Pergamon

Soil Biol. Biochem. Vol. 26, No. 3, pp. 331–337, 1994
Copyright © 1994 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0038-0717/94 $6.00 + 0.00

14108

SOIL SOLUTION CHEMISTRY OF ECTOMYCORRHIZAL MATS IN FOREST SOIL

R. P. Griffiths,[1]* J. E. Baham[2] and B. A. Caldwell[1]

[1]Department of Forest Science, Oregon State University, Corvallis, OR 97331-7501 and [2]Department of Crop and Soil Science, Oregon State University, Corvallis, OR 97331-2213, U.S.A.

(Accepted 16 September 1993)

Summary—Survival and productivity of Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] depend on close association between host trees and ectomycorrhizal fungi. Two of these fungi, *Hysterangium setchellii* (Fischer) and *Gautieria monticola* (Harkness), form extensive hyphal mats with the roots of Douglas-fir and other conifers in the surface of the 'A' horizon, often at the interface between mineral oil and litter. The fungal mat alters the chemistry and mineral nutrition of the soil microenvironment within the rhizosphere, producing conditions that favor increased tree growth by increasing nutrient availability.

Forest soils with or without obvious ectomycorrhizal mats were sampled at two locations in the Pacific Northwest. Cation and anion chemistry, dissolved organic carbon (DOC) and oxalate anions were analyzed. Mean concentrations of DOC, oxalate, PO_4, SO_4, H, Al, Fe, Cu, Mn and Zn were significantly higher in mat than in non-mat soil solutions in both mat types and locations and on both sampling dates. Significant statistical correlations between DOC or oxalate and PO_4 indicate that organic acids influence weathering and solubility of PO_4 in the mat soils. Mean oxalate concentrations were significantly lower in soil solutions from *Hysterangium* mat soils than in those from *Gautieria* mat soils. Organic acids released to the rhizosphere by *G. monitcola* and *H. setchellii* may provide a local weathering environment that increases availability of PO_4, SO_4 and trace nutrients.

INTRODUCTION

Soluble organic acids, especially those that complex with Al or Fe, may perform several critical functions in the biogeochemistry of the rhizosphere and the productivity of the above-ground ecosystem, especially by enhancing dissolution or inhibiting precipitation of soil minerals containing PO_4 or SO_4 (Fox *et al.*, 1990a, b). Such acids have been identified from forest soils in several regions (Hue *et al.*, 1986; Pohlman and McColl, 1988; Fox and Comerford, 1990). The soluble oxalate anion is an effective weathering agent in mineral soils (Henderson and Duff, 1963; Baker, 1973; Boyle *et al.*, 1974; Robert *et al.*, 1979; Furrer and Stumm, 1986; Manley and Evans, 1986; Pohlman and McColl, 1986; Robert and Berthelin, 1986; Tan, 1986; Song and Huang, 1988; Fox *et al.*, 1990a, b) and has been implicated in release of K from a hydroxy-interlayered vermiculite (Comerford *et al.*, 1990). Organic acids (e.g. oxalic, citric) also can form soluble complexes with Al, ameliorating the toxicity of the free metal cations to higher plants and thereby increasing biological productivity (Pavan *et al.*, 1982; Hue *et al.*, 1986).

Certain specialized ectomycorrhizal fungi can form dense perennial fungal mats in forest soils. These are good model systems with which to study the effects of mycorrhizas on soil processes (Cromack *et al.*, 1979; M. A. Castellano, unpublished Ph.D. thesis, Oregon State University, 1988; Griffiths *et al.*, 1990). In some cases, over 25% of the upper 10 cm of the mineral soil in a forest is colonized by rhizomorphs from *H. Setchellii* (Fischer) (Cromack *et al.*, 1979). Fungal mats may accelerate mineral weathering of forest soils (Hintikka and Naykki, 1967; Hintikka *et al.*, 1979), enhancing mobility of important nutrients and their uptake by plants. In particular, the oxalic acid or calcium oxalate produced by various ectomycorrhizal fungi (Graustein *et al.*, 1977; Cromack *et al.*, 1979; Sollins *et al.*, 1981; Malajczuk and Cromack, 1982; O'Connell *et al.*, 1983; Lapeyrie *et al.*, 1984, 1987) probably enhances weathering of soil minerals. Concentrations of exchangeable Al, Fe, Mn, Zn and Cu are higher in soils colonized by *H. setchellii* than in the same mineral soil without dense rhizomorphs (Entry *et al.*, 1987).

Testing geochemical hypotheses about the role of organic acids in PO_4 availability and weathering of soil minerals requires complete chemical analyses of soil solutions. Such analyses are unavailable for soil solutions extracted from soils with fungal mats. The objective of our research, therefore, was to examine the chemistry of soil solutions, with particular attention to oxalate, from two distinct ectomycorrhizal mat communities common in Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] ecosystems of the Pacific Northwest.

---

*Author for correspondence.

MATERIALS AND METHODS

Site description and sample preparation

The Woods Creek (WC) study site is located at *ca.* 460 m elevation on Marys Peak, in the Coast Range of Oregon. The overstory is dominated by a stand of 75–80-year-old Douglas-fir. Dense mats of *H. setchellii* are plainly visible throughout the surface horizons of soils on the site. The major soil series on this site is Slickrock gravelly loam derived from a mixture of highly-weathered colluvial sandstone and basalt. The mean annual precipitation is 1900 mm, mostly occurring as rain in winter and spring. This site has been described in detail by Hunt and Trappe (1987).

The second study area, at the H. J. Andrews Experimental Forest (HJA) in the Cascade Mountains of Oregon, is at 600 m in a stand of 42-year-old Douglas-fir that was precommercially thinned in 1981. The soil is a gravelly loam developed from a mixed colluvium of pyroclastic Mazama volcanic ash. The rhizosphere is colonized by *G. monticola* (Harkness), the dominant mat-forming ectomycorrhizal fungus at this site.

Samples (0–5 cm) from soils colonized by ectomycorrhizal mats and adjacent uncolonized soils were collected from both sites in May and August of 1990. Samples were sealed in plastic bags and transported to the laboratory in ice chests. Soil temperatures (5 cm depth) were 9°C in May and 14°C in August.

Soil solution extraction

After coarse fragments, woody material, and roots had been removed manually, the equivalent of 63 g of soil (dry wt) was packed loosely into a 250 ml centrifuge bottle, similar in design to those used by Adams *et al.* (1980). A 0.22 μm membrane filter supported by a perforated plate separated the bottom of the soil column from the collection cup. The samples were wetted to 100% gravimetric water content with distilled water and allowed to stand 15 min before centrifugation. Soil solutions were extracted by centrifugation in a swinging bucket rotor at 800 *g* for 20 min. A typical yield of soil solution was *ca.* 33% of the soil water content (*ca.* 20 ml). We define the soil solution as the dissolved inorganic and organic constituents in the solution extracted from the soil samples at 100% gravimetric water content. We also assumed that the added deionized water dilutes the soluble species and does not significantly affect the solubility of solid mineral or organic phases. All of the reported concentrations are based on the water content of the soil samples at the time of collection, which was determined by drying separate subsamples in a microwave oven.

Soil solution analysis

The pHs of the soil solutions were determined with a glass combination electrode immediately after centrifugation. Dissolved organic carbon (DOC) was measured in triplicate with a Dohrman DC-80 Carbon Analyzer (Dohrman Instruments, Santa Clara, Calif.). Dissolved total nitrogen (DTN) was determined by a microKjeldahl method (Bremner and Mulvaney, 1982). Nitrate (NO_3^- and ammonium (NH_4^+ were measured colorimetrically with an Alpkem Autoanalyzer (Alpkem Corp., Clackamas, Ore.) Concentrations of Al, B, Ca, Co, Cu, Fe, K, Mg, Mn and Zn were determined with a Jarrell-Ash Model 9000 ICAP (inductively coupled argon plasma) spectrometer (Jarrell-Ash Corp., Waltham, Mass.). Soluble SO_4, Cl, PO_4 and Ox (oxalate anion) were determined with a Dionex 2000i ion chromatograph system. Anions were separated on an AS4A column with NG1 and AG4A guard columns (Dionex Corp., Sunnyvale, Calif.) and detected by conductivity.

3 g of the residual soils was subsequently extracted with 30 mM HCl to dissolve solid-phase calcium oxalate. The oxalate concentrations were measured by IC and expressed in terms of mol kg^{-1}, after correction for the oxalate in the remaining soil solution. Exchangeable cations were displaced with 0.1 M $BaCl_2$ and determined by ICAP (Hendershot and Duquette, 1986).

Data analyses and statistics

Significance of differences was determined by the Wilcoxin nonparametric test (Statgraphics, STSC, Inc., Rockville, Md). Correlations were done with the Spearman rank test (Statgraphics, STSC, Inc., Rockville, Md). Data from sampling period were not pooled.

RESULTS

Soil solution chemistry

Concentrations of inorganic anions and cations, DOC and soluble oxalate were greater in soils dominated by ectomycorrhizal mats than in uncolonized (non-mat) soils on both sampling dates (Table 1); however, the chemistry of the solutions from the *G. monticola* mat and non-mat soils differed more in May. Hydrogen ion concentrations (10^{-pH}) in the *G. monticola* soil solutions were 16 times greater in mat than in non-mat soil in May and 2 times greater in August. The concentration of H^+ in *H. setchellii* mat soil solutions was approx. 6 times greater than in non-mat soil in both May and August. The same general seasonal pattern in soil solution chemistry in both mat types was observed for Al, Ce, Fe, Mn, S, Zn, PO_4, SO_4 and DOC (Table 1).

Soluble oxalate was significantly higher in soil solutions collected in May and August from both mat types than in non-mat soils (Table 1). The mean concentration of oxalate in the *G. monitcola* soil solutions was *ca.* 200 times greater than that in *H. setchellii* mat soils on both sampling dates. The highest values for soluble oxalate (68 mM) were found in the solutions from *G. monticola* mats sampled in

Table 1. Mean concentrations of components of soil solutions isolated from *H. setchellii* (HYST) and *G. monticola* (GAUT) mat soils and adjacent non-mat soils

	May				August			
	Hysterangium		Gautieria		Hysterangium		Gautieria	
Component	Mat	Non-mat	Mat	Non-mat	Mat	Non-mat	Mat	Non-mat
				μmol l^{-1}				
Al	353**	56	8044***	55	1094**	259	2354***	174
Ca	710***	120	2000***	110	2400***	270	1700***	220
Cu	0.56***	0.20	1.83**	0.18	2.12***	0.18	0.73**	0.12
Fe	39*	16	320**	6.3	98	72	117**	36
H	74.1***	10.0	32.4***	2.14	70.8***	10.7	49.0***	27.5
K	470***	120	180***	210	210***	170	1700***	220
Mg	410***	51	1500***	480	1400***	120	1300***	81
Mn	10.3***	2.00	1220***	9.1	81.5***	2.10	972***	15.1
Zn	2.67*	1.13	12.6**	1.23	13.3*	4.34	4.4**	1.93
B	5.12	3.84	5.55**	1.64	13.2	9.59	14.7**	2.43
Cl	682**	204	683**	0	5139**	425	1499**	421
NH_4	< 10	< 10	33	< 10	ND	ND	ND	ND
NO_3	< 3.6	< 3.6	4.3	< 3.6	ND	ND	ND	ND
PO_4	51.8***	35.0	62.1***	3.2	225***	27.3	29.0***	8.4
S	1900***	420	290***	110	7500***	1000	3900***	800
SO_4	140*	52	231**	18	2423*	268	1059**	220
N_T^a	550**	270	1011***	183	ND	ND	ND	ND
Oxyalate	59*	5.2	11,638***	35	352*	0	68,016***	0
DOC^b	67,000**	7300	1888,000***	5200	232,000**	29,000	192,000***	42,000
				μmol kg^{-1}				
Ox^c_{Acid}	7137**	1394	3965**	1409	ND	ND	ND	ND
				mol mol^{-1}				
DOC/NT^d	125	28	193	31	ND	ND	ND	ND

*, **, *** Significance at the 0.05, 0.01, and 0.001 probability levels, respectively, for the comparison of mat and non-mat concentration values.

[a] Total nitrogen in the soil solution.

[b] Dissolved organic carbon.

[c] Oxalate soluble in 0.03 M HCl after removal of the soil solution.

[d] Molar ratio of the dissolved organic carbon to total dissolved nitrogen.

ND = not determined.

August. No oxalate could be detected in the non-mat soils at either site in August.

The concentrations of $BaCl_2$ exchangeable K and Ca were significantly greater in mat soils (Table 2). The reverse trend was observed for Al, Mn and Fe, but these differences were not always significant. Ion concentrations in centrifuged soil solutions were generally lower (<0.1–6%) than those obtained for $BaCl_2$ exchange. Except for Al, Cu and Fe, exchangeable cations displaced in $BaCl_2$ were higher in mat soils. These data show that mat soil solutions contained the largest concentrations of Al and Fe when compared with the $BaCl_2$ exchangeable pools (Table 3). The percentage of ions in soil solution phase relative to total concentration ($BaCl_2$ exchangeable + soil solution) ranged from 0.1% for Ca to 100% for Al, Fe and P (Table 3). This observation is generally true for the transition metals and can be contrasted to Ca, K and Mg, which are mainly present as $BaCl_2$ exchangeable ions.

Concentration of PO_4 was highly correlated with that of oxalate ($r = 0.985$, $P \leqslant 0.05$) or DOC ($r = 0.988$, $P \leqslant 0.01$) in soil solutions from mats of *G. monticola*, but not in solutions of non-mat soils. In

Table 2. $BaCl_2$-exchangeable cations extracted from mat and non-mat soils from which the soil solution was removed

	May				August			
	Hysterangium		Gautieria		Hysterangium		Gautieria	
Element	Mat	Non-mat	Mat	Non-mat	Mat	Non-mat	Mat	Non-mat
					$cmol_c$ kg^{-1}			
Al	0.012*	0.18	0.000**	0.031	0.0093*	0.031	0.00020*	0.055
Ca	32.97**	10.51	14.50**	7.04	23.44**	14.41	9.25**	4.60
Cu	0.0002**	0.0004	0.0002	0.0002	0.0002**	0.0003	0.00028	0.00028
Fe	0.0004	0.0009	0.0000*	0.0008	0.0002	0.0002	6.2E-05	0.0005
K	0.82*	0.60	0.91	0.68	0.93*	0.76	0.67*	0.54
Mg	1.82	1.42	0.87	0.65	1.52	1.49	0.71	0.47
Mn	0.051	0.036	0.028	0.036	0.046	0.17	0.017	0.089
Zn	0.0014	0.0013	0.0004	0.0007	0.0013	0.0006	0.0005	0.0009
Sum cations	35.66	12.74	16.31	8.44	25.94	16.86	10.65	5.75

*, **, *** Significance at the 0.05, 0.01, and 0.001 probability levels, respectively, for the comparison of mat and non-mat concentrations.

Table 3. Percentages of total ions ($BaCl_2$ exchangeable + soil solution) in the soil solution from mat and non-mat soils of *H. setchellii* and *G. monticola*

	May				August			
	Hysterangium		Gautieria		Hysterangium		Gautieria	
Element	Mat	Non-mat	Mat	Non-mat	Mat	Non-mat	Mat	Non-mat
					%			
Al	69.2	3.0	100.0	14.9	82.0	30.6	100.0	12.9
Ca	< 0.1	< 0.1	0.7	< 0.1	0.3	< 0.1	0.4	0.1
Cu	13.5	2.5	27.1	3.2	21.6	1.9	5.7	0.8
Fe	87.0	50.9	100.0	30.1	96.0	92.5	100.0	64.1
K	1.3	0.5	4.5	0.6	3.1	0.4	2.8	0.4
Mg	1.0	0.2	8.9	0.3	2.4	0.3	4.0	0.4
Mn	0.9	0.2	64.0	1.1	4.4	0.2	55.8	0.8
Zn	10.8	4.9	63.4	9.3	25.9	20.0	21.4	7.1

soil solutions from *H. Setchellii*, in contrast, PO_4 was correlated significantly only with DOC and only in non-mat soil ($r = 0.996$, $P \leqslant 0.01$).

DISCUSSION

Soil mineral weathering

Mats of both *G. monticola* and *H. setchellii* contain calcium oxalate (Cromack *et al.*, 1979; Sollins *et al.*, 1981). A large quantity of crystalline calcium oxalate (weddellite) is intimately associated with the rhizomorphs of *H. setchellii* (Graustein *et al.*, 1977; O'Connell *et al.*, 1983). Significant quantities of presumptive calcium oxalate also are visible on the fungal rhizomorphs of *G. monticola* mats. We found that, in contrast to the oxalate concentrations measured in the soil solutions, acid-extractable oxalate was higher in mats of *H. setchellii* than those of *G. monticola*. Possibly the fungi produce different forms of calcium oxalate that vary in crystal structure. The location of the calcium oxalate within the fungal structure also could lead to the differences observed in solubility.

Since the mineralogy of the clay fraction of soils formed under *H. setchellii* mats differs from that of non-mat soils (Cromack *et al.*, 1979), these fungi may be instrumental in pedochemical genesis. Dissolved oxalate concentrations that we measured in non-mat soils were comparable to those measured in solutions collection from forest soils from the southeastern U.S.A. (Fox and Comerford, 1990). The highest oxalate concentrations from *G. monticola* mat solutions (Table 1) were nearly three orders of magnitude greater than those reported by Fox and Comerford (1990), however, and greatly exceeded oxalate concentrations used to study Al and P mobilization (Pohlman and McColl, 1986; Fox *et al.*, 1990a). Dissolved oxalate represented up to 71% of the DOC in soils colonized by *G. monticola*. The total soluble oxalate concentrations (68 and 12 mM) exceeded the value expected in equilibrium with pure calcium oxalate (100 μM; $K_{SO} = 1 \times 10^{-8}$). Thus, the ectomycorrhizal fungi may be secreting oxalic acid in excess of that which can be precipitated with the available Ca in the rhizosphere.

The solution obtained by Entry *et al.* (1992) from extraction with 0.5 N ammonium acetate-0.25 mM diethylenetriamine penta-acetic acid included ions from both the soil solution and the exchangeable pools. One objective of our study was to analyze the soil solution and exchangeable pools separately (Tables 1 and 2). Mat soils tended to have a higher proportion of total (soil solution + 0.1 M $BaCl_2$ exchangeable) cations and anions in the soil solution than in the exchangeable pool; in non-mat soils, in contrast, proportions of the cations and anions generally were higher in the exchangeable pool. Concentrations of Fe, Al and P were significantly greater in the mat soil solution pool than in the exchangeable pool. These results support the hypothesis that oxalate and other organic anions act as ligands forming soluble complexes with Al and Fe, thereby increasing their presence in the soil solution, rather than on exchange sites.

Although oxalate may be a key factor in mineral weathering and nutrient availability in mat soils, other organic acids may also be involved. The pH values of the soil solutions from *H. setchellii* mats were lower than those of the soil solutions from *G. monticola* mats, even though the corresponding DOC values were also lower. This suggests that stronger acids may be present in solutions from the *H. setchellii* mat soils than in those from *G. monticola*. Likely candidates include formic ($K_a^{298} = 1.77 \times 10^4$), acetic ($K_a^{298} = 1.75 \times 10^5$), and citric ($K_a^{298} = 7.45 \times 10^4$) acids, which have been identified in forest soils (Fox and Comerford, 1990). Work is currently under way to identify and measure these organic acids in the mat soil solutions.

Plant nutrient availability

Extraction of air-dried samples of *H. setchellii* and *G. monticola* mat and non-mat soils with 0.1 M $BaCl_2$ produces solutions with strikingly different cation and anion distributions and apparent enrichment of specific elements by the fungal rhizomorphs (Entry *et al.*, 1992). Thus, the fungi may both weather the mineral phase and accumulate cations, providing the host tree with a mechanism for obtaining mineral nutrients.

As a consequence of weathering of the soil mineral phase by formation of soluble metal-oxalate complexes, concentrations of cations and ligands should be higher in mat soil solutions than in non-mat solutions, as we observed. This increase is especially significant in the case of Fe and Al, which are normally present as major ions in primary minerals, secondary oxides, or mineral solids with phosphate and sulfate ligands. The formation of these solids regulates the solubility and, hence, the bioavailability of PO_4, SO_4 and Fe. The soil solutions extracted from the *G. monticola* mats contained as much as 146 times more soluble Al than those from the corresponding non-mat soils, indicating that weathering is more intense in the mat soils (Table 1).

Oxalate forms stable soluble complexes with Fe and Al that can either inhibit precipitation (Struthers and Sieling, 1950) or enhance dissolution of the sparingly soluble Fe and Al phosphates strengite and variscite (Graustein *et al.*, 1977; Earl *et al.*, 1979; Lopez-Hernandez *et al.*, 1986). Oxalate and other low molecular weight organic acids therefore may be primary controllers of PO_4 and SO_4 solubility in acid forest soils and thereby influence plant nutrient availability. Fox and co-workers (1990a, b) demonstrated mobilization of organic and inorganic phosphorus at oxalate concentrations far below those we observed in ectomycorrhizal mat soil solutions. We found that concentrations of soluble PO_4 and SO_4 were significantly higher in both fungal mats than in non-mat soils.

Organic matter cycling

In this study, enrichment of DOC in mat soils relative to non-mat soils ranged from 4.6-fold from samples of *G. monticola* collected in August to over 36-fold in the same mats sampled in May. This is in contrast to previous measurements of total carbon in *H. setchellii* mats, which showed only a 21% enrichment of carbon in mat soils (Griffiths *et al.*, 1990).

Griffiths *et al.* (1990, 1991) also found that the $C_{fum}:N_{min}$ (labile C:labile N) was significantly greater in whole soil samples of mat soils than in non-mat soils. They speculated that this was caused by either (1) an increase in labile carbon resulting from mineralization of recalcitrant organic polymers (where the organic nitrogen component was preferentially removed), or (2) an increase in the fungal production of organic acids, which contain no nitrogen. Thus, the DOC:DTN in pore-water observed in this study reflects the same trend observed in $C_{fum}:N_{min}$ ratios for whole soil samples. On the basis of elevated concentrations of oxalate anions, the high elemental DOC:DTN ratios observed for the mat soils probably resulted in part from organic acid production by fungi.

Concentrations of oxalate in mat soil also may be sufficient to facilitate the solubilization of humic sub-stances by removing the "cation bridges" hypothesized to bind negatively-charged soil organic matter (SOM) to particle surfaces (Greenland, 1965, 1971; Mortland, 1970; Stevenson, 1982). Oxalate concentrations of solutions from *G. monticola* mats sampled in August approach the concentration used by Bremner and Lees (1949) as an organic matter extractant. Oxalate may also solubilize proteins and nucleic acids bound to mineral surfaces or flocculated by metal cations in a similar fashion, thereby increasing accessibility of hydrolytic enzymes to organic nitrogen and phosphorus. Therefore, elevated concentrations of DOC in mat soils may be due to both production of soluble organic acids by fungi and increased solubility of humic polymers containing organic carbon.

Metal toxicity

Formation of complexes with Al and Fe may detoxify the rhizosphere by lowering the activity of the free metal species (Hue *et al.*, 1986; Arp and Strucel, 1989). Reduced growth and nutritional deficiencies in trees occur frequently at Al concentrations well below those we observed in the two ectomycorrhizal mat communities, as discussed in recent reviews (Kelly *et al.*, 1990; Raynal *et al.*, 1990; Sucoff *et al.*, 1990). Apparently, organic acids produced in the rhizosphere can protect plants from the toxic effects of Al and a wide spectrum of heavy metals and may actually reduce the concentration of metals within plant tissues (Bradley *et al.*, 1982; Danielson, 1985; Jones and Hutchinson, 1986). Tree survival may depend, in part, on the establishment of ectomycorrhizal fungi that produce organic acids (Entry *et al.*, 1987; Jones *et al.*, 1986). The formation of Al-organic acid complexes would lower the bioavailability of Al, even though the total concentration of Al may be higher (Hue *et al.*, 1986; Pavan *et al.*, 1982).

Functional differences between G. monticola and H. setchellii mats

On the basis of the relative activities of hydrolytic extracellular enzymes in the two fungi (Griffiths and Caldwell, 1992), *H. setchellii* mats seem better adapted for the processing of detrital nutrients resource in SOM than are those of *G. monticola*. The higher total concentrations of ions in the solutions isolated from its mat soils, however, indicate that *G. monticola* may be better adapted to weathering mineral soil and altering the availability of sulfate and phosphate. Although the precise mechanism is not known, the spatial location of the oxalate within the fungi and the crystal structure may reflect its function in mineral weathering. Much of the oxalate in *G. monticola* mats is in solution, readily available for contact with mineral soil. The oxalate in *H. setchellii* mats, however, is primarily calcium oxalate, which may not be as readily accessible for mineral weathering.

Acknowledgements—We thank Lynne Baham for her technical and editorial assistance. This work was supported in part by the National Science Foundation. This is Paper 2937 of the Forest Research Laboratory and technical paper of the Oregon Agricultural Experiment Station, Oregon State University, Corvallis.

REFERENCES

Adams F., Burmester C., Hue N. C. and Long F. L. (1980) A comparison of column-displacement and centrifuge methods for obtaining soil solutions. *Soil Science Society American Journal* **44**, 733–735.

Arp P. A. and Strucel I. (1989) Water uptake by black spruce seedlings from rooting media (solution, sand and peat) treated with inorganic and oxalated aluminium. *Water, Air and Soil Pollution* **44**, 57–70.

Baker W. E. (1973) The role of humic acids from Tasmanian podzolic soils in mineral degradation and metal mobilization. *Geochimica et Cosmochimica Acta* **37**, 269–281.

Boyle J. R., Voigt G. K. and Sawhney B. L. (1974) Chemical weathering of biotite by organic acids. *Soil Science* **117**, 42–45.

Bradley R., Burt A. J. and Read D. J. (1982) The biology of mycorrhiza in the Ericaceae. VIII. The role of mycorrhizal infection in heavy metal resistance. *New Phytologist* **91**, 197–209.

Bremner J. M. and Lees H. (1949) Studies on soil organic matter. II. The extraction of organic matter from soil with neutral reagents. *Journal of Agricultural Science* **39**, 274–279.

Bremner J. M. and Mulvaney C. S. (1982) Nitrogen-total. In *Methods of Soil Analysis*: *Chemical and Microbiological Properties* (A. L. Page, D. E. Baker, R. Ellis Jr, D. R. Keeney, R. H. Miller and J. D. Rhoades, Eds.), pp. 595–624. Soil Science of America, Madison.

Comerford N. B., Harris W. G. and Lucas D. (1990) Release of nonexchangeable potassium from a highly weathered, forested Quartzipsamment. *Soil Science Society of America Journal* **54**, 1421–1426.

Cromack K., Sollins P., Graustein W. C., Speidel K., Todd A. W., Spycher G., Li C. Y. and Todd R. L. (1979) Calcium oxalate accumulation and soil weathering in mats of the hypogeous fungus *Hysterangium crassum*. *Soil Biology & Biochemistry* **11**, 463–468.

Danielson R. M. (1985) Mycorrhizae and reclamation of stressed terrestrial environments. In *Soil Reclamation Processes*: *Microbial Analyses and Applications* (R. L. Tate III and D. A. Klein, Eds), pp. 173–201. Marcel Dekker, New York.

Earl K. D., Syers J. K. and McLaughlin J. R. (1979) Origin of the effect of citrate, tartrate, and acetate on phosphorus sorption by soils and synthetic gels. *Soil Science Society of America Journal* **43**, 674–678.

Entry J. A., Rose C. L. and Cromack K. (1987) Litter decomposition and nutrient release in ectomycorrhizal mat communities in a Douglas-fir forest soil. *Soil Biology & Biochemistry* **23**, 285–290.

Entry J. A., Rose C. L. and Cromack K. Jr (1992) Microbial biomass and nutrient concentrations in hyphal mats of the ectomycorrhizal fungus *Hysterangium setchellii* in a coniferous forest soil. *Soil Biology & Biochemistry* **24**, 447–453.

Fox T. R. and Comerford N. B. (1990) Low-molecular-weight organic acids in selected forest soils of the southeastern U.S.A. *Soil Science Society of America Journal* **54**, 1139–1144.

Fox T. R., Comerford N. B. and McFee W. W. (1990a) Kinetics of phosphorus release from spodosols: effects of oxalate and formate. *Soil Science Society of America Journal* **54**, 1441–1447.

Fox T. R., Comerford N. B. and McFee W. W. (1990b) Phosphorus and aluminium release from a spodic horizon mediated by organic acids. *Soil Science Society of America Journal* **54**, 1763–1767.

Furrer G. and Stumm W. (1986) The coordination chemistry of weathering. I. Dissolution kinetics of δ-Al_2O_3 and BeO. *Geochimica et Cosmochimica Acta* **50**, 1847–1860.

Graustein W. C., Cromack K. and Sollins P. (1977) Calcium oxalate: occurrence in soils and effect on nutrient and geochemical cycles. *Science* **198**, 1252–1254.

Greenland D. J. (1965) Interactions between clays and organic compounds in soils. Part 1. Mechanisms of interactions between clays and defined organic compounds. *Soils and Fertility* **28**, 415–425.

Greenland D. J. (1971) Interactions between humic and fulvic acids and clays. *Soil Science* **111**, 34–41.

Griffiths R. P. and Caldwell B. A. (1992) *Mycorrhizal Mat Communities in Forest Soils.* (D. J. Read, D. H. Lewis, A. H. Fitter and I. J. Alexander, Eds), pp. 98–105. University Press, Cambridge.

Griffiths R. P., Caldwell B. A., Cromack K. Jr and Morita R. Y. (1990) Douglas-fir forest soils colonized by ectomycorrhizal mats. I. Seasonal variation in nitrogen chemistry and nitrogen cycle transformation rates. *Canadian Journal of Forest Research* **20**, 211–218.

Griffiths R. P., Caldwell B. A., Ingham E. R., Castellano M. A. and Cromack K. (1991) Comparison of microbial activity in ectomycorrhizal mat communities in Oregon and California. *Biology and Fertility of Soils* **11**, 196–202.

Hendershot W. H. and Duquette M. (1986) A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Science Society of America Journal* **50**, 605–608.

Henderson M. E. K. and Duff R. B. (1963) The release of metallic and silicate ions from minerals, rocks, and soils by fungal activity. *Journal of Soil Science* **14**, 236–246.

Hintikka V. and Naykki O. (1967) Notes on the effects of the fungus *Hydnellum ferrugineum* (Fr.) Karst. on forest soil and vegetation. *Communicationes Instituti Forestalis Fenniae* **62**, 1–23.

Hintikka V., Korhonen K. and Naykki O. (1979) Occurrence of calcium oxalate in relation to the activity of fungi in forest litter and humus. *Karstenia* **19**, 58–64.

Hue N. V., Craddock G. R. and Adams F. (1986) Effect of organic acids on aluminium toxicity in subsoils. *Soil Science Society of America Journal* **50**, 28–34.

Hunt G. A. and Trappe J. M. (1987) Seasonal hypogeous sporocarp production in a western Oregon Douglas-fir stand. *Canadian Journal of Botany* **65**, 438–445.

Jones M. D. and Hutchinson T. C. (1986) The effects of mycorrhizal infection on the response of *Betula papyrifera* to nickel and copper. *New Phytologist* **102**, 429–442.

Jones M. D., Browning M. H. R. and Hutchinson T. C. (1986) The influence of mycorrhiza associations on paper birch and jack pine seedlings when exposed to elevated copper, nickel or aluminium. *Water, Air, and Soil Pollution* **31**, 441–448.

Kelly J. M., Schaedle M., Thornton F. C. and Joslin J. D. (1990) Sensitivity of tree seedlings to aluminium: II. Red oak, sugar maple, European beech. *Journal of Environmental Quality* **19**, 172–179.

Lapeyrie F., Chilvers G. A. and Behm C. A. (1987) Oxalic acid synthesis by the mycorrhizal fungus *Paxillus involutus* (Battsch. ex Fr.) Fr. *New Phytologist* **106**, 139–146.

Lapeyrie F., Perrin M., Pepin R. and Bruchet G. (1984) Formation de weddellite ($CaC_2O_4 \cdot 2H_2O$) extracellulaire en culture *in vitro* par *Paxillus involutus*: signification de cette production pour la symbiose ectomycorhizienne. *Canadian Journal of Botany* **62**, 1116–1121.

Lopez-Hernandez D., Siegert G. and Rodriguez J. V. (1986) Competitive absorption of phosphate with malate and oxalate by tropical soils. *Soil Science Society of America Journal* **50**, 1460–1462.

Malajczuk N. and Cromack K. (1982) Accumulation of calcium oxalate in the mantle of ectomycorrhizal roots of

Pinus radiata and *Eucalyptus marginata*. *New Phytologist* **92**, 527–531.

Manley E. P. and Evans L. J. (1986) Dissolution of feldspars by low-molecular-weight aliphatic and aromatic acids. *Soil Science* **141**, 106–112.

Mortland M. M. (1970) Clay-organic complexes and interactions. *Advances in Agronomy* **22**, 75–117.

O'Connell A. M., Malajczuk N. and Gailitis V. (1983) Occurrence of calcium oxalate in karri (*Eucalyptus diversicolor* F. Muell.) forest ecosystems of south western Australia. *Oecologia* **56**, 239–244.

Pavan M. A., Bingham F. T. and Pratt P. F. (1982) Toxicity of aluminium to coffee in ultisols and oxisols amended with $CaCO_3$, $MgCO_3$, and $CaSO_4{\cdot}2H_2O$. *Soil Science Society of America Journal* **46**, 1201–1207.

Pohlman A. A. and McColl J. G. (1986) Kinetics of metal dissolution from forest soils by soluble organic acids. *Journal of Environmental Quality* **15**, 86–92.

Pohlman A. A. and McColl J. G. (1988) Soluble organics from forest litter and their role in metal dissolution. *Soil Science Society of America Journal* **52**, 265–271.

Raynal D. J., Joslin J. D., Thornton F. C., Schaedle M. and Henderson G. S. (1990) Sensitivity of tree seedlings to aluminium. II. Red spruce and loblolly pine. *Journal of Environmental Quality* **19**, 180–187.

Robert M. and Berthelin J. (1986) Role of biological and biochemical factors in soil mineral weathering. In *Interaction of Soil Minerals with Natural Organics and Microbes* (P. M. Huang and M. Schnitzer, Eds), pp. 453–495. Soil Science Society of America, Madison. (Special Publication). **17**.

Robert M., Razzaghe M. K., Vicente M. A. and Veneau G. (1979) Rôle du facteur biochimique dans l'altération des minéraux silicatés. *Science du Sol* **2**, 153–174.

Sollins P., Cromack K. Jr Li C. Y. and Fogel R. (1981) Role of low-molecular-weight organic acids in the inorganic nutrition of fungi and higher plants. In *The Fungal Community: Its Organization and Role in the Ecosystem* (D. T. Wicklow and G. C. Carroll, Eds), pp. 607–619. Marcel Dekker, New York.

Song S. K. and Huang P. M. (1988) Dynamics of potassium release from potassium-bearing minerals as influenced by oxalic and citric acids. *Soil Science Society of America Journal* **52**, 383–390.

Stevenson F. J. (1982) *Humus Chemistry: Genesis, Composition, Reactions*, 433 pp. Wiley, New York.

Struthers P. H. and Sieling D. H. (1950) Effect of organic anions on phosphate precipitation by iron and aluminium as influenced by pH. *Soil Science* **69**, 205–213.

Sucoff E., Thornton F. C. and Joslin J. D. (1990) Sensitivity of tree seedlings to aluminium. I. Honeylocust. *Journal of Environmental Quality* **19**, 163–171.

Tan K. H. (1986) Degradation of soil minerals by organic acids. In *Interaction of Soil Minerals with Natural Organics and Microbes* (P. M. Huang and M. Schnitzer, Eds), pp. 1–27. Soil Science Society of America, Madison.