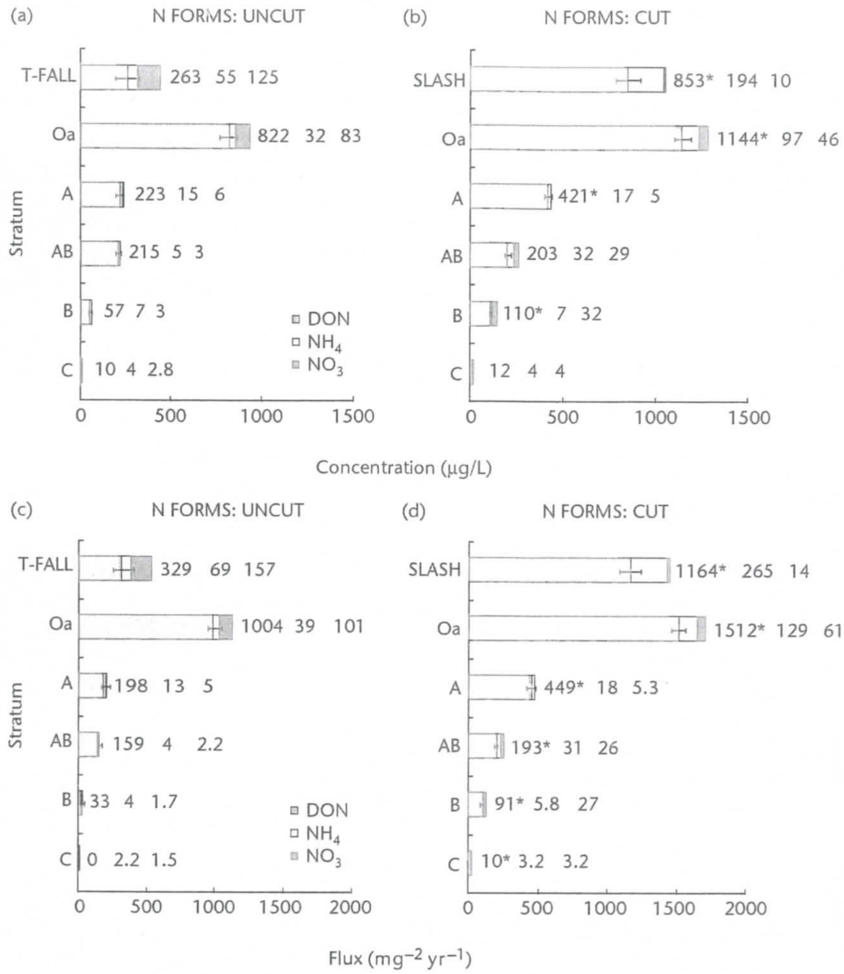

Figure 5.2 Flux weighted average concentrations (figures **a** and **b**) and fluxes (figures **c** and **d**) of N forms for the uncut and cut plots. Asterisks indicate significant ($P < 0.05$) differences (a significant main effect of cutting treatment in the ANOVA) in DON (not inorganic forms) between cut vs. uncut plots, and are placed on the bar that was greater in magnitude. Error bars are standard error of the mean, indicated only for the organic form, and reflect variability among plots, not temporal variability. Numbers on or beside the bars indicate values and are in the same order as the stacking of the bars. From Qualls et al. (2000).

Sources of DOM above the Mineral Soil

Sources of DOM in the cut plots were slash from cutting, other organic debris on the forest floor, and perhaps litter from dead roots. On the other hand, leaching from live canopy leaves and litterfall during the first two years after cutting was greatly reduced. In the mature forest canopy, leaching was an important source of DOC and, in particular, DOP (Qualls et al.1991). In the cut plots, however, fluxes of DOC, DON, and DOP in slash throughfall were much higher than in

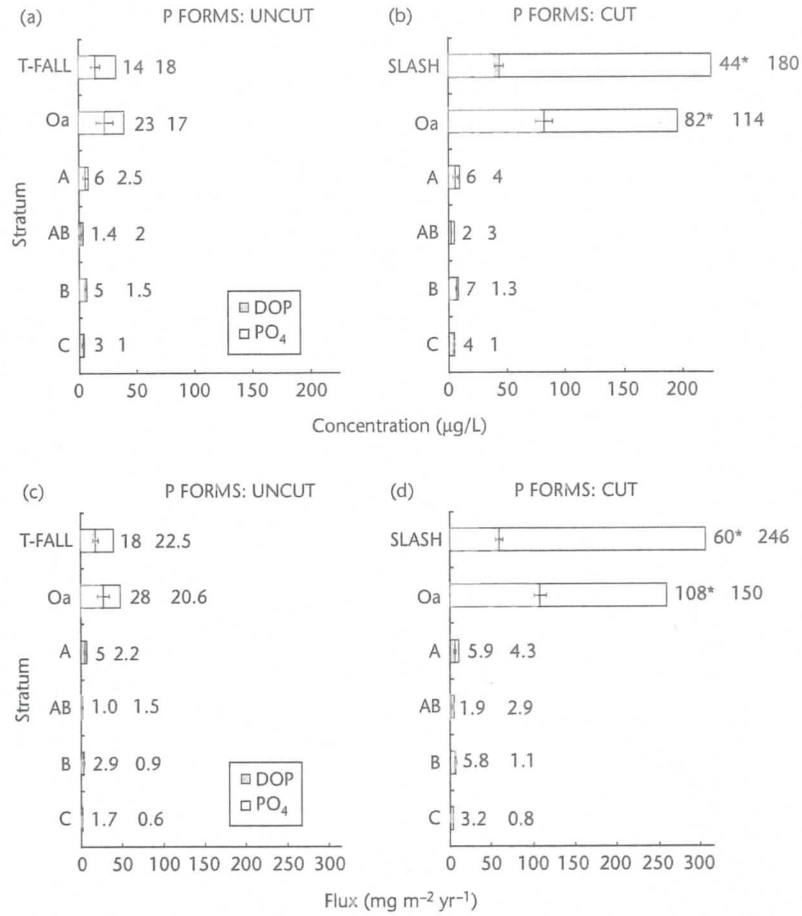

Figure 5.3 Flux weighted average concentrations (a and b) and fluxes (c and d) of P forms for the uncut and cut plots. Asterisks indicate significant ($P < 0.05$) differences (a significant main effect of cutting treatment in the ANOVA) in DOP (not PO_4) between cut vs. uncut plots, and are placed on the bar that was greater in magnitude. Error bars are standard error of the mean, indicated only for the organic form, and reflect variability among plots, not temporal variability. Numbers on or beside the bars indicate values and are in the same order as the stacking of the bars. From Qualls et al. (2000).

throughfall in the uncut plots. Sources of this throughfall in the cut plots may have included: (i) leaching of tannins from dead and fragmented bark, (ii) leaching of soluble organics from porous and fragmented wood, (iii) dissolution of lignin and other constituents by microbial enzymes, and (iv) leaching of microbial biomass such as that of shelf fungi.

Despite greater fluxes from the Oa horizon in the cut plots for all organic nutrients, there was less net leaching (defined as flux from the Oa horizon minus that in throughfall or slash) of DOC and DON from the forest floor in the cut plots compared to the uncut plots. Net leaching of DOC and DON from the Oa horizon was 19% and 48% lower, respectively, in the cut plots compared to the uncut plots (figures 5.1a and 5.2a vs. 5.1b and 5.2b). This was likely due to the loss of most new leaf litter production after cutting.

In a study following three years after clearcutting in a boreal forest, Piirainen et al. (2002) found that DOC and DON fluxes from the Oa horizon nearly doubled, results similar to those of our study but with somewhat greater increases. As in our study, fluxes of DON were greater than those of inorganic N in forest floor of the boreal clearcut. In a Norway spruce forest after clearcutting, Smolander et al. (2001) found that concentrations of DON percolating from the Oa horizon were only 17% higher in clearcut plots compared to intact forest, but concentrations were much higher at the 10 cm depth below the Oa horizon. In another clearcutting experiment in a *Picea abies* forest, Kalbitz and Bol (2004) removed all logging debris, thus removing canopy leaching, fresh litterfall, and logging debris as sources of DOM. Despite the elimination of logging debris in the cut plots, they still found slightly increased concentrations and increased fluxes of DOC and DON from the Oa horizon, mainly due to increased water flux. They attributed this effect to increases in temperature and a greater decomposition rate in the forest floor in cut plots. The Oe and Oa horizons were much thicker in the plots studied by Kalbitz and Bol than in the Coweeta study, and that could have contributed to a more sustained source of DOC than in the Coweeta study. Dai et al. (2001) examined a forest that had been clearcut 15 years earlier at the Hubbard Brook Experimental Forest and found that concentrations of DOC from the forest floor were still much higher than in the intact forest and that the DOC being leached was more aromatic in chemical nature. This chemical difference might reflect the sustained leaching of woody debris and the reduction in canopy leaching that contains more labile, but less aromatic DOC (Qualls et al. 1992b). Mattson et al. (1987) found that concentrations of DOC still averaged 76 mg/L in leachate from decaying logs seven years after clearcutting on the adjacent WS 7 at Coweeta. This suggests that decaying woody residue may remain a source of dissolved organic matter for several years.

The leaching of fine root litter after senescence can be a major source of DOC and DON (Uselman et al. 2007). The mortality of fine roots caused by clearcutting was not measured in this study, but the inputs to the A and AB horizons after clearcutting could contribute to higher concentrations observed in this and other studies (Smolander et al. 2001; Piirainen et al. 2002).

Removal of DOM in the Mineral Soil

Concentrations of DOC and DON declined with depth in the mineral soil, and the greatest difference between the cut and uncut plots occurred in the A horizon (figures 5.1 and 5.2). Physicochemical adsorption, largely by iron and aluminum oxyhydroxides, can rapidly remove DOC from solution and can buffer differences in input concentration (McDowell and Wood 1984; Qualls and Haines 1992b). It is unlikely that large proportions of the DOC and DON were removed by decomposition in the dissolved phase because DOC and DON from the uncut plots was very slow to mineralize (Qualls and Haines 1992b). The unusual degree of retention of soluble organic matter in WS 2 can be explained, in part, by the unusually high content of potentially adsorbing Fe and Al oxyhydroxides. The AB horizon soil used in the adsorption experiments by Qualls and Haines (1992a) had an oxalate extractable Fe and Al content of 1.8 and 2.7 g/kg, respectively, and a citrate bicarbonate dithionite extractable Fe and Al content of 22 and 12 g/kg, respectively. The AB horizon of this same soil from a nearby plot had the highest total Fe and Al contents of all 19 sites in the Integrated Forest Study (April and Newton 1992).

Few studies have measured fluxes of DOM below the forest floor, but Piirainen et al. (2002) found, as we did, that despite much higher fluxes of DOC and DON from the organic horizons these dissolved organic nutrients were mainly retained by the mineral soil in clearcut plots. In a clearcut and control *Pseudotsuga menziesii* forested watershed in Oregon, Sollins and McCorison (1981) monitored DOC (second and third year after cutting only) and DON (third year after cutting only) in soil solution. They found that concentrations of DOC were higher in soil solution in the clearcut by factors ranging from 1.4- to 1.9-fold. The DON comprised from 41% to 58% of total N in soil solution in the third year after cutting. Like the Coweeta site, this clearcut forest exhibited a lag in nitrification and nitrate concentrations that generally remained well below the 1 mg/L level.

In the case of DOP and PO_4, the relatively high concentrations draining from the forest floor of the cut plots were abruptly reduced to low levels in the A horizon, levels that were similar to those of the uncut plots (figure 5.3 a and b). This may reflect the strong tendency of PO_4 (Walbridge et al. 1991) and perhaps organic phosphate esters to adsorb in these Fe- and Al-rich soils.

The increase in water fluxes through the soil was an important factor in causing greater fluxes of organic nutrients from the lower soil horizon; these were more important, in fact, than differences in concentration. This close relationship between nutrient output and water flux is well known for inorganic ions at the watershed level, such as Ca and Na, where concentration is relatively constant and flux is proportional to streamflow (Swank 1988; Likens and Bormann 1995). The estimated increases in annual water flux of 26 cm (a factor of 1.47) due to the cutting of our plots (table 5.1) lies within the ranges found in several studies (Sollins and McCorison 1981; Swank et al. 1988; Likens and Bormann 1995; Arthur et al. 1998).

Streamwater Fluxes of DOC, DON, and DOP

Concurrent with the study of the clearcut plots, the fluxes (export) of DOC, DON, and DOP were measured on the reference watershed (WS 2). Concentration of each species versus streamflow was modeled to estimate the fluxes over the two-year study period. In the case of DOC, during baseflow, DOC concentrations were relatively consistent, averaging 0.63 ($\pm$ 0.1 s.d.) mg/L and showed no seasonal trends. As a first approximation, a simple model of DOC concentration versus stormflow was able to accurately fit the DOC data. The water was assumed to be a mixture of water from two sources: baseflow with a constant concentration of 0.63 mg/L and stormflow (superimposed on baseflow during storms) with a DOC concentration of 5.0 mg/L when rising and peaking and 3.9 mg/L when falling (based on regressions). Plotting DOC concentration versus the ratio of stormflow/baseflow yielded a linear regression line with a y intercept corresponding approximately to the concentration in baseflow (~0.6 to 0.8 mg/L) and the concentration in stormflow corresponding to y at x = 1 (100% stormflow). Fits to this simple model with a simple interpretation were very good, ($r^2 = 0.83$ for rising and 0.77 for falling limbs) but a slightly curvilinear relationship provided a better fit than the linear relationship. Patterns for DON were similar but more variable since DON concentrations were closer to the limit of detection in streamwater.

Fluxes of DOC, DON, and DOP, NH_4, NO_3, and PO_4 in streamwater at the weir of WS 2 are shown in table 5.2. DON comprised 79% of the total dissolved N in streamwater at the weir and 40% of the total N. DOP comprised about 46% of the total dissolved P. Tate and Meyer (1983) showed that four watersheds at the Coweeta Hydrologic Laboratory had a lower export of dissolved organic carbon (DOC) per unit runoff of water than all (15) other watersheds in studies reviewed. In addition, Meyer and Tate (1983) and Meyer et al. (in chapter 6 of this volume) found that the DOC export in the third and fourth year after clearcutting of WS 7 was somewhat lower than the control stream, perhaps due to reduced litter inputs to the stream and near stream source areas. Likewise, the export of DON from WS 2 in our study was unusually low. While the flux of DON from the C horizon of the cut plots was nearly double that of the uncut plots in our study, the contribution of these fluxes from the C horizon would be small in comparison to the DON export of many intact forest watersheds. The mean export of DON and total N from 19 minimally disturbed watersheds in the USA was 1.24 and 2.62 kg ha^{-1} yr^{-1} respectively (Lewis 2002), about 6.5 times that of WS 2. Those studies included some watersheds with considerable wetland area. The mean export of DON from 20 undisturbed tropical watersheds was 2.40 kg ha^{-1} yr^{-1} (Lewis et al. 1999). In the tropical watersheds DON comprised an average of 67% of total dissolved N in first- and second-order streams but was about 50% for all watersheds.

Table 5.2 Fluxes of dissolved organic and inorganic nutrients from the reference watershed (WS 2).

	Flux (kg ha^{-1} yr^{-1})
DOC	4.1
Particulate organic C*	3.6
Total organic C	7.7
DON	0.19
NO_3-N	0.036
NH_4-N	0.014
Particulate N**	0.23
Total N	0.47
DOP	0.011
PO_4-P	0.013

Note: All units are kg ha⁻1 yr⁻1, unlike the figures.
* Estimated using fluxes from Swank and Waide (1988)
** Estimated using fluxes from Monk (1975)
Source: From data reported by Qualls et al. (2002)

Particulate N comprised only 17% of total N in first- and second-order streams ranging to 37% in rivers of the highest order. In a study of nine forested watersheds in New England, the export of DON ranged from 0.5 to 2.4 kg ha^{-1} yr^{-1} with DON comprising the majority most of the total dissolved nitrogen (Campbell et al. 1999). The reasons for this watershed to be unusually retentive for dissolved organic nutrients lay in the high adsorption capacity of the soil and the tendency for most water to drain through the B horizon before entering the stream, as discussed in the following sections.

Retention of Dissolved Organic Nutrients as a Function of Soil Type and Hydrologic Flowpath

The hypothetical relationship of hydrologic flowpath and soil adsorption capacity to the tendency of dissolved organic nutrients to leach from the ecosystem can be illustrated graphically. The diagram in figure 5.4 depicts geochemical and hydrological controls that dominate the tendency of an ecosystem to retain soluble organic nutrients produced by biological processes. Ecosystems can be compared on this diagram with respect to these characteristics. 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 might be represented by sand dunes and other sandy soils, such as the Indiana Dunes chronosequence examined by (Olson 1958). Another end member might be represented by soils high in oxyhydroxides (such as at Coweeta) or volcanic soils with allophane that strongly adsorb humic substances. Hydrologic bypassing 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. The potential decrease in soluble-organic-matter production after cutting is another factor determining export and might be represented along an axis perpendicular to the other two axes in figure 5.4.

Comparison of Mechanisms Controlling Leaching of Dissolved Organic and Inorganic Nutrients

Numerous studies have demonstrated that leaching of inorganic N or P is greater in recently clearcut forests compared to mature reference stands (Sollins and McCorison 1981; Adamson et al. 1987; Stevens and Hornung 1990; Likens and Bormann 1995; Ring 1995). In this study, we also found that fluxes of dissolved organic nutrients were greater in clearcut plots. Indeed fluxes of NO_3, NH_4, and PO_4 were elevated in our cut plots, but the average concentrations did not approach the levels found for NO_3 in, for example, some cut forests (Likens and Bormann 1995). Partly because of this relatively small increase in NO_3 concentrations, the fluxes of DON typically remained greater than those of inorganic forms. The adjacent watershed (WS 7) was experimentally clearcut in 1977 and NO_3 export in streamwater during the first and second year was only about 0.3 and 1.1 kg/ha, respectively (Swank 1988). In our cut plots, the flux of NO_3 from the C horizon was much lower

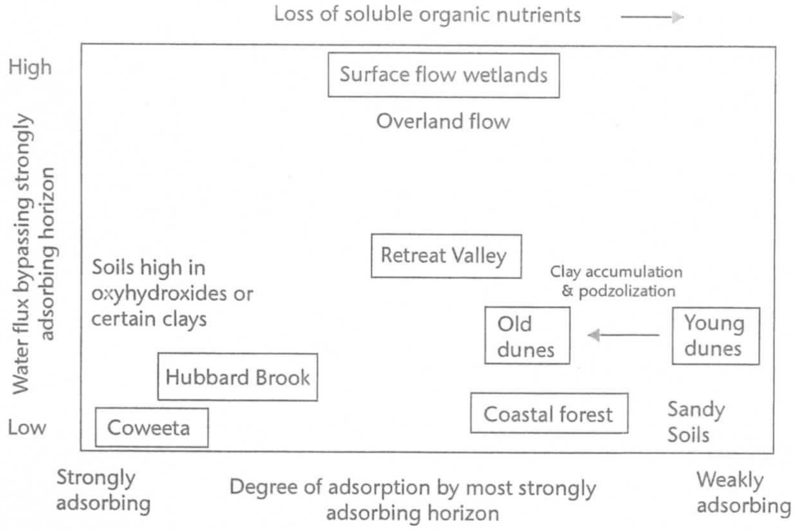

Figure 5.4 Classification of the ecosystems in their tendency to retain soluble organic nutrients as a function of the degree of adsorption of mineral soil and hydrological short circuiting. Ecosystems are placed on this diagram in relative positions since the data needed to quantify their position on the axes were generally not available. "Coweeta" refers to the current study, "Hubbard Brook" to the studies by McDowell and Wood (1984) and McDowell and Likens (1988) who suggested a somewhat lower degree of adsorption of DOC, "Coastal forest" to the study by Seely et al. (1998) where sandy texture appeared to provide a relatively low degree of adsorption but where hydrologic by-passing was not suggested, "Retreat Valley" to the study of Nelson et al. (1996) in which sandy soils overlaying clay soils and portions of the watershed being "poorly drained" suggested some degree of hydrologic by-passing of the clay layer. The hypothetical example of sand dune soil development could be represented by the Indiana Dunes chronosequence (Olson 1958). The "surface flow wetlands" or "overland flow" entry on the diagram represents the extreme example of hydrologic short circuiting which can bypass the adsorbing effects of soils (e.g., Qualls and Richardson 2003). From Qualls et al. (2002).

than that from the B horizon for unknown reasons, but the flux from the B horizon in our cut plots (0.27 kg/ha) was similar to export in streamwater during the first year after cutting on WS 7. However, the export from WS 7 in streamwater the second year after cutting was considerably higher than that from the B horizon in our cut plots. This relatively low export of inorganic nutrients was due to a very rapid recovery of root uptake in stump sprouts and herbaceous plants which recovered to 93% of the precutting N uptake in aboveground NPP only three years after cutting on mesic sites (Boring et al. 1988). A lag in nitrification may also have played a role in delaying nitrate loss from our cut plots, as in the studies of Vitousek et al. (1979). Output of N, especially NO_3, from clearcut forested watersheds varies by nearly two orders of magnitude (Vitousek et al. 1979; Emmett et al. 1990; Ring 1995). Although the data on leaching of dissolved organic nutrients after clearcutting are extremely limited, we hypothesize that the range of increase in concentrations and fluxes of DON is much less than that observed for NO_3.

A set of hypotheses comparing the factors controlling the retention of soluble organic versus inorganic nutrients (table 5.3; Qualls 2000) is applicable to our study. The nutrients considered are forms of nitrogen, phosphorus, and organic carbon only. 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 some plants can take up the smallest amino acids (Kielland 1994).

Perhaps the most important property of the inorganic N and P ions is their small molecular size, which allows transport through cell membranes. In contrast, the soluble macromolecules that carry most of the DOC, DON, and DOP do not pass through the cell membrane without being hydrolyzed first, which in turn requires extracellular decomposition for the assimilation of the nutrient element by microbes

Table 5.3 Factors controlling retention of soluble macromolecular organic vs. inorganic nutrients in terrestrial ecosystems: hypotheses.

Inorganic	Organic
Sources	
Microbial mineralization	Leaching from detritus
Atmospheric input	Direct leaching from plants, exudation
Direct leaching from plants	Microbial dissolution
Properties of molecules	
Small + and - ions	Mostly large molecules
Many salts soluble	Mostly—charged
Some salts insoluble (e.g. salts of PO_4)	Some molecules neutral
	Carboxyl group interactions important
	Multidentate bonding
	Most N in molecules does not act as cation
Removal from solution: Biological	
Root uptake	
Microbial uptake (immobilization)	Microbial hydrolysis and uptake of small molecules
Removal from solution: Nonbiological	
+ Electrostatic	Ligand exchange (regulating concentrations at a low level in mineral soil)
Ligand exchange ($H_2PO_4^-$)	H-Bonding or van der Waals forces
– Electrostatic (minor)	(regulating concentrations at a high level in organic horizons)
Chemical precipitation	
Major factors allowing loss from ecosystem	
Hydrologic short circuiting of root network or adsorbing soil horizon	Hydrologic short circuiting of adsorbing soil horizon
Removal of root uptake	Root uptake less important than for inorganic molecules, only small molecules.
Weak geochemical sorption/ precipitation potential of soil	Absence of a horizon high in Fe and Al oxyhydroxides and certain clays

Source: Qualls (2000).

and roots. Consequently, root uptake and direct microbial uptake, which are important in preventing the loss of soluble inorganic nutrients, are not factors for the macromolecular dissolved organic nutrients. Hence, geochemical factors are more important in controlling the leaching of dissolved organic nutrients.

Electrostatic charge is another property of the predominant soluble inorganic forms of N and P, 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. In addition, the presence of hydroxyl group on the phosphate ions make them susceptible to ligand exchange, which often may be the most important factor in preventing the leaching of phosphate ions.

Properties of the soluble organic macromolecules besides size that determine their behavior are (i) that they are predominately negatively charged, although a significant fraction is neutral (Qualls and Haines 1991); (ii) that the presence of carboxyl and phenolic hydroxyl groups make such interactions as ligand exchange and hydrogen bonding important; and (iii) that molecules are multidentate, making bonds more stable. 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 N 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).

As in the case for phosphate, ligand exchange is likely to be responsible for the removal of a large portion of the macromolecular dissolved organic molecules in mineral soils (Qualls 2000). Thus the geochemical mechanisms for retaining phosphate, DOC, DON, and DOP are similar. These mechanisms are 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 in organic horizons, but these mechanisms function to maintain concentrations at higher levels (Qualls 2000).

We can classify the various mechanisms of retention as *geochemical*, *hydrologic*, and *biological*. In the case of N, the mechanisms controlling the loss of N in the form of nitrate are largely biological and hydrologic. We propose that the loss of DON is controlled by geochemical and hydrologic mechanisms. The production of soluble organic nutrients is, of course, biological, but dissolution and sorption are geochemical mechanisms.

We hypothesize that the most important geochemical mechanisms leading to the retention of dissolved organic nutrients are (i) the slow, sustained release of potentially soluble organic matter caused by slow dissolution, equilibrium-controlled desorption from organic surfaces, and the gradual exposure of surfaces to percolating water during fragmentation; and (ii) equilibrium adsorption to Fe and Al oxyhydroxides and clays. The slow, gradual release of potentially soluble organic matter from detritus can be compared to factors tending to delay nitrification, as in the studies of Vitousek et al. (1979). Sorption helps retain the soluble organic matter to be decomposed slowly on surfaces and finally, hydrologic factors control the capacity for this adsorption capacity to be effective at retaining these organically bound forms of nutrients.

Conclusions

Concentrations of DOC and DON were higher in the cut plots than in uncut plots in solutions from slash leachate (vs. throughfall), the forest floor, the A horizon, and the B horizon. DOP concentrations were higher in the cut plots than in the uncut plots in solutions from slash leachate (vs. throughfall) and the forest floor but not in the mineral soil.

Fluxes of DOC, DON, and DOP in all strata were greater in cut plots than in uncut plots, a product not only of concentration differences in some cases, but also a 1.47-fold greater flux of water. Even in the cut plots, fluxes of the organic forms of nutrients exceeded those of the inorganic forms (except in the case of P in slash leachate and forest floor solution).

Despite greater fluxes of dissolved organic N from the cut plots, over 99% of the DON draining from the forest floor on the cut plots was removed (presumably adsorbed) above the upper C horizon, demonstrating a remarkable degree of retention of this soluble form of N. We hypothesize that the well-recognized retention mechanisms for inorganic nutrients (e.g., uptake by the roots of stump sprouts, adsorption of ions, and immobilization) combined with geochemical adsorption of dissolved organic matter, efficiently buffer against the leaching of either soluble inorganic or organic nutrients after clearcutting.

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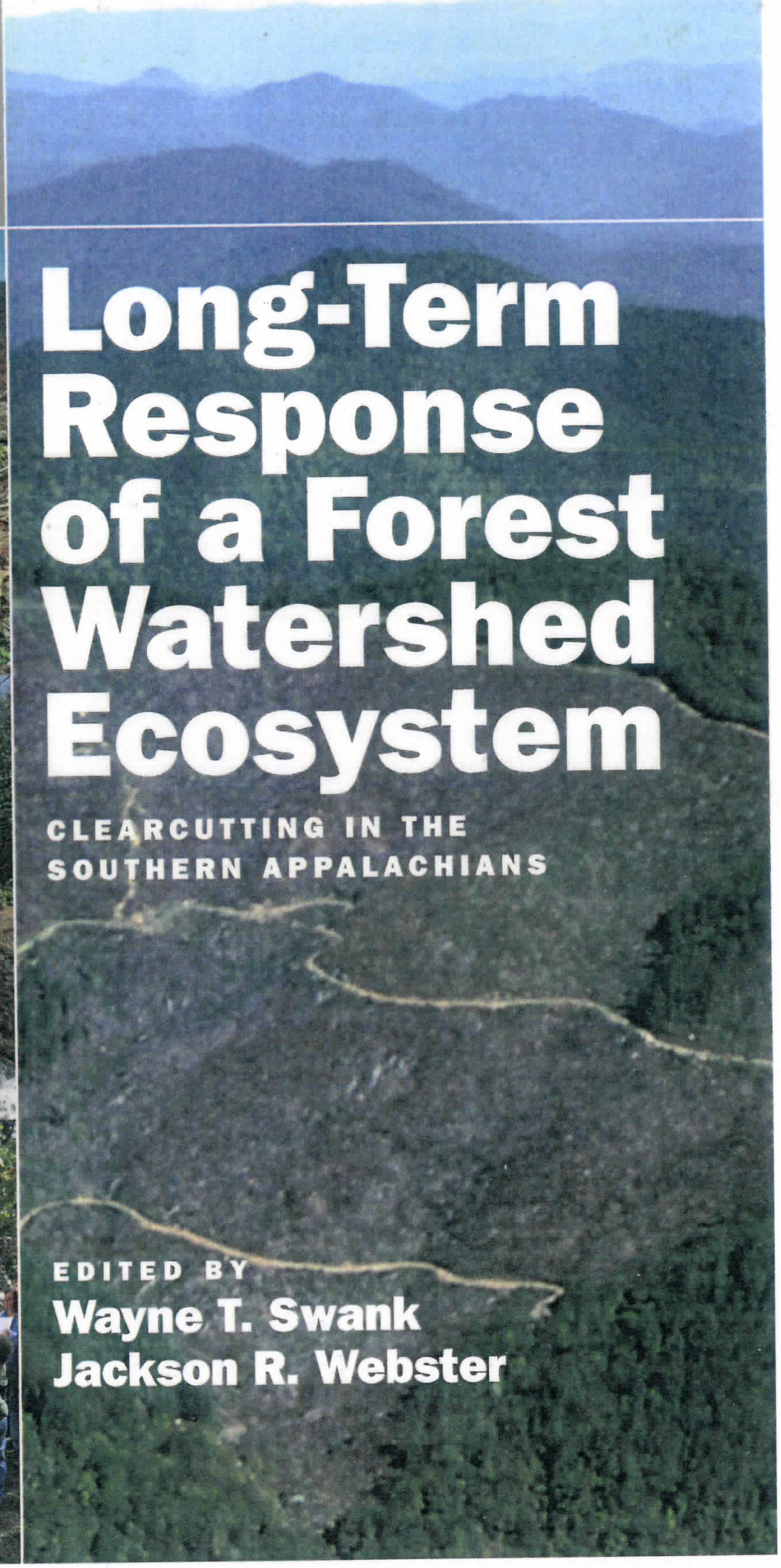

Long-Term Response of a Forest Watershed Ecosystem

CLEARCUTTING IN THE SOUTHERN APPALACHIANS

EDITED BY

Wayne T. Swank

Jackson R. Webster

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Our North American forests are no longer the wild areas of past centuries; they are an economic and ecological resource undergoing changes from both natural and management disturbances. A watershed-scale and long-term perspective of forest ecosystem responses is requisite to understanding and predicting cause and effect relationships. This book synthesizes interdisciplinary studies conducted over thirty years, to evaluate responses of a clear-cut, cable-logged watershed at the Coweeta Hydrologic Laboratory in the Nantahala Mountain Range of western North Carolina. This research was the result of collaboration among Forest Service and university researchers on the most studied watershed in the Lab's 78-year history. During the experiment, a variety of natural disturbances occurred: two record floods, two record droughts, a major hurricane, a blizzard of the century, major forest diseases, and insect infestations. These disturbances provided a unique opportunity to study how they altered the recovery of the forest ecosystem. This book also shows that some long-term forest trends cannot be forecast from short-term findings, which could lead to incorrect conclusions of cause and effect relationships and natural resource management decisions.

Wayne T. Swank is Scientist Emeritus, Coweeta Hydrologic Laboratory, Southern Research Station, USDA Forest Service.

Jackson R. Webster is Professor of Ecology in the Department of Biological Sciences at Virginia Polytechnic Institute and State University.

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