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THE CONCENTRATION AND MOBILITY

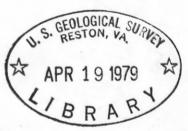
OF ELEMENTS IN SUBALPINE FOREST

SOILS IN COLORADO AND IDAHO

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ABSTRACT

Leaching studies of subalpine forest soils collected at seven sites in Colorado and Idaho show that copper, cobalt, chromium, magnesium, barium, tin, strontium, and yttrium are highly mobile elements in these soils; that zirconium, lanthanum, nickel, and scandium are moderately mobile; and that titanium is rather immobile. Furthermore, the results of the studies indicate that elements are most highly concentrated in the ash of the mull (O2) horizon. In these soils, the mull horizon is a more favorable zone for the accumulation of metals and other elements than are the mineral (A,B,C) soil horizons.

INTRODUCTION

The results of a geochemical survey in a gold district in the Rocky Mountains of Colorado (Curtin and others, 1971) showed that positive metal anomalies in the ash of mull (forest humus)—also denoted herein as the O2 soil horizon—outlined ore zones in bedrock much better than did positive metal anomalies in the underlying mineral soil. In general, the anomalies in mull ash are continuous and correlate well with concealed ore deposits, whereas positive metal anomalies in the underlying predominantly mineral soil horizons are scattered and discontinuous, and do not correlate well with the deposits. Similar geochemical patterns have been described by Boyle and Dass (1967) at Cobalt, Ontario; by Banister (1970) at Stibnite, Idaho; by Rice (1970) in the Orogrande district, Idaho; and by Curtin and King (1974a) in the Stibnite district of Idaho and the Front Range mineral belt of Colorado.

Some insights into those geochemical patterns are given by the studies presented in this report. These studies outline the general distribution and mobility of 25 elements within seven soil profiles and associated vegetation collected in the Rocky Mountains of Colorado and Idaho. The distribution and abundance of four additional elements (tantalum, gallium, lithium, sodium) is shown for the ash of vegetation, mull, and leachate residue. The studies presumably approximate conditions within the vegetation, the mull, and the mineral horizons of the soils in the spring and early summer when, because of snowmelt and frequent rainstorms, the soils are saturated or at least are very wet. The rate of uptake of soil water--as measured by sap velocity (Swanson, 1967)--and presumably of elements in solution by vegetation is highest at this time also.

The data show that a number of elements are leachable in all horizons of subalpine forest soils, but that the mull horizon of these soils apparently is better suited to the fixation and concentration of elements in the biogeochemical cycle than are the mineral horizons of the soil.

The capacity of mull to concentrate elements was first described by Goldschmidt (1937, p. 670-671), who found that the uppermost humus layer of a very old forest of beech and oak in central Germany was enriched in gold, tantalum, beryllium, cobalt, nickel, zinc, boron, germanium, arsenic, cadmium, tin, lead, and silver relative to the underlying soil. Goldschmidt suggested that these elements could be dissolved from the inorganic subsoil by soil solutions, enter plants through the roots, and be deposited in the plants, especially in the leaves. The elements could then become concentrated in the humus as the leaves fall to the ground and decay.

FIELD WORK

Seven soil profiles were sampled. Three profiles were sampled in the Front Range, Colorado and four profiles were sampled near Stibnite, in central Idaho. The soil profiles from Colorado were sampled in an area about 4 km south of Idaho Springs (fig. 1) at elevations ranging from 2,750-2,865 m. Three of the soil profiles from Idaho were sampled in an area south of Stibnite (fig. 2) at elevations ranging from 2,150-2,470 m, and another profile was sampled in an area about 5.3 km northeast of Stibnite, at about 2,320 m elevation. Both areas are forested primarily with Lodgepole pine (*Pinus contorta latifolia* Engelm.), Limber pine (*Pinus flexilus* James), Engelmann spruce (*Picea engelmannii* Parry), Subalpine fir (*Abies lasiocarpa* Hook), and Douglas-fir (*Pseudotsuga menziesii* Franco). The trees range in diameter from 10 to 60 cm adjacent to sample sites, and ground cover consists of grasses and myrtle blueberry (*Vaccinium myrtillus*).

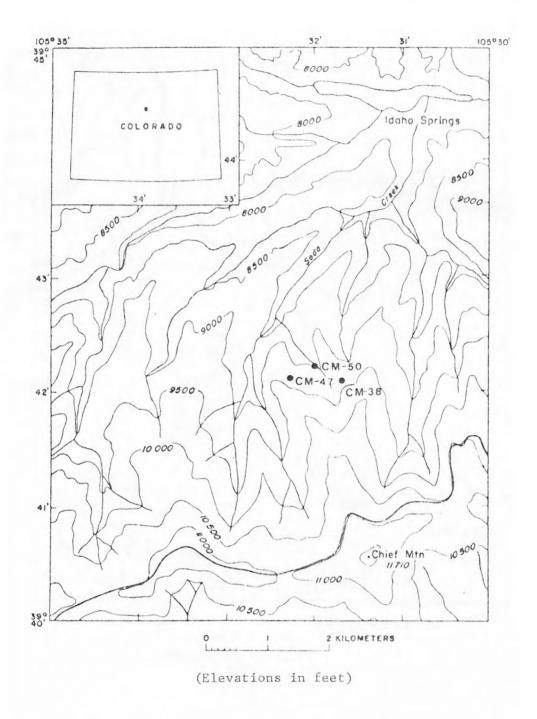


Figure 1.--Index map showing soil-profile sites in Colorado

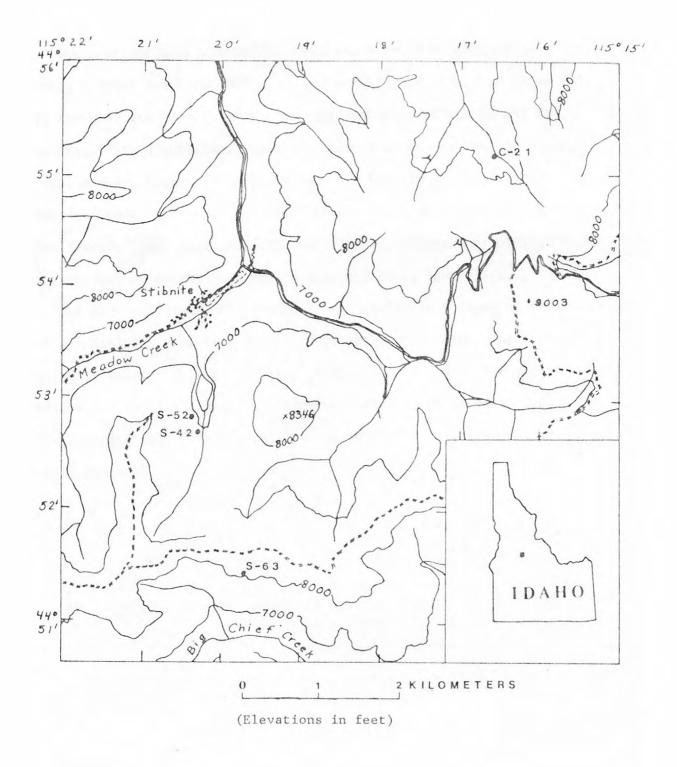


Figure 2.--Index map showing soil-profile sites in Idaho.

The profiles were sampled in areas where previous geochemical testing (Curtin and King, 1974a, b; and unpublished data) had shown that the soil and the ash of the needles and twigs of spruce and fir trees and of mull contained anomalous amounts of several metals (gold, silver, copper, lead, zinc, molybdenum, and bismuth at the Colorado sites; and gold, antimony, arsenic, silver, zinc, and molybdenum at the Idaho sites). Both areas are adjacent to areas of previous mining activity, but no mining has been done in the areas themselves.

The soil profiles were sampled by excavation to a depth of from 0.6 to 1 m. Soil horizons were separated at the sample site. The soil was sampled to bedrock only at locality CM-38; the remainder of the soil profiles are in areas where the bedrock is covered by an estimated thickness of from 1 m to several tens of meters of colluvial and/or glacial material.

SOIL-PROFILE DESCRIPTIONS

Descriptions of the soil profiles are given in Table 1. The soils are classed as inceptisols (U.S.D.A., 1960, p. 136) because they are poorly developed and lack a well-defined illuvial, clay-rich horizon.

Two of the four soil profiles sampled in Idaho (S-42 and S-52) are developing from glacial debris composed primarily of material derived from the Idaho batholith. Soil profile C-21 is developing from glacial debris and alluvium composed of a mixture of volcanics, quartzite, limestone, dolomite, and schist; and soil profile S-63 is developing from granodiorite grus of the Idaho batholith.

Two of the soils sampled in Colorado (CM-47 and CM-50) are developing from colluvium composed primarily of weathered biotite gneiss mixed with minor amounts of weathered granodiorite. CM-38 is developing from colluvium composed of weathered biotite gneiss.

All the soils are well drained with the exception of the Idaho soils C-21 and S-52.

Table 1. -- Descriptions of soil profiles

Horizon	izon Depth (cm) Description		рH				
		Soil Profile C-21 1/					
0212/	12.5- 7.5	Well-formed mat of decomposed litter with sand and silt intermixed	5.6				
022	7.5- 0	Gray to gray-brown sandy loam containing 40 percent organic material (by weight); abundant roots	5.7				
В	B 0 -11.5 Yellow sandy loam						
С	11.5-64	Yellow-brown fine sandy loam (total thickness not determined)	5.8				
		k stand of timber (10-41 cm diam.) composed primarily of Engelmann spruce, Alpine fir and scattered lim w cover of current and willow bushes.					
		Soil Profile S-42					
02	5.0- 0	Mat of decomposed litter with sand and silt intermixed	5.3				
Α	0 -11	Reddish-gray-brown sandy loam; abundant roots					
В			5.5				
	11 -72	Yellow-brown to red-brown sandy loam (total thickness not determined)	5.5				

spruce, Douglas-fir, and limber pine; myrtle blueberry ground cover.

Table 1.--Description of soil profiles--Continued

Horizon	Depth (cm)	Description	pH
		Soil Profile S-52	
021	19.0-11.5	Well-formed mat of decomposed litter with sand and silt intermixed	5.4
022	11.5- 4	Gray-brown decomposed organic material (86 percent organic) mixed with silt and sand; abundant roots	5.4
023	4 - 0	Black, ash-textured, decomposed organic material (60 percent organic) mixed with silt and sand	5:0
Α	0 - 2.5	Yellow-gray to gray silt loam	5.1
В	2.5-48	Yellow, fine sandy loam (total thickness not determined)	5.5

Comment: Soil formed from glacial debris on 15° slope. Soil was saturated. Numerous seeps in area; thick stand of timber (15-60 cm diam.), primarily Engelmann spruce and Douglas-fir, scattered Lodgepole pine, and clumps of alders; myrtle blueberry ground cover.

Soil Profile S-63

02	4.0- 0	Decomposed litter with sand and silt intermixed	5.4
Α	0 - 7.5	Gray to gray-brown sandy loam containing some roots	5.7
В	7.5-56	Yellow-brown sandy loam (total thickness not determined)	6.0

Comment: Soil formed from grus on 30° slope. Scattered timber (10-60 cm diam.), primarily limber pine and Lodgepole pine. Thinly scattered Douglas-fir trees and wax current bushes.

Table 1.--Descriptions of soil profiles--Continued

Horizon	Depth (cm)	Description	рК
		Soil Profile CM-38	
02	5.0- 0	Decomposed litter with sand and silt intermixed	4.9
Α	0 -11	Gray-brown fine sandy loam; abundant roots	5.3
В	11 -40	Gray-brown sandy loam	5.5
С	40 -62	Grayish-orange-brown sandy loam; grades into biotite gneiss bedrock	5.5
Comment:	Soil formed from w	eathered biotite gneiss on 15° slope. Moderately thick stand of timber (3-25 cm diam.),	primarily Lodgepole pine,
	scattered Engelm	ann spruce, Douglas-fir, and aspen. Scattered common juniper, kinnickinnic, wax flower,	ground cover.

	Soil Profile CM-47						
02	5.0- 0	Decomposed litter with sand and silt intermixed	5.9				
Α	0 - 7.5	Orange-brown, fine sandy loam; abundant roots	6.1				
В	7.5-15	Orange-brown sandy loam	6.2				
С	15 -77	Brownish-gray sandy loam; abundant rock fragments (total thickness not determined)	6.1				

Comment: Soil formed from colluvium composed primarily of weathered biotite gneiss on 20° slope, colluvial soil; thick stand of timber (5-30 cm diam.), primarily Lodgepole pine, scattered Douglas-fir and aspen; scattered common juniper, kinnikinnic, wax flower, buffalo berry, and myrtle blueberry ground cover.

Table 1.--Descriptions of soil profiles--Continued

Horizon	Depth (cm)	Description	pH
	III. ja la	Soil Profile CM-501/	
02	3.0- 0	Well-formed mat of decomposed litter with sand and silt intermixed	5.0
Α	0 -30	Gray-brown sandy loam; abundant roots	5.6
В	30 -84	Grayish-yellow-brown sandy loam; abundant pebbles and cobbles; black zones (total thickness not determined)	5.9
Comment:	Soil formed from c	olluvium composed primarily of weathered biotite gneiss. Collected at base of 35° slope near small stream.	Soil
	was saturated.	Discontinuous stand of timber (10-40 cm diam.), primarily Engelmann spruce, Lodgepole pine, and spruce.	

 $[\]frac{1}{2}$ pH determined electrometrically using procedures outlined on page 237 of the U.S. Department of Agriculture $\frac{1}{2}$ Survey Manual (1951).

^{2/} The O2 horizon is also denoted as mull, which is a "humus-rich layer consisting of mixed organic and mineral matter, generally with a gradational boundary to the underlying mineral horizon" (U.S. Department of Agriculture, 1951, p. 245).

LABORATORY PROCEDURES

Each horizon, including the mull (02) layer, of the seven profiles was sieved separately and the plus-2-mm fraction was discarded. The minus-2-mm fraction was then split several times, and two splits of each horizon were further prepared for analysis. Mull splits were ashed, mull-ash and mineral-soil splits were further sieved through a 0.18-mm sieve (80 mesh), and the minus-0.18-mm material was analyzed.

The soil profiles were reconstructed in acid-washed polyethylene columns using varying amounts of the minus-2-mm fraction. This material was packed into the columns until the thickness and degree of compaction of each horizon were roughly similar to that of the soil at the sample sites. The columns were made from 5-cm-inside-diameter polyethylene tubing cut in lengths to accommodate the individual thicknesses of the profiles. The bottoms of the columns were covered with acid-washed nylon bolting cloth. Demineralized water was added to the profiles to saturate the soil material; and an additional 1200 ml of demineralized water was added at the top of the reconstructed profiles, percolated through the soil material, and collected in glass jars placed under the columns. A second 1200 ml of demineralized water was added to the profiles and collected in the same way. Several hours were required to complete each percolation. The resulting suspensions were filtered through 0.2-micron average-pore-diameter membrane filters (rinsed with 500 ml demineralized water) to remove suspended particles; and the filtrates, containing dissolved solids from the soils, were evaporated to dryness. The residues were then ashed at 500°C in a muffle furnace and analyzed. The physical data on the soil-profile leachates are shown on Table 2.

Table 2.--Physical data on soil-profile leachates
using 1200 ml of leach water

Soil profile		Total dissolved solids (g) (g/l)		Weight ashed residue (g)	Ash (%)	
C-21						
lst	leaching	0.675	0.563	0.163	24	
2nd	leaching	. 441	.368	.038	91/	
S-42						
lst	leaching	.379	.316	.123	32	
2nd	leaching	.342	.285	.107	31	
S-52						
lst	leaching	1.218	1.015	.268	22	
2nd	leaching	.868	.723	.175	20	
S-63						
lst	leaching	.768	.640	.169	22	
2nd	leaching	. 584	. 487	.131	22	
CM-38						
lst	leaching	. 555	.463	.128	23	
2nd	leaching	.322	.268	.064	20	
CM-47						
lst	leaching	.745	.621	.155	21	
2nd	leaching	.308	.257	.067	22	
CM-50						
lst	leaching	1.084	.903	.305	28	
2nd	leaching	. 447	.373	.121	27	

^{1/} Part of sample was lost

The remaining splits of the soil horizons, including the unashed organic-rich horizons, are of varying weights (Table 3) and were immersed separately in demineralized water so that thick soil-water slurries were formed. The slurries were allowed to stand, covered except for vigorous stirrings twice each day, for 75 hours. At the end of this period the resulting leachates were decanted, were then filtered through water-rinsed 0.2-micron average-pore-diameter membrane filters, and were evaporated to dryness. The residues, consisting of both dissolved material and solids less than 0.2 microns in diameter, were ashed and analyzed. Physical data on the soil horizons that were leached separately are shown in Table 3.

ANALYTICAL PROCEDURES

All element values for the ash of vegetation and mull were determined by a semiquantitative spectrographic method for organic materials (Mosier, 1972). All elements except antimony, cadmium, molybdenum, and zinc were determined for soil by a semiquantitative spectrographic method for rocks and soils (Grimes and Marranzino, 1968). Antimony and molybdenum were determined in soil by colorimetric methods (Ward and others, 1963). Cadmium and zinc in soil were analyzed by atomic absorption (Ward and others, 1969).

Table 3.--Physical data on soil horizons leached separately

Soil Profile	Soil Horizon	Soil Weight (g)	Leachate Volume (recovered) (ml)		tal ed solids (g/l)	Weight ashed residue (g)	Ash of residue (%)
C-21	021	500	550	2.700	4.909	0.430	16
	022	1000	700	.695	.993	.222	32
	В	1000	1050	.212	.202	.068	32
	С	1000	700	.231	. 303	.059	26
S-42	02	1000	910	2.006	2.204	. 398	20
	А	1000	1040	. 290	.279	.088	30
	В	1000	1050	. 466	. 444	.129	26
S-52	021	500	650	1.141	1.755	.760	66
	022	1000	960	3.640	3.792	.772	21
	023	600	1220	.779	.639	.427	55
	A	1000	1430	.229	.160	.174	76
	В	1000	1640	. 481	.293	.080	17
S-63	02	400	580	1.857	3.202	.289	16
	А	1000	1030	.810	.786	.219	27
	В.	300	470	.093	.198	.019	20
CM-38	02	1000	960	3.453	3.597	.467	14
	А	900	1070	.388	.363	.090	23
	В	800	1050	.162	.154	.040	24
	С	500	930	.090	.097	.021	23
M-47	02	1000	1030	5.136	4.986	.645	13
	А	1000	970	.197	.203	.045	23
	В	1000	930	.142	.153	.030	21
	С	500	800	.740	.925	.171	23
M-50	02	1000	1010	4.098	4.057	.628	15
	А	400	720	.270	.375	.070	26
	В	400	740	.075	.101	.015	16

ELEMENT CONCENTRATION

A comparison of element concentration in media of such varied composition as vegetation, organic-rich soil, leachate residue, and mineral soil is not completely satisfactory because these media cannot be reduced to a similar compositional state and still accurately represent their role in the geochmemical cycle. Ashing of the organic-rich samples (vegetation, organic-rich soil, leachate residue), however, produces material that is roughly similar compositionally to the mineral soil horizons in that all samples are largely inorganic and free of water. The mineral fraction of the organic samples is composed of material that has been mainly derived from the underlying soil. Thus, a comparison of the relative amounts of elements in the inorganic phase of the different media gives an estimate of where certain elements are being concentrated as they move from the soil to the vegetation and back to the soil again.

The data shown in figure 3 and table 4 demonstrate that most elements are primarly concentrated in the ash of the organic samples—vegetation and mull 0 horizons—in relation to the mineral soil horizons (A, B, or C). The elements silver, manganese, magnesium, boron, barium, cadmium, copper, molybdenum, lead, tin, zinc, and strontium show a definite affiliation with the ash of the mull horizons and vegetation. Antimony, which was detected in measurable amounts only in the Idaho profiles, was most highly concentrated in the mull horizons of the soil profiles. Using the spectrographic method, it was not detected in vegetation at the sensitivity limit (50 ppm).

Iron is most highly concentrated in the mineral soil horizons

(A, B, or C); and beryllium, yttrium, chromium, lanthanum, and vanadium are the only other elements that show a tendency to be most highly concentrated in the mineral soil.

Titanium, scandium, nickel, and zirconium show more of an affiliation for either the mull horizons or the mineral (A, B, or C) horizons of the soil than for the vegetation.

ELEMENT MOBILITY

In order to estimate the mobility of elements in subalpine forest soils, we assumed that element values in the ash of the leachate residue represented elements in the soil which had gone into solution in the demineralized water as it percolated through the soil profile. We then compared the concentrations of certain elements in the ash of the leachate residue to those of the same elements in the mineral soil horizons and ash of the mull horizons (table 4). This comparison allowed us to determine the amount of an element leached from the mineral soil horizon and mull horizon relative to the amount of that element potentially available in the mineral soil horizon and mull horizon. In this way we were able to estimate the relative mobilities of the various elements in these various soil horizons. Elements which showed a high concentration in the ash of the leachate residue relative to that in the mineral soil horizon and ash of organic soil horizons were judged to be highly mobile, whereas those which showed a relatively low concentration in the residue ash were judged to have a low mobility.

Leachate residue, ash2	Cr, Li, Mg, Mn	Ba,Co,Cr,La,Mn, Sc,Sr,Y	Co, Cu, La, Mo, Ni, Sr, Y	Be,Co,Cr,Qu,La, Ni,Sc,Sn,Sr,Y	Be , Co , Cu , La ,Mg, Ni , Sn , V , Y	Co, Cr, Mn, Sr, Y, Zr	As,Cd, Co,Cu,Mg, Mn,Ni,Sr,Y
Leochate residue, ash l	As,Co,Cu,Mg,Sc, Sn,Y,Zr	Mg , Mn	B, Cu, La, Ni, Sn, Y	Ba,Cr	Ba, Be, Cr, Ni, Sc, Sr, Y	B, Ba, Mn, Sc, Sn, Sr, Zr	Mn, Sn, Sr
С				Fe, V	Fe ·		Ag, Be
В	Be, Fe, La V	Be,Fe,V	Be,Cr,V			Fe, La, V	Cr
А	Be	Be, Mo	Be,Fe,Sc,V			Be -	(A horizon not recognized)
02	Ti, Mn, Sb,	021 Mn,Ag,Cd,Sb, 022 Mn,Cd,Ni, 023 Ti,Mn,Cd,Mo,Zr	Ti, Mg, Ag,Cd,	Ti, Ag, Pb, Zr,	Ti, Cd, Mo, Pb, Zr, V	Fe,Ti,Mn,Ag,Cd, Mo,Ni,Pb,Sb,Zr	021 Sb 022 Fe, Ti, Be, La, Ma Sc, V, Zr
	English Man Monday Man Man Agent Man Man Agent Man Man Agent Man	Mn, B, S Twigs Ag, Cu Ag, C	ir S S Mn	S. Needles	Needles	Zn (Pg Twigs	

Figure 3.--Location of highest concentration of certain elements in the soil profiles (including mull ash), ash of vegetation, and ash of leachate residue. Element values are shown in table 4.

Table 4.--Spectrographic and chemical analyses of the ash of vegetation and mult and of soil samples collected at seven sites in Colorado and Idaho, and of the ash of leachate residue

[All values shown in ppm; Cd and Zn in soil analyzed by atomic absorption; Sb and Mo in soil analyzed by colorimetric methods; spectrographic values shown for ash of mull and soil are the average of two analyses; -- * insufficient data. One number in parentheses after element symbol indicates lower sensitivity limit is the same for all materials analyzed. Where more than one number is shown in parentheses the number in the first parentheses indicates lower sensitivity limit for elements in the ash of vegetation, mull, and leachate residue; number in second parentheses indicates lower sensitivity limit for elements in soil. L = undetermined amount present below sensitivity limit; N = element was looked for but not found; G = undetermined amount present above upper sensitivity limit. Spectrographic analyses by J. M. Nishi and C. L. Forn; atomic absorption and chemical analyses by R. L. Turner, J. D. Hoffman, R. B. Carten, and E. P. Welsch]

Element	Alpine F Needles	ir Ash Twigs	021 (Ash)	Soil Horizons 022 (Ash)	В	C i	Ash of leach	ate residue 2nd leach
			Idaho, C	-21, Soil Profile				
Fe (500)	1,000	5,000	30,000	G50,000	40,000	17,000	700	500
Mg (200)	20,000	50,000	12,500	11,000	5,000	2,500	50,000	100,000
Ti (20)	70	300	4,000	8,500	2,000	1,750	30	30
Mn (10)	G10,000	5,000	7,500	2,500	600	1,750	G10,000	610,000
Ag (0.1) (0.5)	N	L	0.4	0.2	N	0.7	0.2	0.5
As (200)	N	N	700	850	500	1,000	2,000	5,000
B (5) (10)	200	200	100	70	40	30	10	20
Ba (20)	2,000	3,000	850	850	150	100	300	500
Be (1)	N	N	1.5	2	1.5	2	L	L
Cd (2) (0.5)	N	1.0	N	N	N	N	10	20
Co (10) (5)	N	10	70	60	15	150	200	G1,000
Cr (5) (10)	L	10	30	40	85	50	15	10
Cu (1) (5)	70	100	125	125	70	150	300	500
La (20)	N	N	25	40	L	L	N	L
Mo (2)	N	N	N	4	2	2	N	-1
Ni (5)	10	20	60	60	20	50	50	100
Pb (1) (10)	10	100	50	20	L	L.	7	10
Sb (50) (1)	N	N	225	60	10	8	L	N
Sc (5)	N	N	5	10	6	6	N	N
Sn (5) (10)	N	10	L	L	N	N	15	10
Sr (100)	300	500	175	125	N	N	500	500
V (10)	N	5	50	125	70	50	15	L
Y (10)	N	N	L	18	10	50	50	100
Zn (100) (5)	1,000	500	600	300	25	100	100	100
Zr (10)	N	20	125	400	125	75	15	20
T1 (2)	100	70	9	4			15	10
Ga (2)	N	2	13	13			N	N
Li (200)	N	N	N	N			1,500	5,000
Na (100)	70	300	1,000	700			15,000	10,000

Table 4.--Spectrographic and chemical analyses of the ash of vegetation and mull and of soil samples collected at seven
sites in Colorado and Idaho, and of the ash of leachate residue--Continued

Element	Engelmann Spruce Ash Needles lwigs		02 (Ash)	Soil Horizons A	В —	В		ate residue 2nd leac
			Idaho, S-4	42, Soil Profile				
Fe (500)	700	5,000	40,000	40,000	50,000		1,000	5,000
Mg (200)	30,000	50,000	12,500	5,000	10,000		70,000	70,000
1 (20)	50	500	6,000	3,000	3,000		50	50
Mn (10)	G10,000	G10,000	G10,000	1,750	700		10,000	G10,000
Ag (0.1) (0.5)	L	0.7	0.5	N	N		L	0.
As (200)	N	N	N	N	N		700	N
B (5) (10)	500	700	70	10	10		50	50
Ba (20)	3,000	7,000	1,750	500	600		2,000	2,000
Be (1)	N	L	1.5	2.5	2.5		L	L
Cd (2) (0.5)	2	10	5	N	N		3	2
Co (10) (5)	N	L	15	5	9		100	30
Cr (5) (10)	L	15	15	70	70		20	200
Cu (1) (5)	100	200	70	15	30		300	100
La (20)	L	L	L	50	60		L	L
Mo (2)	7	3	. N	2	2		L	L
N1 (5)	15	50	20	9	13		30	10
Pb (1) (10)	10	500	25	L	13		5	7
Sb (50) (1)	N	N	200	2	1		50	L
Sc (5)	N	N	5	5	7		10	7
Sn (5) (10)	N	15	23	N	N		70	10
Sr (100)	1,000	1,000	300	200	300		700	500
V (10)	N	10	40	50	70		10	15
Y (10)	N	N	L	15	13		30	15
Zn (100) (5)	1,500	2,000	1,000	70	70		N	100
Zr (10)	N	20	150	100	150		200	150
T1 (2)	N	N	L				N	N
Ga (2)	L	3	13				N	N
Li (200)	200	300	N				2,000	3,000
Na (100)	2,000	5,000	5,000				G50,000	G50,000
(100)	2,000	0,000	12.000	17a				

Table 4.- τ Spectrographic and chemical analyses of the ash of vegetation and mull and of soil samples collected at seven sites in Colorado and Idaho, and of the ash of leachate residue--Continued

Element	Engelmann Needles	Spruce Ash Twigs	021 (Ash)	Soil He 022 (Ash)	023 (Ash)	A	В	Ash of leach	and lead
		***	Ida	ho, S-52, Soil	Profile				
2 (500)	1,000	2,000	30,000	25,000	30,000	50,000	60,000	7,000	50,000
g (200)	30,000	30,000	15,000	17,500	8,500	8,500	10,000	70,000	50,000
1 (20)	30	300	5,000	3,000	7,000	3,000	5,000	100	700
n (10)	G10,000	10,000	G10,000	G10,000	G10,000	700	1,000	G10,000	G10,000
g (0.1) (0.5)	N	1.5	1.8	1.5	0.6	N	N	L	0.
s (200)	N	N	N	N	N	N	N	N	N
(5) (10)	500	300	100	150	85	13	15	100	70
a (20)	2,000	3,000	2,000	1,750	1,000	500	600	3,000	5,000
e (1)	N	N	1	1.3	1.8	2	2	1	1.
d (2) (0.5) (20)	N	2	3	3	3	N	N	L	N
0 (10) (5)	N	N	10	L	15	6	10	50	100
r (5) (10)	5	15	18	15	23	85	85	200	1,000
Cu (1) (5)	100	200	85	100	60	18	18	100	70
à (20)	N	N	L	L	25	25	30	20	50
0 (2)	N	N	N	N	3	3	L	N	N
1 (5)	7	20	20	30	25	13	18	15	20
b (1) (10)	3	70	60	60	25	13	15	7	7
5b (50) (1) (100)	N	K	1,000	300	50	2	1	L	50
Sc (5)	N	N	L	6	8	7	6	7	10
Sn (5) (10)	, L	70	15	13	5	N	N	10	10
Sr (100)	1,000	700	500	500	400	300	300	700	1,000
V (10)	N	L	30	35	50	60	85	20	70
(10)	N	N	ı	L	10	10	13	30	15
(n (100) (5) (200)	1,000	1,500	500	50	30	80	90	N	N
(10)	N	15	70	125	225	100	180	150	200
(1)	N	N	N	N	N			N	N
Ga (2)	N	2	7	10	13			N	N
1 (200)	N	N	N	N	N			1,500	2,000
Na (100)	1,000	3,000	4,000	3,000	4,000			50,000	15,000

Table 4.--Spectrographic and chemical analyses of the ash of vegetation and mull and of soil samples collected at seven sites in Colorado and Idaho, and of the ash of leachate residue--Continued

Element	Louglas- Needles	Fir Ash Twigs	02 (Ash)	Soil Horizon	s B	 Ash of leachate residue 1st leach 2nd leac		
			Idaho, S	-63, Soil Profi	le			
e (500)	2,000	1,500	50,000	40,000	50,000	10,000	30,000	
lg (200)	70,000	30,000	12,500	4,000	5,000	50,000	50,000	
1 (20)	200	100	8,500	3,000	5,000	500	300	
In (10)	G10,000	7,000	G10,000	1,250	500	G10,000	G10,000	
kg (0.1) (0.5)	L	L	0.3	N	N	N	0.	
As (200)	N	500	N	N	N	N	N	
3 (5) (10)	300	500	100	10	13	500	70	
Ba (20)	1,500	1,500	1,500	600	700	7,000	5,000	
Be (1)	N	N	2	3	2	1.5	2	
Cd (2) (0.5) (20)	1	3	5	N	N	2	N	
Co (10) (5)	N	N	15	L	L	70	150	
Cr (5) (10)	10	L	18	60	70	200	1,000	
Cu (1) (5)	150	200	85	8	10	150	70	
La (20)	N	N	40	30	85	50	50	
Mo (2)	N	L	2	L	N	N	L	
Ni (5)	10	7	25	5	5	15	20	
Pb (1) (10)	30	50	85	13	13	10	10	
Sb (50) (1) (100)	N	N	125	3	2	N	N	
Sc (5)	N	N	8	L	5	20	10	
Sn (5) (10)	5	7	9	N	N	70	10	
Sr (100)	500	500	500	200	250	1,500	1.500	
V (10)	N	L	50	50	70	30	50	
Y (10)	N	N	13	10	15	30	50	
Zn (100) (5) (200)	700	1,500	600	90	55	100	L	
Zr (10)	L	N	300	150	200	300	300	
T1 (2)	N	N	N			N	N	
Ga (2)	N	N	20			L	N	
Li (200)	N	N	N			1,500	1,500	
Na (100)	3,000	2,000	3,000			50,000	10,000	

Table 4.--Spectrographic and chemical analyses of the ash of vegetation and mull and of soil samples collected at seven sites in Colorado and Idaho, and of the ash of leachate residue--Continued

	Lodgepole			Soil Horizons			Ash of leachate re	
Element	Needles	Twigs	02 (Ash)	A	В	С	1st leach	2nd leac
			Colorado, (CM-38, Soil Prof	ile			
Fe (500)	3,000	10,000	50,000	60,000	70,000	85,000	20,000	20,000
Mg (200)	70,000	50.000	12,500	6,000	10,000	10,000	50,000	50,000
1 (20)	300	1,500	G10,000	5,000	7,000	7,000	200	200
Mn (10)	G10,000	5,000	4,000	500	500	500	1,000	1,000
Ag (0.1) (0.5)	L	1	3	0.5	N	N	L	L
As (200)	N	N	N	N	N	N	N	N
3 (5) (10)	500	700	70	L	L	L	50	100
Ba (20)	200	700	850	400	300	200	5,000	2,000
Be (1)	N	0.5	2	2	2	2	3	7
Cd (2) (.5)	10	20	13	N	N	N	5	2
Co (10) (5)	10	15	15	13	13	15	20	30
Cr (5) (10)	10	15	30	175	175	200	500	500
Cu (1) (5)	150	200	85	13	10	9	200	300
La (20)	N	L	40	50	60	70	70	200
Mo (2)	5	7	4	N	L	L	L	2
Ni (5)	30	30	30	30	30	30	20	50
Pb (1) (10)	300	700	700	50	25	20	50	50
Sb (50) (1)	N	N	N	L	N	L	N	1
Sc (5)	N	N	13	13	15	15	20	30
Sn (5) (10)	L	50	10	N	N	N	15	,50
Sr (100)	200	500	250	100	125	100	1,500	2,000
V (10)	L	20	70	85	125	150	50	50
Y (10)	N	5	15	40	50	40	30	10
Zn (100) (5)	1,500	2,000	850	75	65	70	100	20
Zr (10)	L	70	500	200	200	200	100	20
T1 (2)	N	N	N				N	
Ga (2)	L	5	15				N	
Li (200)	N	N	N				700	1,50
Na (100)	2,000	3,000	3,000				20,000	20.00

Table 4.--Spectrographic and chemical analyses of the ash of vegetation and mull and of soil samples collected at seven sites in Colorado and Idaho, and of the ash of leachate residue--Continued

Element	Lodgepole P Needles	Pine Ash Twigs	02 (Ash)	Soil Horizons A	В -		Ash of leach 1st leach	ante residue 2nd leach
			Colorado,	CM-47, Soil Profi	le			
e (500)	7,000	10,000	G50,000	60,000	60,000	85,000	20,000	15,000
g (200)	50,000	50,000	15,000	7,000	7,000	12,500	100.000	100,000
1 (20)	500	1,000	10,000	5,000	5,000	7,000	200	300
n (10)	G10,000	7,000	2,250	400	250	600	700	1,500
g (0.1) (0.5)	0.7	7	3	N	N	N	L	0.1
s (200)	N	N	N	N	N	N	N	N
(5) (10)	700	300	85	L	L	L	50	30
a (20)	200	500	850	600	500	400	1,500	1,000
e (1)	L	0.7	2	1.5	1.5	2	5	5
d (2) (.5)	10	10	18	N	N	N	2	L
0 (10) (5)	15	10	15	10	10	15	70	100
r (5) (10)	20	15	65	150	150	200	500	50
u (1) (5)	150	150	100	13	15	30	100	200
a (20)	L	L	50	60	75	100	300	500
0 (2)	2	7	7	L	L	N	L	2
1 (5)	30	20	50	30	30	30	70	70
b (1) (10)	300	500	850	40	30	20	30	50
b (50) (1)	N	N	N	L	N	1	N	N
c (5)	N	5	15	7	7	15	30	20
n (5) (10)	5	10	13	N	N	N	10	30
r (100)	300	300	225	175	125	100	2,000	1,500
(10)	10	20	150	100	85	125	30	150
(10)	N	10	50	25	25	25	150	150
n (100) (5)	1,500	1,000	1,000	55	65	100	L	300
r (10)	50	70	650	175	175	175	300	300
1 (2)	N	L	N				N	N
a (2)	5	15	18				N	L
1 (200)	N	L	ι	~~			1,500	1,500
a (100)	2,000	3,000	3,500				50,000	20,000

Table 4.--Spectrographic and chemical analyses of the ash of vegetation and mull and of soil samples collected at seven sites in Colorado and Idaho, and of the ash of leachate residue--Continued

Element	Engelmann Needles	Spruce Ash Twigs	02 (Ash)	Soil Horizons A	8	 Ash of leachar	2nd leach
			Colorado, CM	-50, Soil Profile			
e (500	1,000	10,000	50,000	85,000	70,000	10,000	5,000
g (200)	15,000	15,000	17,500	8,500	8,500	7,000	7,000
1 (20)	30	2,000	8,500	7,000	6,000	70	70
n (10)	10,000	7,000	8,500	1,000	1,000	700	1,500
g (0.1) (0.5)			2	N	N	0.15	N
s (200)	N	N	N	N	N	N	N
(5) (10)	200	200	100	10	10	500	150
a (20)	3,000	7,000	1,750	700	700	1,500	2,000
e (1)	N	1	1.5	2	2	1.5	1.
d (2) (0.5) (20)	3	10	9	N	N	N	N
o (10) (5)	N	15	15	15	15	15	20
r (5) (10)	5	20	50	150	200	30	15
u (1) (5)	20	200	110	20	25	200	200
a (20)	L	L	65	70	70	150	150
0 (2)	N	10	3	2	2	3	10
i (5)	15	30	50	30	40	100	100
b (1) (10)	20	500	300	40	50	10	2
b (50) (1) (100)	N	N	N	L	L	N	N
c (5)	N	N	13	15	13	5	N
n (5) (10)	N	7	9	N	N	10	5
r (100)	1,000	1,000	600	175	125	1,000	1,500
(10)	L	30	60	100	125	15	15
(10)	N	10	15	50	40	\$0	50
n (100) (5) (200)	1,500	2,000	850	115	95	N	L
r (10)	N	70	250	175	150	70	70
1 (2)	N	N	N			N	N
a (2)							
i (200)	N	N	N			300	300
a (100)	200	2,000	2,500			50,000	20,000

In most or all of the soil profiles, the elements copper, cobalt, chromium, magnesium, barium, tin, strontium, and yttrium were highly concentrated in the ash of the leachate residue relative to the mineral soil horizons and to the ash of the mull (fig. 3, table 4), indicating that they are highly mobile in these soils. The elements zirconium, lanthanum, nickel, and scandium are noticeably concentrated in the ash of the leachate residue relative to the soil (table 4), indicating that they are at least moderately mobile in these soils. The indicated mobility of zirconium in the soils is supported by data from previous studies (Curtin and others, 1974, p. 254-259). The concentration of titanium is low in the ash of the leachate residue compared to that in the mineral soil and mull ash, indicating that titanium may be relatively immobile in these soils.

The results of the leaching studies on individual soil horizons (table 5) indicate that most of the elements studied are mobile in all horizons of these subalpine soil profiles. Further, that the elements were mobile as organic complexes is suggested by the relatively low ash content (25 percent or less) of most of the total dissolved solids. The low ash content indicates the loss on ignition of organic carbon—presumably in the form of soluble organic complexes.

Table 5.--Spectrographic analyses of the ash of the residue of soil leachates

[All values in ppm. After element symbol, the number in parentheses indicates lower sensitivity limit for elements; -- = insufficient data; L = undetermined amount present below sensitivity limit;

N = element was looked for but not found; G = undetermined amount present above upper sensitivity limit. Analyses by J. M. Nishi.]

		Soil hor	izone		Cod 1 hardware				
Element	021	022	В	С	02	Soil horizons	C		
Fe (500)	5,000	15,000	15,000	2,000	1,500	7,000	7,000		
Mg (200)	30,000	30,000	30,000	70,000	50,000	30,000	50,000		
Ti (20)	70	50	70	50	70	300	200		
Mn (10)	10,000	G10,000	G10,000	G10,000	G10,000	G10,000	5,000		
Ag (0.1)	1.5	L	0.1.	1.5	L		N		
As (200)	1,500	700	2,000	5,000	N	N	N		
B (5)	300	150	300	300	200	200	300		
Ba (20)	1,000	700	500	300	1,000	700	1,000		
Be (1)	L	1	1.5	L	N	1	1		
Cd (2)	N	N	N	N	N	3	N		
Co (10)	100	100	300	500	L	20	50		
Cr (5)	5	10	15	7	L	7	10		
Cu (1)	100	30	150	300	50	150	70		
La (20)	20	20	30	L	N	N	50		
Mo (2)	L	L	2	2	7	2	20		
Ni (5)	30 .	30	50	50	7	15	30		
Pb (1)	200	7	10	70	10		2		
Sb (50)	50	L	L	L	N		N		
Sc (5)	N	5	20	N	N	15	5		
Sn (5)	7	N	N	10	N		N		
Sr (100)	500	500	500	500	700	500	1,000		
V (10)	10	10	30	30	N	20	30		
Y (10)	10	10	50	100	N	15	20		
Zn (100)	500	150	100	100	700	200	L		
Zr (10)	10	15	100	20	L	200	30		
T1 (20)	10	10	L	3	N	N	٨		
Ga (2)	N	N	N	N	N	2	N		
Li (200)	L	N	N	L	200	300			
Na (100)	20,000	3,000	10,000	20,000	20,000	30,000	10,000		

Table 5.--Spectrographic analyses of the ash of the residue of soil leachates-Continued

Idaho, S-52, Soil Profile

Idaho, S-63, Soil Profile

lement		Soil		Soil horizons				
	021	022	023	A	В	02	A	В
Fe (500)	1,000	7,000	3,000	30,000	15,000	1,500	10,000	15,000
Mg (200)	30,000	50,000	50,000	30,000	30,000	30,000	50,000	30,000
Ti (20)	70	50	200	700	500	100	300	700
Mn (10)	G10,000	G10,000	G10,000	10,000	G10,000	G10,000	G10,000	10,000
Ag (0.1)	0.5	1	5	N	N	0.5	1	0.7
As (200)	N	L	200	N	N	N	N	N
B (5)	300	200	300	300	300	300	150	1,000
Ba (20)	1,500	1,500	1,000	700	1,000	1,000	1,500	2,000
Be (1)	N	N	N	2	1.5	N	L	3
Cd (2)	N	L	L	L	N	5	N	3
Co (10)	L	10	10	50	30	10	20	10
Cr (5)	L	L	7	20	10	5	. 5	15
Cu (1)	150	150	70	100	150	150	30	200
La (20)	L	N	N	N	L	L	L	50
Mo (2)	L	2	2	5	3	2	3	7
Ni (5)	10	10	10	20	15	10	15	20
Pb (1)	5	150	200	15	50	50	100	50
Sb (50)	100	. 50	N	L	N	L	L	N
Sc (5)	L	5	5	5	15	N	N	30
Sn (5)	. N	7	20	N	N	10	10	15
Sr (100)	700	1,000	1,000	700	500	700	700	1,000
V (10)	N	L	15	50	30	N	20	50
Y (10)	N	N	N	L	20	N	10	70
Zn (100)	200	300	200	200	150	500	100	300
Zr (10)	10	N	20	200	200	15	50	700
T1 (2)	N	N	N	N	N	N	N	N
Ga (2)	N	N	L	2	3	N	L	5
Li (200)	200	200	200	200	N	200	500	L
Na (100)	30,000	5,000	10,000	20,000	30,000	5,000	70,000	50,000

	Col	orado, CM-38,	Soil profile		Co	olorado, CM-47	, Soil profi	le	Colorado, CM-50, Soil profile		
		Soil horizo	ons			Soil hori	zons			Soil horizo	ns
Element	02	A	В	С	02	A	В	С	02	A	В
Fe (500)	10,000	30,000	20,000	20,000	5,000	50,000	30,000	20,000	500	7,000	10,000
Mg (200)	50,000	50,000	30,000	15,000	70,000	50,000	50,000	50,000	50,000	50,000	50,000
Ti (20)	500	500	300	700	100	700	300	300	30	100	200
Mn (10)	G10,000	G10,000	3,000 •	500	10,000	10,000	1,500	G10,000	7,000	1,500	1,000
Ag (0.1)	L	0.1	L	2	L	20	20	30	2	L	0.3
As (200)	N	.N	N	N	N	N	N	N	N	N	N
B (5)	500	200	300	700	700	700	500	300	200	500	500
Ba (20)	1,500	1,000	700	1,000	700	1,000	1,000	700	1,000	1,000	700
Be (1)	1.5	1	1.5	2	1	1.5	1.5	1	N	1.5	1.5
Cd (2)	20	3	3	7	15	3	5	L	N	3	5
Co (10)	30	30	15	L	20	50	30	20	L	15	30
Cr (5)	10	15	20	70	7	50	30	. 7	N	20	50
Cu (1)	100	100	150	300	100	200	200	100	150	200	300
La (20)	30	L	L	50	L	L	50	N	N	150	100
Mo (2)	5	5	3	10	2	10	3	2	N	7	5
Ni (5)	30	20	15	20	20	30	20	15	10	100	20
Pb (1)	500	100	20	500	1,000	2,000	5,000	2,000	15	10	50
Sb (50)	N	N	N	N	N	N	N	N	N	N	N
Sc (5)	5	10	20	30	N	20	20	N	N	15	30
Sn (5)	7	N	N	20	5	150	200	100	N	L	7
Sr (100)	1,000	1,000	500	1,000	700	1,000	1,500	700	1,000	1,500	1,500
V (10)	30	100	50	50	20	150	50	30	N	20	20
Y (10)	20	15	15	30	15	20	20	N	N	50	70
Zn (100)	2,000	300	200	300	2,000	200	500	200	200	100	700
Zr (10)	30	50	100	. 150	20	150	100	70	N	100	200
T1 (2)	N	N	N	N	Ν -	N.	N	N	N	N	N
Ga (2)	L	N	N	5	L	2	2	L	N	N	3
Li (200)	L	200	N	200	N	200	700	700	N	L	500
Na (100)	5,000	20,000	100,000	20,000	7,000	30,000	50,000	50,000	20,000	20,000	30,000

The mobilization of elements in soils is most likely accomplished primarily by the complexing action of (1) fulvic acid (Schnitzer, 1969, p. 80), which constitutes as much as 87 percent of the water-soluble organic matter in some soils (Schnitzer and Desjardins, 1969, p. 154); and (2) oxalic acid, which is an exudate of forest tree roots (Smith, 1976, p. 327) and is apparently produced by fungi in forest soils (Graustein and Cromack, 1977, p. 1253).

Fulvic acid presumably can be generated in the humus (Davies, 1971, p. 82), can dissolve elements in the humus and in the A horizon, and can transport them downward in the profile. Likewise, oxalic acid can mobilize elements within the soil. Polyphenols, organic acids, and other organic compounds from canopy drip also can mobilize iron, aluminum, and presumably other elements in the soil (Malcolm and McCracken, 1968, p. 838).

In these studies, the elements presumably were mobilized primarily as complexes with fulvic acid, oxalic acid, polyphenols, and other water-soluble organic compounds. The data in table 5 indicate that, for most of the elements, differences in element values between the ash of the leachate residue from the 0 horizons and that from the mineral soil horizons are not great enough to establish well-defined trends. The data show, however, that, with the exception of zinc, antimony, and manganese, element values for the ash of the leachate residue from the mull horizons are either the same as or less than those for the ash of the leachate residue from the mineral soil horizons. These data indicate that there is no increase in the amounts of elements leached from the mull horizons relative to the mineral soil for those elements that are concentrated in the mull (except zinc, antimony, and manganese).

This relationship can probably best be explained by considering the nature of these soils. Because the soil profiles below the mull horizon are poorly developed and lack a well-defined illuvial, clay-rich B horizon, they lack the capacity to fix elements that are in the soil solutions. The mull horizon has the capacity to fix elements because it contains both soluble organic complexing agents and insoluble organic compounds that form complexes with various elements. The principal organic compounds that fix elements in the mull horizon are humic acids. Humic acids are able to fix iron, manganese, zinc, and molybdenum (Salazy, 1969, p. 34), and presumably other elements.

The data suggest that this process takes place in these soils. The uptake and accumulation of elements from the soil and subsoil, by conifers and other species of vegetation, apparently provide an abundant supply of elements to the mull, as fallen needles, leaves, and other parts of the vegetation are added to the mull and decay. Although part of the element contribution from decaying vegetation would be leached from the mull horizon, the remaining elements would be concentrated in the mull by the complexing action of the humic acids. The mineral soil, however, would be resupplied with only those elements which can be leached from the mull horizon.

CONCLUSIONS

Most leaching and movement of elements in the soil probably takes place in the spring and early summer when snowmelt and heavy rains provide enough water to saturate and flush the soil. Sap movement and, therefore, the uptake of soil solutions by Lodgepole pine, Engelmann spruce, and presumably other species of conifer trees are highest at this time (Swanson, 1967, p. 432). The elements in the mull horizon which are leached from the mull and migrate downward in the soil are probably primarily recycled back into the vegetation and mull, thus leaving the mineral soil horizons depleted in elements relative to the mull horizon. Under these conditions, the mull would continually concentrate elements, whereas the mineral soil would act mainly as a medium through which elements travel in the biogeochemical cycle. Furthermore, this process would explain why, in geochemical exploration, the B horizon of subalpine forest soils similar to those discussed herein yields only weak and erratic anomalous patterns. The process would also explain why mull is an effective medium for element accumulation and possibly the most reliable indicator of concealed mineral deposits.

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