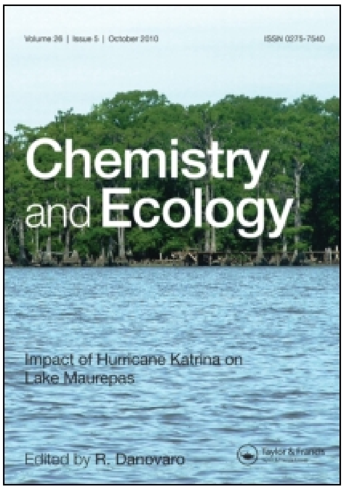

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Processes Influencing Dissolved Organic Nitrogen, Phosphorus and Sulphur in Soils

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PROCESSES INFLUENCING DISSOLVED ORGANIC NITROGEN, PHOSPHORUS AND SULPHUR IN SOILS

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The influence of different plant and soil processes on the concentrations of soluble organic forms of carbon, nitrogen, phosphorus and sulphur in soil and drainage waters is reviewed. Current knowledge about soluble organic matter is restricted mainly to dissolved organic carbon. Comparable information about soluble organic nitrogen, phosphorus and sulphur in processes such as eutrophication, plant uptake and decomposition is limited. Data are presented to highlight the potential sources of soluble organic components together with a discussion of their likely fate within the soil profile. The implications of changes in land use and management practices on dissolved organic matter are discussed.

KEY WORDS: carbon, nitrogen, phosphorus, plants, soil, soluble organic matter, sulphur

INTRODUCTION

The total amount and chemical composition of dissolved organic matter (DOM) in a terrestrial ecosystem varies considerably as rainwater passes down through the vegetation canopy and infiltrates the soil profile (Qualls *et al.*, 1991). The important role played by DOM in many soil processes, e.g. podzolization, has been recognised for a long time. This soluble and, in the case of non-humic substances, often extremely labile organic component, is the subject of wide ranging chemical, physical and biological modifications. Pronounced seasonal variations in their supply and the extent of any transformational process (Figure 1) can occur as a direct consequence of changing biological, climatic and hydrological conditions.

The nutrient composition of rain-water is dominated by inorganic forms of nitrogen and sulphur and normally contains very low levels of phosphorus (Miller *et al.*, 1990). During its passage through vegetation canopies and surface organic horizons, the concentration of dissolved organic components often tends to increase, reaching high levels in litter and upper soil horizons before declining again as it interacts with the mineral soil (McDowell and Likens, 1988).

While numerous studies have attempted to quantify the changes in dissolved organic carbon (DOC) that are likely to occur (McDowell and Wood, 1984), their significance in terms of the organically associated nitrogen, phosphorus and sulphur has, until recently, been largely ignored. In particular, the role of their soluble organic forms in nutrient cycling has received scant attention when compared to their inorganic counterparts. This low level of scientific interest in soluble organic forms reflects the greater importance of inorganic forms in plant uptake and nutrition. A general lack of suitable analytical procedures for distinguishing routinely between

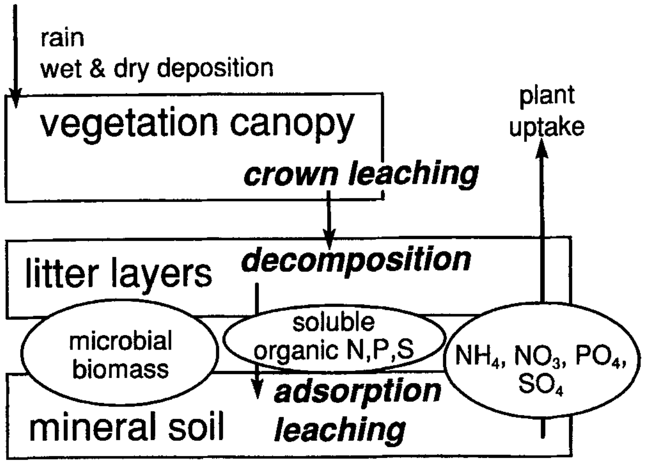

Figure 1 Principal processes influencing concentrations of soluble organic matter in the soil plant system

different organic components is a major limitation. Where progress on the role of DOM in nutrient cycling has been made, it is in studies of forested or semi-natural ecosystems (Qualls *et al.*, 1991). This reflects a greater need to understand the processes controlling nutrient availability and transport in plant communities growing on impoverished soils, and contrasts with agricultural crop production with its greater reliance on fertilizer applications.

Dissolved organic compounds can play a significant role in nutrient cycling as a result of their influence on:

1) the supply of readily hydrolyzed sources of nitrogen, phosphorus and sulphur which then become potentially available for plant uptake
2) chelation and complex formation with polyvalent ions, particularly transition metals, which can markedly change their biological toxicity and availability (Vaughan *et al.*, 1993)
3) competitive interaction with inorganic species for sorption sites.

Soil organic matter, which originates primarily from the biological activity of plants, microorganisms and animals, varies widely in chemical composition and rates of production and decomposition. A typical soil profile can be conveniently divided into an upper biologically active zone and an underlying mineral soil where geochemical processes are dominant (Ugolini *et al.*, 1977). It will be readily apparent, therefore, that hydrological factors such as depth of water percolation and residence time in individual horizons are key factors in determining the chemical composition of the soil solution at any particular point in the soil profile.

The downward passage of soil water through the biologically active surface zone into lower mineral soil horizons usually results in removal of DOC (Spycher *et al.*, 1983) through a combination of adsorption and precipitation type reactions. The extent of any reduction in DOC concentrations will be highly dependent upon the chemical and mineralogical properties of the soil (Evans, 1985) in addition to hydrological factors.

This paper considers the processes that are likely to have a direct influence on soluble forms of organic nitrogen, phosphorus and sulphur in the plant-soil system. These processes are discussed in relation to land use and management issues together with their possible consequences for surface water quality.

PLANT PROCESSES

Crown Leaching

Interaction of rainwater with various components of the vegetation canopy can cause rapid and highly significant changes in composition of DOC (Seastedt, 1985). This results either from interactions (uptake or release) with the leaf surface or the washing-off of previously deposited atmospheric aerosols. Carlisle *et al.* (1966) reported a transfer of up to 174 kg C ha^{-1} yr^{-1} from the canopy of sessile oak (*Quercus petraea*) to the forest floor. Most of this transfer occurred during the summer period June–August (30–45 kg ha^{-1} $month^{-1}$) and decreased to less than 5 kg C ha^{-1} $month^{-1}$ during winter.

These data included particulate material (<0.2 mm) and the quantities of dissolved substances are generally smaller in solutions filtered through a 1 μm filter (Adamson *et al.*, 1993). In a comparison of throughfall beneath heather (*Calluna vulgaris*) and *Sphagnum* mosses during September, DOC amounts were 5.5 and 10.5 kg C ha^{-1} $month^{-1}$, respectively (Edwards, unpublished results).

Various organic components identified in throughfall or canopy drip from trees include carbohydrates (Mahendrappa, 1974), simple organic acids and saturated fatty acids (Ugolini *et al.*, 1977). McDowell and Likens (1988) reported that 26% of DOC in throughfall was in the form of carbohydrates and phenolic acids, and a further 8% was present as aliphatic carboxylic acids and aldehydes. Primary amines were also detected, but contributed less than 1% to the DOC. Marked seasonal variations in composition have been reported with late summer inputs dominated by carbohydrates (Carlisle *et al.*, 1966). Numerous site specific factors will interact to influence the amount and composition of throughfall, including plant species, climate, nutrient status and soil type. In forest stands for example, individual tree species can display widely different efficiencies for intercepting and passing on ions deposited from the atmosphere in throughfall (Miller *et al.*, 1991). Age and structure of tree stands may also influence the interaction between vegetation and precipitation (Miller and Miller, 1983). The spatial distribution of throughfall can be highly heterogeneous, creating sampling difficulties when assessing the impact of throughfall on soil processes.

Plant Uptake

The major contribution to nutrient availability and plant uptake is via inorganic NH_4^+, NO_3^-, PO_4^{3-} and SO_4^{2-} nutrient pools. Increasingly, there are reports in the literature that soluble organic substances may also contribute directly to plant uptake under specific circumstances. Chapin *et al.* (1993) showed that under certain conditions the uptake of amino acids by non-mycorrhizal *Eriophorum vaginatum* growing in Arctic tundra accounted for at least 60% of the total nitrogen absorbed. Furthermore, the *Eriophorum* showed a clear preference for amino acids over mineral-N. Obtaining unambiguous experimental evidence that direct uptake has occurred is difficult because of the activity of extracellular enzymes and the modifying action of mycorrhizal fungi (Abuzinadah and Read, 1989). Mycorrhizal fungi infecting roots of native plants, e.g. *Calluna vulgaris, Betula* sp. and *Pinus* sp., have been identified as having proteolytic activity that provides the plant with low molecular weight organic forms of nitrogen for uptake (Leake and Read, 1989). Not only can ectomycorrhizas in pure culture utilize amino acids (Alexander, 1983), but ericaceous plants infected with the mycorrhizas are also able to use the organic-N source (Stribley and Reid, 1980). Thus, plants that can utilize low molecular weight soluble organic compounds will have a competitive advantage in conditions where nutrient mineralization is incomplete or the availability of inorganic forms is low.

Decomposition of Plant Material

The return of plant material to the soil represents a major transfer of organic matter and Kuiters (1993) has indicated the effects of this transfer on DOM. Levels of DOC increase sharply as throughfall passes through the litter layer (Brown and Iles, 1991). Release of mineral-N and PO_4^{3-} from decomposing litters is controlled by the microbial demand for these elements indicated by the C:N and C:P ratios of the litters (Staaf, 1980). Consequently, during the first two years of decomposition litters may release very small quantities of NH_4^+, NO_3^- and PO_4^{3-}. During this lag period, prior to the release of inorganic forms, organic-N can still be leached from litters by water (Williams and Griffiths, 1989). This suggests that leaching of DOM is not necessarily constrained by C:N:P ratios which are unfavourable to net mineralization (Table I). The chemical nature of organic-N leached from decomposing plant material has not been fully identified, but free amino acids such as aspartic acid, glutamic acid, alanine, glycine and serine were found to be widely distributed in waters extruded from a range of peats (Dadd *et al.*, 1953). These amino acids also included sulphur containing molecules such as cystine and methionine.

Root exudates form the second major source of DOM likely to be present in soil solution (Vaughan *et al.*, 1993). These are released into the rhizosphere which becomes a region of localized biological activity in the soil. Recent studies have claimed that up to 10% of carbon released into the soil as low molecular weight organic compounds may be reabsorbed by the root (Jones and Darrah, 1992).

Table I Mean accumulated amounts, mg/column, of nitrogen and phosphorus fractions leached from Sitka spruce litter in glass columns with distilled water at 20°C after incubation for 8 and 16 weeks. Standard errors of the means shown in parentheses.

	WEEK 8	WEEK 16
NH_4-N	0.27 (.061)	2.04 (0.179)
NO_3-N	0.09 (0.014)	13.33 (1.09)
ORGANIC-N	6.18 (0.339)	9.36 (0.313)
PO_4-P	10.83 (0.263)	17.02 (0.471)
ORGANIC-P	7.08 (0.515)	8.22 (0.539)

SOIL PROCESSES

Soil Solution Chemistry and Leaching

There are reports of the dissolved organic fractions of nitrogen, phosphorus, and sulphur (N_0, P_0 and S_0) in soil solution being found in greater amounts than their inorganic counterparts. Thus, for example, Stevens and Wannop (1987) reported that N_0 was the dominant form of nitrogen in soil solution in a profile beneath an area of clear-felled Sitka spruce. Nitrate concentrations and its contribution to the soluble-N increased in lower parts of the profile suggesting that NO_3^--N was leached, as well as being produced by gradual transformation of N_0 to NO_3. Samples of runoff collected from the surface of reseeded blanket bog contained greater concentrations of N_0 than either NH_4^+ or NO_3^- (Figure 2). Moreover, concentrations of N_0 increased during the growing season, indicating control by biological activity, and appeared to be unaffected by fertilization with urea. The significance of the influence of seasonal factors on soil solution P_0 and P_i under temperate climatic conditions has been well documented by Magid and Nielsen (1992). Ron Vaz *et al.* (1993) reported greater concentrations of soluble organic P than P_i in a soil solution extracted from an acid mineral soil under permanent pasture (Table II). While a sharp decline in P_i and P_0 was apparent for solution collected in the sub-soil, concentrations of P_0 remained relatively greater.

The amounts of S_0 can also be significant, often exceeding the quantity of SO_4^{2-}-S leached in the Oa horizon of a spodosol (Schindler and Mitchell, 1987). In a stand of Sitka spruce in central Scotland, concentrations of total-S increased sharply in throughfall as rain passed through the tree canopy and then to the litter layer (Edwards *et al.*, 1992). Organic-S accounted for up to 35% of dissolved sulphur

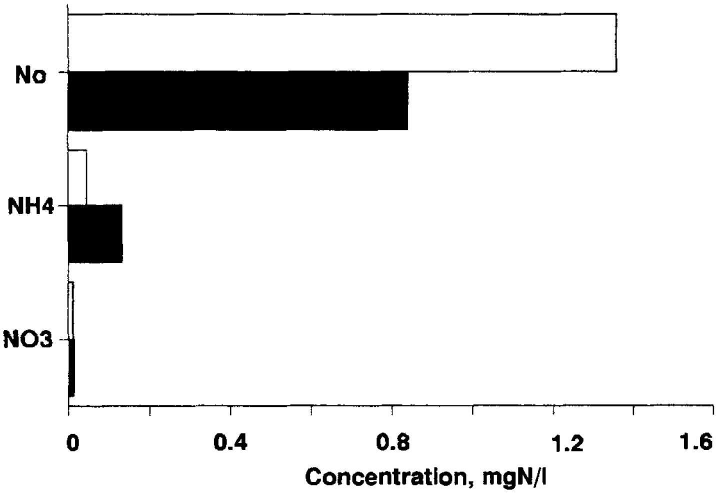

Figure 2 Mean concentrations (mg N l^{-1}) of NH_4^+, NO_3^- and soluble organic-N (N_0) in surface runoff samples collected on 23 sampling occasions from the upper 5 cm of reseeded blanket bog treated with P+K (☐) and N+P+K (■). Nitrogen applied as urea, phosphorus as granular superphosphate, and potassium as potassium chloride.

Table II Concentration (mg P l^{-1}) of soluble organic-P (P_o) and inorganic-P (P_i) in soil solution collected from different depths of an iron humus podzol (Typic Fragiorthod).

Depth (mm)	Soluble P_o	Soluble P_i
0–50	10.4	4.6
50–100	10.0	5.0
100–150	10.2	3.8
Sub-soil	6.0	2.0

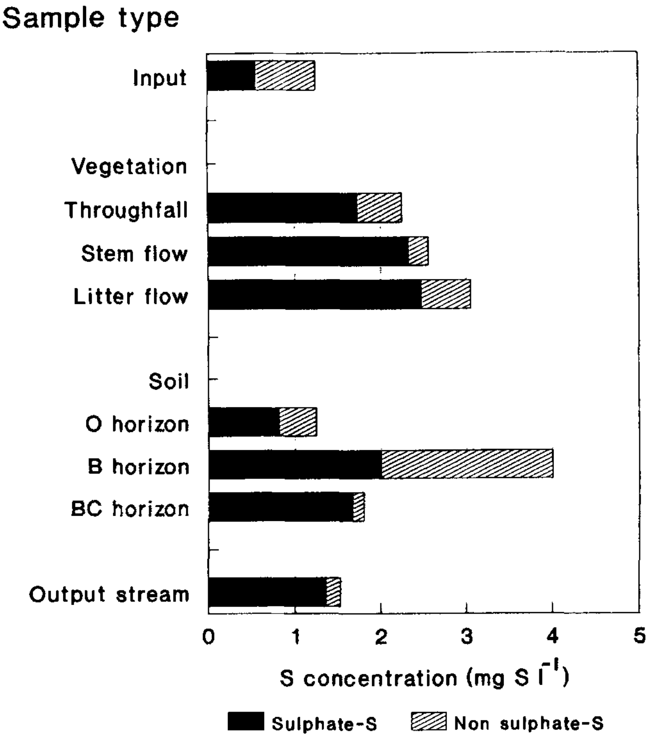

Figure 3 Concentrations (mg S l^{-1}) of inorganic- and organic-S in water samples collected beneath vegetation and at different depths of the soil profile in a stand of Sitka spruce in Central Scotland (Edwards *et al.*, 1992).

in waters draining the O horizon compared with 10% in the stream output (Figure 3). Forest soils differ from agricultural soils in that C-bonded sulphur is a major component of throughfall beneath hardwood species (Fitzgerald *et al.*, 1984), but is of minor significance beneath agricultural crops. The C-bonded sulphur includes sulpholipids and the amino acids, methionine and cystine, derived from proteins. Similar water extractable organic compounds were found to incorporate ^{35}S labelled SO_4^{2-} in the forest floor (Fitzgerald *et al.*, 1982) and also to form ester linkages with polysaccharide materials.

Table III DOC mg C l^{-1}, total-S, inorganic-S (S_i), organic-S (S_o) concentrations (mg S l^{-1}) in soil solution from an altitudinal sequence in NE Scotland (Arowolo, 1992).

	DOC	TOTAL-S	S_i	S_o	DOC/S_i
HEATHER	237	13.3	12.1	1.2	201
PERMANENT	36	4.8	3.5	1.3	28
ARABLE	70	8.4	6.0	2.4	29

The relative proportions of soluble organics-(S_o) and inorganic-S (S_i) compounds in soil solution can vary considerably over short distances as shown by Arowolo (1992) in a study of the forms of sulphur in soil solution isolated from soil collected along a short altitude/climatic sequence in NE Scotland. All soils had initially been derived from the same granitic parent material, but had widely differing chemical properties including organic matter contents and type of vegetation cover. The soils were also subject to an increasing degree of land management and agricultural inputs in the order, moorland < permanent pasture < arable/grass rotation. Dissolved organic-C concentrations displayed considerably more variation (Table III) than any of the sulphur components; this resulted in a significantly greater C:S_o ratio for the soil solution from heather moorland. Inorganic-S (S_i) concentrations were generally greater than S_o, being 91, 73 and 71 % of the total S in solution for heather moorland, permanent pasture and arable/grass rotation, respectively. The corresponding values of inorganic phosphorus (P_i) were 80, 21 and 48 % of the total-P (Ron Vaz, unpublished data).

Adsorption

The decline in DOM within the mineral part of the soil profile depends on depth of percolation and residence times in any particular horizon. Cresser and Edwards (1988) demonstrated changes in DOC concentrations of leachates percolating through intact cores from a *Calluna* heath. Soluble-C declined sharply from 18 to 3 μg ml^{-1} as the depth of mineral soil and the number of soil horizons increased. Abiotic control of DOC in river stream water was highlighted by McDowell and Wood (1984), with measured values of DOC absorption by the B2 horizon of >0.3 mg DOC g^{-1} soil. Separation of soil particles into light and heavy fractions indicated that the carbon and nitrogen associated with the heavy fraction were originally soluble organic matter leached down the soil profile (Spycher *et al.*, 1983). At 60–80 cm depth, the heavy fraction accounted for about 80% of soil carbon and 90% of soil nitrogen, and the carbon and nitrogen at this depth were approximately 13 and 16 %, respectively, of the total in the soil profile. The capacity of the mineral soil horizons to retain organic carbon and nitrogen in this way has very important implications for the eutrophication of surface waters in situations where atmospheric inputs of nitrogen are high. The importance of soil type, pH and chemical form of DOM in determining the extent of any adsorption have been reviewed for P_o by McKercher and Anderson (1989).

Death and Turnover of Soil Microbial Biomass

The soil microbial biomass has a relatively short turnover time compared with more stable humus (Jenkinson and Ladd, 1981) and is therefore a potentially important

Table IV Mean amounts of total-N (mg kg^{-1} dry soil) and the proportion (%) in organic form sequentially extracted with 0.01M $CaCl_2$ and 0.5M K_2SO_4 from unfumigated samples and from the same samples fumigated with chloroform for 18 hrs and extracted with 0.5M K_2SO_4 (Hill, 1992). Standard errors of the means shown in parentheses.

Sample	Unfumigated		Fumigated	
	mg kg^{-1}	%	mg kg^{-1}	%
Spruce litter	890 (72.7)	71.6	960 (31.7)	82.1
Spruce humus	298 (23.1)	19.5	139 (13.8)	59.0
Blanket peat	184 (4.6)	39.2	81 (9.2)	42.0
Grassland soil	81 (4.0)	29.7	129 (16.7)	90.7

source of dissolved organic-N, -P and -S. Fumigation of soils with chloroform to kill the biomass increases appreciably the amount of extractable-N, -P and -S. A large proportion of the extracted elements is inorganic, especially in the case of phosphorus, but for nitrogen a significant part is organic including ninhydrin positive compounds (Amato and Ladd, 1988). In a comparison of different soils, extractable-N from unfumigated samples was mainly inorganic except for spruce litter (Table IV). On fumigation of pre-extracted soils, the organic-N component increased, as might be expected, but there was marked variation in the proportions of organic-N between different soil types (Hill, 1992). Enzyme activity released during the physical collapse of cells may be responsible for the degradation and partial transformation of cell constituents to inorganic forms (Williams and Sparling, 1984). Alternatively, these enzyme activities may be synthesized with growth of new biomass (Amato and Ladd, 1988). The large proportion of microbial nitrogen, phosphorus and sulphur not recovered by extraction may still be in organic forms either adsorbed to the surfaces of soil components or present in suspension. Other processes that cause microbial death, such as soil drying and freeze-thaw cycles, also release soluble organic matter. Ivarson and Sowden (1970) reported releases of free amino acids and sugars when soils were frozen and thawed. Drying followed by rewetting has marked effects on the release of nutrients from tropical soils (Birch, 1964) including the release of free amino acids (Payne *et al.*, 1956). Effects of soil drying are not confined to tropical soils and Van Cleve and White (1980) described reductions in water extractable organic-N in Alaskan soil beneath birch as drying occurred during summer. Then, when the soil rewetted, concentrations increased though the origin of the organic-N is uncertain. Ivarson and Sowden (1966) ascribed these changes to liberation of energy sources available for microbial activity which is enhanced. The source of this organic matter could very well be a fraction of microbial biomass killed by the perturbation (Sparling and Ross, 1988).

Turnover of the microbial biomass is naturally enhanced by the grazing activities of protozoa and fauna. For example, protozoa grazing bacterial cells released surplus nitrogen as NH_4^+ (Zwart and Darbyshire, 1992), but only if the supply of N was adequate to maintain growth (Darbyshire, pers. comm.). In the coniferous forest floor, where the microbial biomass is predominantly fungal, faunal grazing stimulated leaching of organic-N (Setala *et al.*, 1990) as well as the release of inorganic forms of nitrogen and phosphorus.

Humification

The DOM in surface waters is chemically complex including low molecular weight components as well as high molecular weight humic substances (Qualls and Haines, 1991). Anderson *et al.* (1991) fractionated these substances into fulvic and hydrophilic acids. Fulvic acid-N in stream water accounted for about 12 % of the total dissolved-N in stream waters. In the soil drainage waters the relative contributions varied seasonaly, with fulvic accounting for almost 50 % of the total-N during summer and making a greater contribution than in the litter layer. Some humified substances may be formed during microbial degradation of plant material whereas others may be the result of abiotic processes (Benzing-Purdie *et al.*, 1986).

In general, humic substances are considered to be decomposed only slowly. Cook and Allen (1992) fractionated DOC compounds from old field soils into five categories on the basis of molecular size and surface charge to compare substrate quality. The proportion of each fraction did not change after incubation for 7 months, indicating that there was little difference in relative decomposability.

LAND USE CHANGES AND MANAGEMENT

Ploughing

Ploughing of arable soils and grasslands in lowland conditions increases the levels of potentially mineralizable-N in the soil almost two-fold to over 350 kg N ha^{-1} (Richter *et al.*, 1989). The effects increased rapidly for up to 9 years after ploughing and then more slowly up to 18 years, suggesting ongoing, dynamic processes in the soil as organic matter is decomposed. Techniques to improve the quality of the vegetation on upland soils have included removal of the vegetation by either burning or disc harrowing and losses of inorganic forms of nitrogen in stream water have increased from 10 to about 22 kg N ha^{-1} yr^{-1} (Roberts *et al.*, 1989). Some loss of nutrients in soluble organic forms is inevitable under these circumstances if it is accepted that the production of low molecular weight compounds is an essential part of the overall mineralization process.

Afforestation

Afforestation of nutrient poor peatlands and upland soils causes marked changes in the physical and chemical conditions in a soil, some of which are irreversible (Williams *et al.*, 1978). Hughes *et al.* (1990) reported increases in DOC in an afforested podzol soil compared with a grassland soil. However, there is little information about changes in the leaching of organic-N, -P and -S immediately following afforestation.

Cropping

Harvesting of tree crops has a profound impact on the forest soil environment by;

1) physical disturbance and soil compaction
2) increase in the supply of woody plant residues
3) change in the temperature and moisture regimes of the soil
4) interruption in the uptake of plant nutrients from the soil.

In general, inorganic-N leaching is enhanced by tree harvesting, whereas concentrations of dissolved organic-N can remain unchanged (Sollins and McCorison, 1981). In contrast, DOC can increase and mobilize iron and aluminium (Hughes *et al.*, 1990) when a tree crop is harvested. Carbon and nitrogen appear to behave quite differently under these conditions. Much less is known about the movement of dissolved organic matter after cropping agricultural soils.

Fertilization and Liming

Applications of fertilizer-N to forest stands increase the concentrations of total-N in throughfall, but not necessarily in stemflow (Mahendrappa and Ogden, 1973). Fertilizer-N, particularly urea, can also have a direct impact on soil organic matter. Ogner (1972) reported leaching of organic matter from forest soil receiving the equivalent of 400 and 1600 kg N ha^{-1}. The DOM included amino acids and carbohydrates and may account for the longer term effects of urea as a fertilizer compared with inorganic-N (Williams, 1972).

Liming acid soils can have profound changes on soil microbial activity and it may be expected that this will strongly influence the soluble organic components. Marschner and Wilczynski (1991) noted a reduction of 7 t C ha^{-1} in the organic-C pool of limed forest floor beneath pine compared with untreated controls. This reduction which occurred during a 3-year period was attributed to increased microbial respiration. Hornung *et al.* (1986) reported significant reductions in DOC in the soil solution of stagnopodzols treated with lime. However, in limed areas ploughed or surface cultivated, the concentration of DOC was significantly greater than in the unimproved control. These effects were detectable 10–40 years after treatment.

PRIORITIES FOR FUTURE RESEARCH

There is little doubt that where the transport and transformations of carbon, nitrogen, phosphorus and sulphur are being studied, their organic components should also be included. At present, analytical methods such as Inductively Coupled Plasma Emission Spectroscopy (ICP) with acid digestion are available for the analysis of the total contents of the elements in vegetation throughfall, runoff and drainage waters, soil solution and soil extracts. Well established methods are also at hand for the analysis of the inorganic forms though some are subject to interference from low molecular weight organic molecules. Such interference in the colorimetric analysis of P_i and NH_4^+-N prevent measurement of organic forms by difference and there is a need for quantitative analytical methods to determine organic forms directly and also to have a high throughput of samples.

Identification of the different chemical forms in solution (speciation) also seems important particularly if transformations are likely. For phosphorus, it is far from clear that the difference between total dissolved-P and orthophosphate-P corresponds to organic forms alone. Polyphosphates and P_i associated with organic molecules and adsorbed at surfaces through iron and aluminium prevent clear distinctions between organic and inorganic forms. Assays to determine bio-availability of the different forms in the soluble fraction may be more desirable in the future, in aquatic systems as well as in the soil.

The present practice of disposing of organic wastes such as sewage sludge and straw on land requires closer examination of the DOM contents of drainage and surface waters. This cannot be achieved without a better understanding of the processes involving the production and consumption of DOM at different levels in terrestrial and aquatic ecosystems. Such information will also benefit the study of nutrient cycling in agricultural systems where sustainability and extensification are key objectives.

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