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Metals in Low-elevation, Southern Appalachian Forest Floor and Soil

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ABSTRACT

Litter and humus, and surficial (0-5 cm) and deeper (25-30 cm) mineral soil were collected from two, 90-yr-old forests to measure readily-available, potentially-available, and total-pool quantities of metals in low elevation, southern Appalachian soils. Soils of the two forested watersheds are either in the Evard or Tate series, a fine-loamy, mesic family of Typic Hapludults. Concentrations of Ca, K, Mg, Mn, Cd, Co, Cu, Pb, and Zn in soils were determined by three extraction methods (water soluble, weak acid, and total dissolution). Total soil Ca, K, Mg, and Mn pools were two or more orders of magnitude greater than trace metal pools. Total soil metal pools at both depths followed a trend of $K \gg Ca \geq Mg > Mn \gg Zn > Cu \gg Pb \geq Co \gg Cd$. Fractions of the total metal pools that were readily and potentially available generally decreased with depth.

Litter and humus trace metal concentrations of two low elevation watersheds in the Coweeta Basin contain lower concentrations of Cu, Zn, and Pb than commonly reported for the northeastern USA. Aerial deposition of Cd, Co, and Pb was indicated by the surficial forest floor enrichment in those elements compared to the mineral soil. The largest trace metal pool in forest floor litter and humus was for lead, and was presumably from long-range transport, deposition and subsequent retention on humic materials. Metals measurement in the relatively pristine organic forest floor and mineral soil at Coweeta will be useful for future evaluations of trace metal impacts on southern Appalachian forest ecosystems.

Additional Index Words: trace metals, lead, cadmium, pollution.

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Many phytotoxic trace metals have anthropogenic sources. Increases in ambient levels of toxic trace metals are directly attributable to coal combustion, metal smelting, waste disposal, and the use of leaded gasoline. The release of SO₂ and trace metals in toxic amounts from smelters can result in complete denudation of forest vegetation and eroded landscape downwind of smelter emissions. Effects of small trace metal quantities are less well delineated, but low-level metal contamination may reduce forest floor decomposition rates and disrupt nutrient transfer mechanisms (Tyler, 1972; Ruhling and Tyler, 1973; Jackson and Watson, 1977; Doelman and Haanstra, 1984). Ever-increasing fossil fuel consumption signals the possibility of continued increases in trace metal accumulations in forested ecosystems.

The documentation of existing elemental baselines at relatively pristine locations will be critically important in future evaluations of potential trace metal impacts on forest dynamics. Long-Term Ecological Research (LTER) sites such as the Coweeta Hydrologic Laboratory, are excellent locations for such baseline investigations. The objectives of this investigation were to com-

pare baseline organic forest floor and near-surface soil metal pools in two oak-hickory forests in the southern Appalachian Mountains and to partition the metal pools into three forms: metals readily-available to plants; metals potentially-available for plant uptake (weak-acid extractable); and total metals.

MATERIALS AND METHODS

Study Area

Forest floor and soil were sampled in the Spring of 1983 in two control (unmanipulated) watersheds at the U.S. Forest Service, Coweeta Hydrologic Laboratory, near Otto, NC. The Coweeta Basin lies within the Nantahala Mountains, part of the Blue Ridge Province of the southern Appalachians. The mean annual temperature is about 13°C (Day, 1974), while annual precipitation averages about 170 cm at elevations < 1000 m (Swank and Henderson, 1976). Land use in the area is generally rural farmland in the valleys with forested tracts on the mountain slopes; the closest large city, Asheville, NC, is located 80 km to the northeast.

Schist and gneiss bedrock has weathered into deep soils, except on ridge tops (Hatcher, 1974). Soils of the two forested watersheds are either in the Evard or Tate series, a fine-loamy, mesic family of Typic Hapludults. The watersheds are both approximately 12 ha, but have contrasting aspects: watershed 18 (WS18) is north facing, while watershed 2 (WS2) is south facing. Both watersheds are vegetated by oak-hickory forest. Common species include white oak, *Quercus alba* L., scarlet oak, *Q. coccinea* Muenchh., chestnut oak, *Q. prinus* L., red oak, *Q. rubra* L., and black oak, *Q. velutina* Lam., pignut hickory, *Carya glabra* (Miller), and mockernut hickory, *C. tomentosa* (Poiret) Nuttall, yellow poplar, *Liriodendron tulipifera* L., red maple, *Acer rubrum* L., Rhododendron, *Rhododendron maximum* L., and mountain laurel, *Kalmia latifolia* L. These watersheds were selectively logged prior to 1927. They have remained free of major disturbance since the cessation of logging and the demise of American chestnut, *Castanea dentata* (Marshall) Borkh., during the late 1920's and early 1930's.

A square, 1-ha reference plot, field marked to 5-m intervals, has been established on both watersheds based on a design used at H.J. Andrews Forest. The reference plots were used for sampling, since they facilitate sample randomization and future sample relocation. Even though the overall vegetation patterns on the two watersheds are very similar, some differences were noted based on the 1-ha plots. Watershed 18 has higher total tree basal area, diversity, and density, and a greater evergreen shrub layer than WS2.

Sampling Procedures

Sixteen sites were randomly chosen in each of the two watersheds. Litter (0i) and humus (0a and 0e) were each sampled volumetrically at each site within a 25-by-25 cm template frame. Mineral soil was sampled at the same random location used for the forest floor collection. At each site, three soil samples were composited after collection with a 5-cm diameter plastic (pvc) pipe at two depths, 0-5 cm and 25-30 cm. The 0- to 5-cm depth encompassed the organically enriched A horizon of the mineral soil. The 25- to 30-cm depth was selected to represent characteristic B horizon mineral soil. No estimate was made of below-ground woody root and debris mass within the soil depths sampled. Two litter and one humus samples from WS18 were found to be contaminated and their elemental concentrations are not reported.

Analytical Procedures

Litter and humus samples were dried to a constant mass at 105°C, weighed, and ground finely in a Wiley mill. Weighed, 1-g samples were ashed at 400°C (Webber, 1974). Five milliliter of concentrated (16 N) HNO₃ were added to the cooled ash which was heated for 30

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min at 80°C. After cooling, the solutions were filtered through acid-leached filter paper, brought to volume, and analyzed by atomic absorption spectrophotometry.

Each soil sample was mixed, oven dried at 70°C, and passed through a plastic 2-mm sieve. Soil carbon was determined by a Leco carbon auto-analyzer. Concentrations of metals (Ca, K, Mg, Mn, Cd, Co, Cu, Pb, and Zn), described as readily-available, were determined by atomic absorption spectroscopy (AAS) following water extraction (4.0 g soil + 100 ml. deionized-distilled water, shaken at constant revolution for 2 h). Drying the soil samples possibly reduced readily-available nutrient concentrations. Metal concentrations considered as potentially-available were extracted with a (0.1 M) double acid (Mehlich, 1953) method and determined by AAS. Total amounts of cations (Ca, K, Mg, Mn, Cd, Co, Cu, and Zn) were determined from soil extract samples digested by concentrated (16 M) nitric-perchloric-hydrochloric acids (5:3:2 ratio) (Jackson, 1958; Beaton et al., 1968). Total Pb was determined by AAS on extracts of soils digested in concentrated nitric acid (Sealy et al., 1972).

Chemical element analyses were performed on a Perkin-Elmer 306 Atomic Absorption Spectrophotometer. Sample solutions for Cd, Co, Cu, and Pb analyses were injected by an automatic-pipetter into an HGA-2100 graphite furnace, dried, charred and atomized according to optimized conditions. Calcium, K, Mg, Mn, and Zn were determined with flame analyses by optimized conditions. Triplicate analyses were performed for each sample. As a quality control measure, standards of all elements were compared to National Bureau Standards reference materials (SRM-1571, SRM-1573) before analyses (NBS, 1981). All standard reference material concentrations were within the 10% range of accepted NBS values.

All statistical analyses were performed using standard *t*-tests which were calculated using the Statistical Analysis System (SAS, 1979).

RESULTS AND DISCUSSION

Metals in Litter and Humus

Analyses of randomly collected forest floor samples from each watershed showed that concentrations of macrometals (Ca, K, and Mg) were not significantly ($p < 0.01$) different between litter and humus on either

watershed (Table 1). Concentrations of Co, Cu, Mn, Ni, Pb, and Zn were significantly higher in humus than in litter. Cadmium was the only trace metal which had similar concentrations in litter and humus. Copper, Co, Mn, and Ni concentrations were approximately 30% greater in humus than in litter. Lead concentrations in humus were almost double those in litter. Higher trace metal concentrations in humus relative to litter reflects the low input of metals to Coweeta as well as the tendency of many trace metals, especially Pb, to adsorb onto the humic material (Schnitzer and Skinner, 1967; Tyler, 1972). In contrast, macrometals did not adsorb onto persistent humic materials. Litter and humus concentrations of Cu, Pb, and Zn from WS2 and WS18 were lower than most forest floor metal concentrations reported for 51 sites in the northeastern USA (Andresen et al., 1980).

Watershed Comparison of Litter and Humus

Forest floor samples showed no differences between watersheds for litter and humus mass, nor for concentrations of Ca, K, Mg, Co, Cu, Ni, Pb, and Zn (Table 1). Manganese differed in that litter and humus concentrations were approximately 20% higher in WS2 than in WS18. The general similarity of the forest floor mass and chemical composition allowed calculation of mean metal content of the forest floor.

Metal content of the organic forest floor was calculated by multiplying individual litter and humus mass values by their corresponding elemental concentrations. Late spring litter mass ranged from 805 g/m² on WS2 to 922 g/m² on WS18; humus ranged from 244 to 340 g/m² on WS18 and WS2, respectively. Litter pools of Ca, K, Mg, and Mn were at least twice as large as humus pools (Table 2).

The largest watershed trace element pool in the organic forest floor (litter and humus) was 18.0 mg/m² for Pb (Table 2). Lesser organic forest floor pools were determined for Cu, Zn, Ni, Co, and Cd (approximate pools were 8.5, 5.3, 4.1, 1.7, and 0.3 mg/m², respectively); the Cd pool was < 2% of the Pb pool. Mean organic forest floor pools of Cu, Pb and Zn at Coweeta were more than 20 times smaller than similarly calculated metal pools for the northeastern USA (Andresen et al., 1980). Low metal forest floor pools at Coweeta indicate that Coweeta has metal inputs comparable to other remote locations (Hendry et al., 1984). In addition, metal transport out of the organic forest floor may

Table 1. Mean forest floor mass, elemental concentrations, standard error of mean, and number of samples†

Variable	Sample	WS 2			WS 18		
		X	SE	N	X	SE	N
Mass	Litter	805.40	(70.58)	16	921.60	(94.89)	16
	Humus	339.50	(47.36)	16	244.30	(49.98)	16
Soil	0-5 cm	4.59	(0.21)	16	5.48	(0.52)	16
	25-30 cm	1.10	(0.11)	16	1.32	(0.20)	16
Ca	Litter	14 402.54	(999.93)	16	11 004.51	(748.26)	14
	Humus	11 952.88	(1 143.49)	16	11 111.51	(1 868.82)	15
Cd	Litter	0.28	(0.01)	16	0.27	(0.02)	14
	Humus	0.32	(0.02)	16	0.32	(0.01)	15
Co	Litter	1.32	(0.15)	16	1.49	(0.20)	14
	Humus	1.96	(0.30)	16	2.37	(0.36)	15
Cu	Litter	5.82	(0.43)	16	5.96	(0.65)	14
	Humus	9.00	(0.71)	16	8.90	(0.92)	15
K	Litter	1 021.46	(37.24)	16	972.08	(23.41)	14
	Humus	992.20	(43.68)	16	928.47	(40.49)	15
Mg	Litter	2 033.88	(109.78)	16	1 952.00	(134.55)	14
	Humus	2 327.15	(136.25)	16	1 842.35	(179.73)	15
Mn	Litter*	1 130.87	(80.08)	16	894.18	(78.86)	14
	Humus*	1 694.20	(136.41)	16	1 391.66	(84.40)	15
Ni	Litter	2.78	(0.21)	16	3.63	(0.60)	14
	Humus	4.57	(0.76)	16	6.13	(0.96)	15
Pb	Litter	13.11	(0.77)	16	13.60	(0.89)	14
	Humus	23.86	(1.37)	16	26.11	(1.62)	15
Zn	Litter	4.69	(0.33)	16	4.65	(0.28)	14
	Humus	5.88	(0.41)	16	5.74	(0.34)	15

* Significant difference detected ($p < 0.05$) between litter and humus in the watersheds (*t*-test, SAS, 1979).

† Values for litter and humus mass are (g/m²), soil carbon (%), and elemental concentrations (mg kg⁻¹).

Table 2. Forest floor potentially available metal pools. Soil metal pools were calculated from double-acid extraction data and average bulk density values of McGinty (1976).†

Metal pools	Ca	K	Mg	Mn	Cd	Co	Cu	Pb	Zn
	g/m ²								
Forest floor									
Litter	12.45	0.83	1.62	0.87	0.0002	0.0011	0.006	0.011	0.004
Humus	4.07	0.26	0.60	0.48	0.0001	0.0006	0.003	0.007	0.002
Soil									
0-5 cm	42.91	9.02	10.23	17.96	0.01	0.09	0.10	0.07	0.47
5-30 cm	32.52	3.19	21.99	35.71	0.01	0.49	0.53	0.30	0.59
Total	91.95	13.30	34.44	55.02	0.0203	0.58	0.639	0.388	1.066

† Concentrations of the 25-30 cm soil layer were used to estimate burdens between 5 and 30 cm.

be rapid due to high rainfall and organic matter decomposition rates. The low elevation forests of the Coweeta Basin have not, therefore, been significantly impacted (in terms of metal pools) by urbanization.

Watershed Comparison of Soil Metals

Soil macrometal concentrations were generally similar between the two watersheds: differences are related to bedrock geology (B. Grant, 1985, personal communication) (Table 3). Manganese differed in that Mn concentrations were higher for all soil extractions at both depths in WS2 than in WS18. Similarly, litter and humus had approximately 20% higher Mn concentrations in WS2 than in WS18 (Table 1). Concentrations of soil Mn in WS2 are well below Mn toxicity levels commonly associated with highly weathered, acidic (pH below 5.5), tropical soils (Schmehl et al., 1950).

Soil trace metal concentration differences between the two watersheds were more common than macrometal concentration variations. Higher potentially-available Co and Zn in the surficial soil, Co, Cu, and Zn in the deeper mineral soil of WS18, were correlated with the higher soil organic matter content of WS18. Higher total Pb concentrations at both soil depths in WS18 than in WS2 (9.4 to 6.7 mg kg⁻¹ at 0-5 cm, and 6.1 to 5.5 mg kg⁻¹ at 5-30 cm) may result from the higher organic matter of WS18.

Soil metal concentrations decreased with depth on both watersheds. Concentrations of Ca, Mg, and Mn for the three availability fractions were higher in the

surface soil. Conversely, more total K was present in the deeper, clay-enriched mineral soil than in the shallow, organic soil layer. Total litter-humus pools of Ca, K, Mg, and Mn were less than half of the potentially-available, 0- to 5-cm soil pools of those same metals (Table 3). Nevertheless, the large forest floor pools of Ca, K, and Mg illustrate the importance of litter mineralization in replenishing plant-available metals.

Trace metal concentrations resulting from the three soil extraction methods were more similar between soil depths than were macrometal concentrations, especially on WS2 (Table 3). Generally, more readily and potentially available Cd, Zn, and Pb were present in the surficial soil layer than in the deeper soil layer.

Lead, Cd, and Co concentrations were higher in the 0- to 5-cm soil horizon than in the deeper mineral soil. Enrichment of surficial soil horizons with trace metals indicates that deposition was probably aerial (Burton and John, 1977). In contrast, Cu, Mn, and Zn concentrations were not surficially enriched. Similar metal concentrations in the A and B horizons indicate that present concentrations of metals are primarily the result of bedrock weathering and soil-forming processes (Burton and John, 1977).

Total Forest Floor Metal Pools

Potentially available forest floor metal pools, excluding roots and woody debris, were estimated as the sum of litter, humus, and soil pools to a depth of 30 cm. The estimate is conservative because metals sequestered in

Table 3. Soil elemental concentrations from Watersheds 2 and 18. Values are mean element fraction (mg kg⁻¹) and (SE) from 16 composite samples.

Soil depth, cm	Extraction type†	Ca	K	Mg	Mn	Cd	Co	Cu	Pb	Zn
WS 2										
0-5	r-avail	106.15 (10.61)	77.43 (5.68)	65.77 (4.89)	63.33* (8.46)	< 0.01 (- 0.01)	0.58 (0.08)	0.20* (0.02)	BD†	1.76 (0.19)
0-5	p-avail	746.75 (94.20)	152.39 (8.30)	179.39 (14.27)	352.45* (29.69)	0.09 (0.03)	1.06* (0.07)	1.40 (0.14)	1.10 (0.14)	5.76* (0.32)
0-5	Total	1 515.88 (197.59)	11 012.67* (585.63)	636.29 (31.33)	533.29 (56.30)	0.05 (- 0.01)	5.09* (0.29)	28.53 (2.23)	6.70* (0.44)	69.79* (3.14)
25-30	r-avail	24.70 (4.99)	34.51 (3.06)	32.18 (4.04)	33.55* (5.98)	< 0.01 (- 0.01)	0.47* (0.10)	0.08* (0.01)	BD	0.63* (0.07)
25-30	p-avail	95.99 (20.7)	59.28 (7.36)	75.02 (9.32)	138.76* (15.17)	0.02 (- 0.01)	1.28 (0.09)	1.38* (0.11)	0.95 (0.09)	0.75* (0.06)
25-30	Total	770.01 (187.16)	13 647.80* (601.84)	712.15 (42.29)	521.84* (44.89)	0.01 (- 0.01)	4.10* (0.41)	35.06* (2.57)	5.47 (0.36)	89.52* (7.91)
WS 18										
25-30	r-avail	92.91 (11.19)	73.87 (4.99)	57.90 (6.90)	41.20* (4.69)	0.01 (- 0.01)	0.81 (0.12)	0.14* (0.01)	BD	1.94 (0.25)
0-5	p-avail	566.39 (100.99)	138.55 (5.53)	150.61 (18.24)	241.12* (26.85)	0.09 (- 0.01)	1.73* (0.07)	1.70 (0.10)	1.02 (0.11)	8.68* (0.55)
0-5	Total	1 520.07 (263.06)	9 127.41* (470.70)	748.18 (88.10)	495.18 (44.50)	0.06 (- 0.01)	7.53* (0.61)	34.69 (4.37)	9.41* (0.62)	105.42* (5.59)
25-30	r-avail	26.96 (4.28)	29.92 (2.53)	27.67 (2.05)	19.55* (2.86)	< 0.01 (- 0.01)	1.02* (0.17)	0.12* (0.01)	BD	0.98* (0.13)
25-30	p-avail	71.84 (11.27)	41.79 (4.90)	60.32 (6.86)	80.97* (9.30)	0.02 (- 0.01)	1.74 (0.16)	1.88* (0.13)	0.80 (0.09)	1.53* (0.18)
25-30	Total	719.97 (194.47)	10 094.78* (631.18)	853.44 (106.39)	383.06* (41.02)	0.03 (- 0.01)	5.80* (0.65)	56.41* (7.23)	6.83 (0.45)	117.59* (6.87)

* Indicates ($p < 0.05$) difference in elemental concentration between watersheds for each fraction (SAS, 1979).

† BD = Below detection limits.

‡ r-avail = water extraction, p-avail = double-acid extraction, Total = total dissolution.

woody debris and large roots were not determined. Thus, our estimated soil pools are based on a soil block filled with soil, but without roots. The Coweeta oak-hickory forest floor pools followed the trend of $\text{Ca} > \text{Mn} > \text{Mg} > \text{K} \gg \text{Zn} \gg \text{Cu} > \text{Co} \geq \text{Pb} \gg \text{Cd}$ (Table 3). Forest floor pools should include woody debris and roots, since Smith and Siccama (1981) have shown that root tissue may be associated with high concentrations of trace metals such as Pb.

Potentially available pools of macrometals (Ca, K, Mg, and Mn) were at least an order of magnitude greater than trace metal pools. Soil pools of Ca and K were greater within the A horizon; other metals pools, with the exception of Cd, were greater within the larger mineral soil horizon.

Ecosystem Comparison of Soil Metals

Trace metals in the surficial and deeper mineral soil at Coweeta are at the low range of trace metals reported for sites throughout the world (Aubert and Pinta, 1977; Nakos, 1983; Reaves and Berrow, 1984; Domingo and Kyuma, 1983). For example, Pb in the mineral soil at Coweeta is present in concentrations of approximately 6 mg kg^{-1} , lower than the world average soil concentration ($15\text{--}25 \text{ mg kg}^{-1}$) reported by Aubert and Pinta (1977). Low soil trace metal pools in conjunction with the lack of historically detectable trace metal increases in tree rings (*sensu* Baes and McLaughlin, 1984; Berish and Ragsdale, 1985) indicate that Coweeta has not been significantly impacted by southern smelters or by local urbanization. Baseline trace metal concentrations at Coweeta indicate that the soils are relatively pristine, and will be useful in monitoring environmental changes in ambient southern Appalachian soil trace metal pools.

Chemical Partitioning of Soil Metals

The understanding of mineral cycling processes are enhanced with an estimate of the element flux among pools that are readily available, potentially available, and essentially unavailable. Various sequential extractants have been used to fractionate heavy metals from contaminated media (LeRiche and Weir, 1963; Kuo et al., 1983; Hickey and Kittrick, 1984), but little research has been applied to chemical partitioning of uncontaminated soils. Metal partitioning data for Coweeta soils are presented based on average watershed soil values since the two watersheds have generally similar soil metal concentrations (Table 3).

The fractions of the total pool of Ca, Mg, and Mn which were readily and potentially available were similar within the surface soil. For these three elements, the readily available fractions ranged from 7 to 10%, whereas between 23 and 55% of the total pool was potentially available. In the deeper mineral soil, the readily available fractions of these elements were similar to the surface horizon (range 2 to 6%), but the potentially available fractions (range 9 to 23%) were about one-half of surface soil values. Presumably, fine roots should be located throughout the soil layer with a high ratio of "readily and potentially available" to "total nutrient pools" for an optimum nutrient absorbing capacity.

Direct documentation of root-to-soil nutrient pools are lacking. Fine roots in most ecosystems at Coweeta are, however, located primarily within surficial soil horizons (McGinty, 1976). Similar situations exist in many temperate (Santantonio et al., 1977; Santantonio, 1982) and tropical forests (Berish, 1982; Jordan and Herrera, 1981). Surficial rooting patterns would thus correspond with soil layers of maximum nutrient availability.

The largest total pool of any measured metal was recorded for K. Fractions of the total K pool that were readily and potentially available were $< 2\%$. Absolute amounts of readily and potentially available K were less than Ca and Mg pools. Available K pools decreased with depth, even though the total pool size increased. The relatively small readily and potentially available K pools indicate that K is bound largely in forms unavailable for plant uptake.

Total soil pools of Zn and Cu were two or more orders of magnitude smaller than Ca and Mg pools. Moreover, fractions of the total Zn and Cu pools that were readily available were much smaller than for Ca and Mg, and similar to K. Total Pb, Co, and Cd soil pools were extremely low. Lead was below routine detection limits ($< 0.003 \text{ mg kg}^{-1}$) for the water soluble soil extraction.

CONCLUSIONS

Litter, humus, and soil representative of two low-elevation watersheds in the Coweeta Basin contain lower concentrations of trace elements (Cu, Zn, Pb, and Cd) than commonly reported for northeastern forests of USA. The trace element concentrations in organic forest floor and mineral soil at Coweeta are similar to remote, nonpolluted areas. Forest floor pools of Cu, Pb, and Zn were 20 times smaller than metal pools found in forests of the industrialized northeastern USA.

Aerial deposition of Pb, Cd, and Co was indicated by forest floor enrichment of these elements relative to mineral soil metal concentrations. In contrast, higher concentrations of Cu, Mn, and Zn in the deeper mineral soil emphasizes mineral weathering processes as the primary metal source. The largest trace metal pool in forest floor litter and humus was for Pb, and was presumably from long-range transport, deposition, and subsequent retention on humic materials. Macrometal pools of Ca, Mg, Mn, and K were two or more orders of magnitude greater than trace metal pools at Coweeta.

Readily and potentially available metal concentrations were higher in the organically enriched surface soil than in the deeper mineral soil. Proportions of the total metal pools that were readily and potentially available generally decreased with depth.

The low concentrations of trace metals in the forest floor at Coweeta indicate that, presently, atmospheric inputs of metals are low. This agrees with historical analyses which show low trace metal deposition at Coweeta based on low mineral soil trace metal concentrations and low concentrations of trace metals in tree rings. The relatively pristine organic forest floor and soil at Coweeta will be useful for future evaluations of trace metal impacts on baseline southern Appalachian forest ecosystems.

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