FOUR-DECADE RESPONSES OF SOIL TRACE ELEMENTS TO AN AGGRADING OLD-FIELD FOREST: B, MN, ZN, CU AND FE

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Abstract. In the ancient and acidic Ultisol soils of the Southern Piedmont USA, we studied changes in trace element biogeochemistry over four decades, a period during which formerly cultivated cotton fields were planted with pine seedlings that grew into mature forest stands. In 16 permanent plots, we estimated 40-yr accumulations of trace elements in forest biomass and O horizons (between 1957 and 1997), and changes in bioavailable soil fractions indexed by extractions of 0.05M HCl- and 0.2 M acid ammonium oxalate (AAO). Element accumulations in 40-yr tree biomass plus O horizons totalled 0.9, 2.9, 4.8, 49.6 and 501.3 kg ha^{-1} for Cu, B, Zn, Mn, and Fe, respectively. In response to this forest development, samples of the upper 0.6-m mineral soil archived in 1962 and 1997 followed one of three patterns: 1) Extractable B and Mn were significantly depleted, by -4.1 and -57.7 kg ha^{-1} with AAO, depletions comparable to accumulations in biomass plus O horizons, 2.9 and 49.6 kg ha^{-1}, respectively. Tree uptake of B and Mn from mineral-soil greatly outpaced resupplies from atmospheric deposition, mineral weathering, and deep-root uptake. 2) Extractable Zn and Cu changed little during forest growth, indicating that nutrient resupplies kept pace with accumulations by the aggrading forest. 3) Oxalate-extractable Fe increased substantially during forest growth, by +275.8 kg ha^{-1}, about 10-fold more than accumulations in tree biomass (28.7 kg ha^{-1}). The large increases in AAO-extractable Fe in surficial 0.35-m mineral soils were accompanied by substantial accretions of Fe in the forest's O horizon, by 473 kg ha^{-1}, amounts that dwarfed inputs via litterfall and canopy throughfall, indicating that forest Fe cycling is qualitatively different from that of other macro- and micro-nutrients. Bioturbation of surficial forest soil layers can not account for these fractions and transformations of Fe, and we hypothesize that the secondary forest's large inputs of organic additions over four decades has fundamentally altered soil Fe-oxides, potentially altering the bioavailability and retention of macro- and micronutrients, contaminants, and organic matter itself. The wide range of

responses among the ecosystem's trace elements illustrates the great dynamics of the soil system over time scales of decades.

Key words: ecosystem ecology; nutrient cycling; trace elements; Fe oxides; soil organic matter; reforestation; Southern Piedmont USA.

INTRODUCTION

Iron, Mn, Cu, Zn and B are required for plant growth and development and are indeed essential micronutrients for all living organisms (Boardman and McGuire, 1990; Knight, 1975). Deficiencies and toxicities of micronutrients occur widely in urban, agricultural, and forest ecosystems (Bartlett and James, 1979; Karamanos et al., 1986; Stone, 1990; Kabata-Pendias and Pendias, 1992; Alloway, 1995), yet ecosystem cycling of trace elements has received limited study and too often has been considered of secondary importance in the functioning of terrestrial ecosystems. A survey of 1945 of the most recent papers on nutrient cycling in the leading ecological journals indicated that <1% examined trace elements (J. Li, unpublished data, Durham, NC).

The complex of biogeochemical processes that controls the distribution and sustainability of mineral-soil nutrients including trace elements, includes: (1) input processes, such as atmospheric deposition and mineral weathering release; (2) recycling processes, such as litterfall, root turnover, canopy leaching, organic matter decomposition, and within-plant retranslocation; (3) retention processes, such as cation and anion exchange and sorption reactions; and (4) removal processes, such as plant root uptake, harvesting, fire, erosion, and hydrologic leaching. How these processes affect the sustainability of soil's *macro*-nutrients N, P, Ca, or K over decades of ecosystem functioning is not well quantified (Finzi et al., 1998; Richter and Markewitz 2001; Dijkstra and Smits, 2002; Nezat et al., 2004; Schroth et al., 2007); how these processes affect soil B, Mn, Zn, Cu, and Fe is almost entirely a matter of speculation.

Plant requirements for trace elements are supplied by the mineral soil's readily bioavailable fractions, but also by atmospheric deposition, mineral weathering, and deep root uptake. The accumulations of trace elements in tree biomass (Morrison and Hogan, 1986;

Bergvist, 1987; Stone, 1990; Zayed et al., 1992) and O horizons (Stark, 1972; Louiser and Parkinson, 1978; Staaf, 1980; Rustad, 1994) are often substantial compared with soil contents that are readily extractable, and therefore leads to the hypothesis that rapidly aggrading forests place acute demands on trace elements in mineral soils and thereby affect significant changes in trace element biogeochemistry. We also hypothesize those temporal changes in the biogeochemistry of chemical elements, as wide ranging in their chemistry as B, Mn, Fe, Zn, and Cu, will be highly element dependent.

Cycles of nutrients and non-nutrient chemical elements have been studied over five decades (1957 to present) at a field experiment at the Calhoun Forest Experiment in South Carolina. This long-term field study and its sample archive were used to quantify how tree seedlings planted on old cotton fields accumulated trace elements in forest biomass and forest floor and altered trace-element biogeochemistry in mineral soils. Such a study is challenging because soil trace elements typically exist at relatively low concentration and content, are often redox active, and can interact electrostatically with soil cation exchange sites, and complex in various configurations with Fe and Mn oxides and organic matter. Because trace elements exist in a variety of forms in soil: 1) as free ions and complexes in soil solution, 2) as nonspecifically and specifically adsorbed ions, 3) as ions occluded in soil hydrous oxides and carbonates, 4) organically bound in microbial and plant biomass, detritus, and humic substances, 5) substituted in Al-Si minerals, and 6) as precipitates (Martens and Lindsay, 1990), we can expect that root uptake affects resupply from slowly cycling fractions at a wide range of rates depending on chemical element.

In this paper, we examine trace elements in the O, A, E, and upper B soil horizons, to evaluate decadal biogeochemical change in the bioavailability of trace elements in mineral soils.

Specifically, we examined 35-year changes in extractable B, Mn, Zn, Cu, and Fe in the upper 0.6-m mineral soils in relation to four-decade accretions in vegetation biomass and surficial O horizons. We quantified rates of atmospheric deposition inputs of trace elements and sampled soil waters over a two-year period to evaluate trace-element atmospheric inputs, solubility in soil, and hydrologic leaching losses. The study was aimed at quantifying the resilience and sustainability of soil trace elements in a forest ecosystem developed for five decades.

METHODS

The Calhoun ecosystem

The soil-ecosystem experiment at the Calhoun Experimental Forest is located on the Southern Piedmont in Union County, South Carolina, at about 34.5° N, 82° W (Richter and Markewitz 2001). The 16 permanent plots are on broad geomorphically stable interfluves (with < 2% slopes), all underlain by the Piedmont's most common bedrock, partly metamorphosed granitic gneiss. Soils are deep acidic Ultisols (Table 1), specifically, fine, kaolinitic, thermic Typic Kanhapludults (Soil Survey Staff 2003) of the Appling series. Surficial A and E horizons are sandy loams or loamy sands and have mineralogy dominated by quartz but with secondary Kaolin and Fe and Al oxide component (Table 2). Soil organic matter has accumulated only modest concentrations due to coarse soil texture and long-term cultivation between approximately 1800 to 1955. Below are acidic, clayey Bt-horizons, dominated by kaolinite clay, quartz, and Fe and Al oxides, prominent low-CEC kandic subsoils. The main crystalline framework of Fe and Al oxides indexed by DCB-extractable Fe and Al closely tracks soil clay fraction within the upper 3-m of soil (Table 1). Percent clay and DCB-Fe and Al have correlation coefficients >0.89 in samples throughout the upper 3-m. The oxides are highly reactive with anions as indicated by correlations of DCB-Fe and VO_3-extractable SO_4 that exceed >0.95. Physical, chemical and biological data on the soils have been previously described (Richter et al. 1994; Richter and Markewitz 1995b; Markewitz et al. 1998; Richter et al. 1999; Richter and Markewitz 2001; Callaham et al. 2006; Richter et al., 2006). Human influences have been prominent in these soils, especially after about 1800 and the boom for cotton in South Carolina, when physical soil attributes made upland sites attractive for cultivation. With the expansion of cotton, upland hardwood forests were extensively cleared to agricultural fields. After forest clearing, sites were often burned (Ruffin 1852; Gray 1933), with ash promoting nutrient bioavailability, including that of trace elements (Matsi and Keramidas, 2001; Khan and Singh, 2001). Following several years of cropping, farmers shifted from cotton and corn to less demanding crops such as wheat before abandoning fields and moving on to "fresh soil" (Gray 1933; Richter and Markewitz 2001) or uncultivated land. Soil micronutrient availability probably shifted prominently given inputs of ash, changes in pH and harvest removals.

After the U.S. Civil War, the Southern Piedmont was more extensively and continuously cropped (Vance 1929). Phosphorus fertilization and liming became more standard farm practices (Sheridan 1979), with fertilizers containing variable but largely unknown contents of trace elements as secondary constituents (Raven and Loeppert, 1997; McBride and Spiers, 2001). Secondary forests growing on old fields have substantially taken up and recycled macronutrients and hypothetically micronutrients derived from past agricultural inputs (Richter et al. 2000; Richter et al. 2006).

The specific soils in this study are located in Cross Keys, SC on two old cotton fields formerly cultivated on a plantation managed by Rev. Thomas Ray and his family through much of the 19th century. In the early 1930s, the USDA Forest Service purchased the property for the Sumter National Forest, and from the 1930s to 1955, the two fields were cultivated for cotton by a local tenant farmer. In the winter of 1956-1957, after a two-year fallow, the fields were planted with loblolly pine seedlings (*Pinus taeda* L.) in 16 permanent plots that were arranged in a randomized complete block design with four blocks of four plots each (Fig. 1). Blocks represented different soil-landform and erosion conditions, and plots (each about 0.1-ha in area) within each block were in close proximity and planted at one of four spacings.

Tree biomass and forest floor sampling and analysis

To estimate trace element accumulation in trees and forest floor from planting in 1957 to 1990s, tree biomass was sampled in 1991 and forest floor in 1997. Samples of stemwood, stembark, foliage, dead branches, and live branches were composited from samples of 10 individual trees that ranged across the diameter distribution of the stand. Each sampled tree was divided into stemwood, stembark, foliage, dead branch and live branch for estimation of aboveground biomass and nutrient content, and biomass estimated by allometric equations. Root biomass was estimated from loblolly pine allometric equations by Shelton et al. (1984). Root samples were obtained from soil-core samples (6-cm dia) of coarse lateral roots (>2-mm) and fine roots (<2-mm dia) from the O horizon and 0- to 0.15- and 0.15- to 0.30-m mineral-soil depths. Subsamples of each tree component were oven dried, ground with a Wiley mill, and stored in capped bottles. Taproots were not sampled and the concentrations were assumed to be equal to stemwood and bark.

To estimate trace elements accumulated in the O horizon, five 30-cm diameter samples were collected from each of the 16 plots in 1997 from three layers representing Oi, Oe, and Oa horizons, which correspond approximately to L (fresh litter several years in age), F (fermentation horizon) and H (humic horizons) of the forest floor, respectively. We also collected litterfall monthly over one year in 1991 and 1992 with five 0.7 m^2 collectors in each of 8 plots.

To estimate trace element concentrations in tree biomass, O horizon, litterfall, and roots samples, 0.5-gram powderized material was weighed into Teflon tubes, mixed with trace metal grade acids (5 ml HNO_3 and 3 ml $HClO_4$), and carefully boiled for nine hours at 138 ^{o}C (±3^{o}C) and for three additional hours at 208^{o}C (±3^{o}C). After cooling, the digests were diluted to 50 ml in polypropylene centrifuge tubes with deionized water (Zasoski and Buran, 1977). Concentrations of Fe, Mn, Zn, Cu and B were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). Organic matter mass and nutrient contents of roots and basal O horizons were corrected if necessary for mineral constituents.

Water sampling and analysis

To evaluate trace elements in atmospheric deposition, collections were made every three weeks during a two-year period in 2004 to 2006 with an Aerochem Metrics wet-only precipitation sampler. This sampler was co-located with a bulk precipitation gage, constructed with a 15-cm diameter glass funnel and 4-L amber bottle. Both the wet-only and bulk precipitation collectors were located in a field about 100 m from the experimental forest plots. Canopy throughfall was collected with five bulk-throughfall gages located in each of 12 of the 16 permanent plots, also using 15-cm diameter glass funnels and 4-L amber glass bottles. Every three weeks, funnels and bottles were collected for cleaning in the lab, volumes of each bottle's collection were measured gravimetrically, and throughfall collections composited within each of the 12 plots. Elemental fluxes of wet-only and bulk precipitation and canopy throughfall were estimated from products of water volumes per unit area and trace element concentrations.

Multiple field blanks were used during nearly all 3-week collections to confirm that the collection system was absent of significant contamination.

To evaluate trace-element solubility and fluxes in soil water, lysimeters collected soil water in the 12 plots every three weeks from beneath O horizons and at 0.075-, 0.6-, and 2-m depths within the mineral soil; and from a local seep (Calhoun Seep) and perennial stream (Sparks Creek), both of which drain from a fraction of the long-term Calhoun plots. Both the seep and stream are on the order of 20-m in vertical elevation below the Calhoun plots' mineral soil surface. Under O horizons and at 0.075-m depths, PVC pipes (7.5-cm dia, with two under O horizons, one at 0.075-m depth) collected water by gravity, which drained into 4-L amber bottles installed belowground. Similar bottles collected water at 0.6- and 2-m depths using Prenart lysimeters (Teflon plus stainless steel) that collected water in response to a vacuum that was established in the 4-L bottles every three weeks. These latter samplers collected water in year one. Grab samples were taken every three weeks from the Calhoun Seep and Sparks Stream over the two years.

After each three-week collection, all water samples were returned to the laboratory, refrigerated, and nearly always within one day of returning to the lab, solutions were passed through prewashed 0.4-µm Millipore-isopore membrane filters and 15 mL solution acidified with 45-µL HNO_3 (Trace element grade, ultrapure) in preparation for analysis of Mn, Zn, Cu and Fe by Atomic Absorption Spectrophotometry. Dissolved organic C (DOC) was analyzed by combustion and infrared analysis with prior acidification to pH 2 using HCl and sparging with N_2 to degas dissolved inorganic carbon (Mobley et al., 2008).

Mineral soil sampling, archiving, and analysis

In the Calhoun soil archive, samples were taken from the 1962 and 1997 collections, both made in the dormant with similar protocols. Field composite samples were made by compositing at least twenty individual 2-cm-diameter punch-tube cores within each of the 16 permanent plots. Individual sample points were located within each plot with a stratified random design and samples were taken from four depths (0 to 0.075, 0.075 to 0.15, 0.15 to 0.35, and 0.35 to 0.6-m). Samples are air-dried, sieved through a 2-mm screen, and stored in the dark. The 1962 samples were archived by storing air dry in stout cardboard containers until the late 1980s when they were transferred to capped glass bottles. The 1997 samples were prepared and stored air dry in capped glass bottles. Bulk density was sampled with 6-cm diameter cores in the early 1990s (Richter et al. 1994). Total elemental concentrations were measured following Li-metaborate fusion (Hossner, 1996), and actively cycling or "labile" concentrations were extracted with 0.05 M HCl (Lovely and Phillips, 1986) and 0.2 M acid ammonium oxalate (AAO) at pH 3.0 (Carter, 1993; Loeppert and Inskeep, 1996). While AAO extracts short range ordered (SRO-) Fe oxides (Thompson et al. 2006), HCl extractions target the most soluble SRO- oxides (Kostka and Luther, 1994, Thompson et al. 2006). Soil samples (1.0 g) were weighed into 50-ml polypropylene centrifuge tubes, mixed with 5 ml HCl or AAO solution, and shaken for 90 minutes for HCl extraction and 4 hours for AAO extraction (Ponnamperuma et al. 1981; Cox, 1968; Shuman and Anderson, 1974). Suspensions were centrifuged for 25 minutes at 3400 rpm, after which centrifugates were pipetted into 15-ml plastic tubes (BD Falcon ® Conical-Bottom Disposable Plastic), and Fe, Mn, Zn, Cu analyzed with an atomic absorption spectrophotometer (5100 PC, Perkin-Elmer), and B analyzed with Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES). All AAO extractions were shaken and centrifuged in the dark (Siffert and Sulzberger, 1991).

In the acidic Calhoun Ultisols, soil extraction by HCl recovers trace elements in soil solution, and nonspecifically adsorbed trace elements bound in outer-sphere complexes with organic matter, clays, and oxides (Sposito, 1981). HCl recovered probably small fractions of specifically adsorbed cations from hydrous oxides (Fe, Mn and Al oxides) and phyllosilicates, and occluded and precipitated trace elements during partial acid decomposition of minerals (Martens and Lindsay, 1990). In contrast, AAO extraction solubilizes SRO- and micro- and non-crystalline forms of Fe and Al oxides, and displaces organic-complexed Fe, Mn, Cu, and Zn, all without dissolving much crystalline oxide of Fe and Al (McKeague, 1967; Parfitt and Child 1988; Loeppert and Inskeep, 1996). In at least some soils, AAO may attack some crystalline oxide forms of Mn (Carter, 1993).

Statistical analysis of changes in soil trace elements (1962 to 1997)

Changes in mineral-soil trace elements were estimated from archived soil samples collected in all sixteen plots in 1962 and 1997, all extracted with HCl and AAO. Paired-t tests were used to evaluate changes in concentrations by pairing samples from each plot and depth collected in 1962 and 1997. If distributions of concentrations violated assumptions of normality, data were log transformed. Changes of contents during the 35 years of forest growth were estimated only if the 1962 to 1997 differences in concentration departed from zero with a significance level of $p < 0.05$. This approach to estimating changes in soil nutrients followed from other soil-change studies of macronutrients, Si, Al, C, and pH conducted at Calhoun and at other long-term soil experiments (Richter et al., 1994; Markewitz and Richter, 1998; Richter et al., 1999; Richter et al., 2006).

RESULTS

Trace-element transfers from mineral soil to biomass and O horizons

During 40 years of forest development, aggrading tree biomass and forest floor accumulated a total of 0.9, 2.9, 4.8, 49.6, and 501.3 kg ha^{-1} of Cu, B, Zn, Mn and Fe, respectively (Table 2). Annual fluxes of mineral-soil trace elements to aggrading tree biomass and O horizons over the 40 years thus averaged 0.023, 0.072, 0.120, 1.24, and 12.5 kg ha^{-1} y^{-1} in Cu, B, Zn, Mn and Fe, respectively. Of the total elemental transfers from mineral soil to plant biomass plus O horizons, plant biomass accounted for 33.3, 72.4, 52.1, 49.8, and 5.7%, respectively. The wide range of trace element partitioning between tree biomass and forest floor is suggestive of contrasting rates and processes of nutrient cycling (plant-soil exchange) among the trace elements.

Mineral-soil responses to forest growth and development

Combining 40-year accretions of trace elements in forest biomass and O horizons and mineral-soil changes indicates that bioavailable fractions of the five trace elements have responded with one of three patterns to forest growth and development: (1) mineral-soil B and Mn were depleted by tree uptake and little affected by processes leading to resupply; (2) mineral-soil Zn and Cu were little changed and therefore were resupplied by inputs and recycling despite removals, and (3) mineral-soil Fe was greatly accumulated due to four-decade transformations in the biogeochemical soil environment. A conceptual diagram of the three patterns is presented in Fig 2.

Mineral-soil depletions of B and Mn

Of the five elements under study, soil-extractable B and Mn decreased significantly from 1962 to 1997 (Table 3). Moreover, these reductions of content were comparable to B and Mn transfers from mineral soils to tree biomass and forest floor (Table 2), a pattern we refer to as "mineral-soil depletion".

Boron.--- Throughout the upper 0.6-m of mineral soil, substantial decreases were observed in concentrations of HCl- and AAO-extractable B (Table 3). In 1962, soil concentrations of B averaged up to 0.70 ug g-1, but by 1997, most of this was no longer extractable by HCl or AAO. Concentrations of AAO-extractable B were depth-dependent in both 1962 and 1997, with higher concentrations of B recovered in more organic-enriched surficial layers. In contrast, HCl-extractable B was not depth dependent in either 1962 or 1997 (Table 3). Hypothetically, AAO more efficiently recovers B from surface soils with solid interfaces dominated by organic matter, than in subsoil with interfaces dominated by oxides and kaolinite.

In 1962, contents of HCl- and AAO-extractable B amounted to about 3.0 and 4.6 kg ha^{-1} in the 0.6-m layers, respectively. About 80% of extractable B was depleted from the two deeper mineral-soil layers (0.15 to 0.35 and 0.35 to 0.6-m), indicating the significance of deep roots and deeper soil layers to the nutrient supply of the aggrading forest (Table 3). Overall, B was depleted from the upper 0.6-m mineral soil by about 2.5 kg ha^{-1} via HCl and by 4.1 kg ha^{-1} via AAO, contents that were comparable to the 40-year accretions in tree biomass and O horizons, 2.9 kg ha^{-1}. Such patterns indicate that there has been little if any resupply of soil-extractable B to compensate removals affected by forest development.

Manganese.--- In contrast to B, concentrations of extractable Mn were depleted only from the upper 0 to 0.15-m, rather than from the entire 0.6-m. Even still, Mn decreases were substantial with both HCl- and AAO-extractions (Table 3). Although AAO recovered 4- to >5-fold more Mn than HCl, both extractants tended to recover Mn more readily from surficial layers than from deeper layers. Forest growth altered this depth-dependent pattern by depleting extractable Mn in the 0 to 0.075-m layer, such that in 1997, concentrations of HCl- and AAO-extractable Mn were reduced in these layers well below those at 0.075 to 0.35-m (Table 3). In the upper B horizons between 0.35 and 0.6 m, however, concentrations of extractable Mn were notably low in samples from both 1962 and 1997, probably a consequence of the strength of Mn sorption to Fe and Al oxides and clay (Brown and Parks, 2001; Sparks, 2003). Concentrations of Mn in natural waters collected by lysimeters were also highest in surficial soils (Table 4) and extremely low at depth (e.g. 0.6-m), patterns that suggested strong sorption of Mn to oxides and clays as drainage waters entered upper B horizons. For example, soluble Mn exceeded 125 µg L^{-1} in forest canopy throughfall, O horizons, and in mineral soils at 0.075-m depth, but averaged <8 ug $^{-1}$ at 0.6 and 2-m (Table 4, Fig. 3). Concentrations and fluxes of soluble Mn are strongly correlated with those of dissolved organic carbon (DOC) suggesting a chelating and mobilization effect by DOC in the upper layers of the Calhoun soil (Fig. 3, Table 4). Subsequent adsorption to solid phases and decomposition of DOC may well be associated with concurrent decreases in Mn concentration in upper B horizons.

During 35 years of forest growth, contents of HCl- and AAO-extractable Mn decreased significantly by 20.2 and 57.7 kg ha^{-1}, respectively. Depletions in AAO-extractable Mn were thus entirely commensurate with accretions in tree biomass and forest floor, estimated to be 51.9

kg ha^{-1} (Table 2). About 67% of this Mn depletion was estimated to be from the surficial 0 to 0.075-m layer (Table 3), a much more surficial pattern of depletion compared with B.

Mineral-soil resupply of Zn and Cu

Of the five elements under study, soil-extractable Zn and Cu changed relatively little or have increased slightly from 1962 to 1997 (Table 3). The patterns are impressive in contrast to the depletions observed with B and Mn, as replenishments of soil Zn and Cu appear to have kept pace with removals (Table 2). We call this pattern "mineral-soil resupply".

Zinc. --- Throughout the four soil layers sampled in the upper 0.6 m of mineral soil, relatively small changes were observed in the concentrations of HCl- and AAO-extractable Zn (Table 3). Although statistically significant decreases in concentrations of HCl-extractable Zn amounted to 0.166 and 0.050 μg g^{-1} in the two most surficial layers sampled, there were no significant changes in concentrations of AAO-extractable Zn (Table 3). Both extractions indicated strong depth dependence of concentrations of extractable Zn, with much higher concentrations of Zn recovered in surficial 0 to 0.15-m layers compared with 0.15 to 0.6-m. Like Mn, HCl and AAO more efficiently recovered Zn from surface soils with surfaces dominated by organic matter. Like Mn, extractable Zn at 0.35 to 0.6-m depths, the upper B horizons, was notably low in both 1962 and 1997.

During 35-year of forest growth, contents of HCl-extractable Zn decreased significantly by about 0.32 kg ha^{-1} in the upper 0.6-m layers or by 27%. This reduction, however, amounted to only about 6.7% of the Zn transferred to biomass and O horizons, about 4.8 kg ha^{-1}. Resupplies of soil Zn removed by forest growth appeared to have several sources. Atmospheric deposition alone, i.e., at 0.19 kg ha^{-1} y^{-1} in wet-only deposition (Table 4), represented an input of

6.6 kg ha^{-1} to the ecosystem if averages over two years of measurement (2004 to 2006) are scaled over the age of the forest, 35 years. Moreover, Zn in natural soil waters collected in the field appeared soluble throughout the upper 2-m soil, with little obvious soil sorption as rainwater moved through the O, A, and upper B horizons (Table 4). In contrast to solution concentrations of Mn, Zn concentrations in natural waters were greatly elevated above atmospheric deposition through 2-m depths, suggesting that clay and oxide surfaces were much stronger sinks for Mn than for Zn, and that Zn, despite its relatively small extractable contents, was relatively bioavailable throughout the rooting zone.

Copper. -- Concentrations of extractable Cu increased slightly between 1962 and 1997 (Table 3). HCl-extractable Cu significantly increased by about 0.098 ug g^{-1} in both 0.075 to 0.15- and 0.35 to 0.6-m layers, and by about 0.207 ug/g for AAO in the 0.35 to 0.6-m layer. Neither HCl nor AAO data indicated much depth dependence to extractable Cu. Both extractions recovered Cu from surface layers with organic matter and from deeper layers more affected by kaolinite and oxides.

Contents of both extractable Cu fractions (in 1962, about 1.4 and 4.4 kg ha^{-1} in the 0.6-m layers, respectively) increased by about 11 and 18% over the 35 years of forest growth. The resupply and accretions of soil Cu appears to have several sources. Atmospheric deposition appeared to be only a small source of Cu (Table 4), thus soil resupply hypothetically came from mineral dissolution and deep root uptake. Like Zn, concentrations of Cu in natural soil waters collected in the field increased as precipitation moved into the soils, and Cu remained relatively soluble throughout the upper 2-m (Table 4). Considering that transfers into plant biomass and O horizon amounted to 0.9 kg ha^{-1}, the increases of 0.8 kg ha^{-1} in AAO-soil Cu would seem to be ecologically significant.

Soil accumulation of Fe

Remarkably, concurrent with Fe accumulations in biomass and forest floor, HCl- and especially AAO-extractable Fe increased substantially throughout the upper 0.35-m mineral soil layers. Increases in extractable Fe far exceeded uptake and recycling during 35 years of forest growth. We thus call this pattern "mineral soil accumulation."

Significant increases were observed in extractable Fe in the most surficial 0.35-m layers of mineral soil (Table 3). Whereas HCl-extractable Fe increased by up to 5 ug g^{-1} in the upper 0.15 m, AAO-Fe increased between 50 to 65 ug g^{-1} in the upper 0.35 m. The magnitude of the increases in AAO-Fe concentrations in the upper 0.35-m mineral soil suggests that transformations of Fe oxides are an important part of the restructuring of soil chemistry that is affected by forest growth and development.

Among all trace elements under study, the greatest changes over the 35 years were with AAO-extractable Fe. Mineral-soil contents of AAO-Fe increased by 276 kg ha^{-1} during forest growth (Table 3), a 27% gain from 1962 to 1997 in the upper 0.35-m layer. HCl-extractable Fe also increased in surficial soil layers, by 37% or by about 9.6 kg ha^{-1} compared with contents in 1962.

Fe fluxes in tree uptake, litterfall and throughfall were small compared with changes in AAO-extractable Fe in the mineral soil. Trees accumulated 28.7 kg ha^{-1} of Fe, 92% of which was in root biomass by age 40 years in 1997, and canopy litterfall and throughfall averaged only 0.19 and 0.11 kg ha^{-1} y^{-1} in the mid-1990s and from 2004 to 2006 (Table 4). Given the relatively small Fe uptake by vegetation and Fe return in litterfall and throughfall, the very substantial increases of Fe in the 40-year-old O horizons, 472.6 kg ha^{-1} (Table 2), are as remarkable as the

Fe-oxide changes in mineral soil. Because chemical elements in O horizons typically derive from inputs in canopy litterfall and throughfall, Fe cycling seems altogether different, as annual Fe fluxes in litterfall and throughfall represent <0.07% of the total Fe accumulated in the 40-year-old O horizons. We discuss mechanisms and consequences of these changes in soil Fe more thoroughly later in this paper.

DISCUSSION

Changes in Calhoun soil's trace and major chemical elements

Table 5 combines decadal patterns of soil change in trace elements with those in major elements previously reported at the Calhoun ecosystem: for C, N, P, Ca, Mg, K, and Al. Overall, the changes are driven by cycling processes such as nutrient uptake and accumulation in forest biomass and O horizon, mineral weathering, atmospheric deposition, organic matter sequestration, hydrologic leaching, and ecosystem acidification.

Like soil extractable B and Mn, major soil depletions during forest growth have been observed for total N, (Richter et al. 2000), Ca-associated P (Richter et al. 2006), exchangeable Ca and Mg (Richter et al. 1994; Markewitz et al. 1998). Major soil resupply via mineral dissolution is notable for exchangeable K (Richter et al. 1994; Markewitz and Richter 2000) and labile P (Richter et al. 2006), and based on the present study, we can add HCl- and AAO-extractable Zn and Cu. Finally, patterns of accumulation of HCl- and AAO-Fe are shared by organic C (Richter et al., 1999; Richter et al. 2006) and exchangeable- and AAO-Al (Markewitz and Richter, 1998)..

Trace element cycling and soil change

Great element-dependent variation is observed in trace-element cycling and provides perspective to the patterns of soil and ecosystem change through time (Table 6).

The partitioning of trace elements between plant biomass and O horizon ranges widely, between 2.5 for B to 0.06 for Fe (Table 6). Relative to the other trace elements, B is notable for the contents stored in biomass and Fe is notable for the contents stored in the O horizon. Even still, both B and Fe appear to immobilize relatively large contents in both plant biomass and O horizons. For B, noted for its relatively large sink in plant biomass, the accumulated O horizon contains 20-fold the inputs of litterfall, indicating relatively slow turnover of B within the O horizon, and much slower than for Mn and especially Zn. For Fe, noted for its large contents that accumulate in the O horizon, plant biomass contains 95.7-fold more Fe than that annually recycled in litterfall and throughfall, suggesting that once Fe is associated with plant biomass it tends not to turnover.

In contrast to B and Fe, Mn and Zn cycle rapidly through biomass and O horizons. Both Mn and Zn accumulated in 40-year old forest biomass and O horizons in about equal amounts, but Mn and Zn in O horizons are only 5.1- and 2.3-fold larger than annual inputs to the O horizon from canopy litterfall plus throughfall (Table 6). That O horizons contain only 2.3-fold more Zn than the yearly O-horizon inputs tells much about the rapid rate of Zn recycling. Similarly, the basal Oea horizon contains only 1.3- and 3.3-fold more Mn and Zn than the superficial Oi layer (Tables 5, 6).

In contrast to B, Mn, and Zn, O horizons contain more Cu and Fe than that contained in plant biomass, with ratios of biomass to O horizons for Cu and Fe that average 0.53 and 0.06 (Table 6). Relatively high Cu and Fe in O horizons are attributed to the affinity with which these metals are complexed by organic matter. But overall, Table 6 illustrates how greatly Fe cycling contrasts with the cycling behavior of the other four trace elements. The various ratios for Fe tend to be extremely different from the other four trace elements, and they illustrate the strong sink strength of biomass and O horizon for Fe.

Forest interactions with Fe oxides

Past studies of Fe cycling in forests are not well quantified, although several indicate substantial accretions of Fe in O horizon, similar to the Calhoun forest. Iron accretion in O horizons of various forests (eg. maple, pine, and fir) of a wide range of age totaled 199 kg ha^{-1} to 423 kg ha^{-1} (Vogt et al., 1987; Morrison, 1990 and 1991; Arocena and Sanborn, 1999; Brockley and Simpson, 2004).

Four decades of Calhoun forest growth have altered soil micronutrients in significant and various ways (Table 3). One most significant outcome of this experiment is what it reveals about the ecosystem-driven transformation of Fe oxides. Because Fe oxides are some of the most important soil components for sorption and transformation of nutrients, organic matter, and contaminants (Schwertmann 1991), the decadal transformations in soil Fe oxides have many potential implications. Long-term cultivation reduced organic matter in the old field Calhoun soils (Richter et al., 1999), likely disrupting organic-bound Fe and SRO-Fe oxides, leaving behind largely crystalline, low surface area materials. Results from this experiment demonstrate that secondary forest-drivers can transform relatively large contents of soil Fe oxides into hypothetically reactive biomaterials in both O horizons and surface mineral soils over a matter of a few decades.

The source of Fe accumulated in O horizons and in mineral soil as SRO-Fe recovered by AAO extraction is attributed to the very large pool of Fe contained in crystalline “free” oxides and mineral-bound (Table 1). These fractions range from 10- to 35-fold greater than AAO-extractable Fe in the upper 0.15-m soil and thus represent the reservoir of Fe that is transformed during forest development. A portion of crystalline and mineral-bound Fe fractions are hypothetically transformed into more SRO- or AAO-extractable components by organo-Fe interactions assisted by pronounced acidification (Markewitz et al. 1998). The surficial 0 to 0.075-m of Calhoun mineral soil has increased its organic C concentrations by about 35% in four decades (Richter et al. 1999) at the same time that soil pH of these environments plummeted by more than a pH unit (Markewitz et al. 1998).

Because atmospheric deposition, litterfall, and throughfall add relatively little Fe to the forest floor (Table 2), the source of Fe in O horizons must be from upward translocation from the mineral soil. Several processes may be involved, the most obvious being bioturbation by macroinvertebrates that physically mixes O and A horizons. Bioturbation, however, is not considered a very active process in the Calhoun pine ecosystem, given relatively low populations of macroinvertebrate populations (Callahan et al. 2006). Radiocarbon in Oi, Oe, and Oa horizons (Richter et al. 1999) confirm the general absence of prominent mixing and development of a strongly stratified structure in these pine O horizons, the structure of a classic mor O horizon, first described by P. E. Müller in the late 19th century. Moreover, if the O horizon's content of Si and Al at 3055 and 109 kg ha^{-1} (Markewitz and Richter, 1998) is assumed to result entirely from bioturbation's mixing of A horizon materials with the O, <60 kg ha^{-1} of Fe would have been translocated upward by bioturbation (based on Fe/Si and Fe/Al ratios in A horizon materials). This leaves well over 400 kg ha^{-1} of Fe in the O horizon to be accounted for by a process of upward translocation other than bioturbation.

Total Fe in fresh canopy litterfall averages 40 ug g^{-1} which very rapidly increases nearly 17-fold to 680 ug g^{-1} as it resides in superficial Oi horizons during the course of a few years (Table 7). Overall, Fe increases by 120-fold as canopy litterfall is incorporated into Oe and Oa horizons (4755 ug g^{-1}). We hypothesize that Fe enrichment in O horizons results from the four-decade influx of forest organic matter with various functional groups that strongly complex and mobilize Fe. Over the decades, as litterfall is deposited and decomposed in the forest floor, Fe is hypothetically drawn upward from surficial A horizons into the aggrading blanket of decomposing O horizons via a combination of complexation, diffusion of aqueous complexes, and possibly evaporation. The Fe in the O horizon far exceeds concentration increases expected due to C loss during decomposition. For example, a model of the decomposition of Calhoun litterfall C (Richter et al. 1999), estimates that about 105 Mg ha^{-1} of organic C has been added to the O horizon during 40 years; if all of this litterfall averaged 40 ug g^{-1} in total Fe (Table 7), over the life of the forest litterfall would have added <8.5 kg ha^{-1} of Fe. Adding the Fe in canopy throughfall only doubles the small amount of Fe added in litterfall (Table 2).

We further hypothesize that Fe accretion of the O horizon (Table 6) is closely associated with the substantial increases and transformations of SRO-Fe in the underlying 0.35 m of mineral soil. Taken together, what seems most striking is that SRO- Fe in A horizons has increased by 276 kg ha^{-1} during a period in which O horizons accumulated 473 kg ha^{-1} of Fe. These data suggest that over three to four decades, crystalline Fe oxides and otherwise low solubility mineral-bound Fe compounds in A horizons have been the source of about 780 kg ha^{-1} of Fe (sum of Fe in plant biomass, O horizons, and increases in AAO-Fe in mineral soil). On a mass basis, this is in the same order of magnitude as the transfer of mineral-soil N into forest biomass plus O horizon (Richter et al. 2000), indicating clearly that Fe in this terrestrial ecosystem has fluxes with magnitude of a major chemical element rather than a trace- or micro-element. The rapid rates of these fluxes suggest new mechanisms by which plants and mineral soils interact ecosystem-driven transformations of Fe oxides may affect the bioavailability, sorption, and retention of organic matter, macronutrients, and chemical contaminants as well, and therefore, the implications are well worth further study

CONCLUSION

This study found that four decades of forest growth and development affect soil trace elements in diverse ways, and in ways that illustrate not only ecosystems but also soils that support them are highly dynamic on time scales of decades. In response to four decades of forest development, trace elements followed one of three patterns: 1) Extractable B and Mn were significantly depleted in amounts comparable to accumulations in biomass plus O horizons. Tree uptake of B and Mn from mineral-soil thus greatly outpaced resupplies from atmospheric deposition, mineral weathering, and deep-root uptake. 2) Extractable Zn and Cu changed little during forest growth, indicating that nutrient resupplies kept pace with accumulations by the aggrading forest. 3) Short-range order or oxalate-extractable Fe increased substantially during forest growth, by about 10-fold more than accumulations in tree biomass, indicating that forest Fe cycling is qualitatively different from that of other macro- and micro-nutrients. The contrasting patterns of soil change were determined by contrasting rates of inputs, translocations, transformations, and removals, or more specifically transfers into plant biomass and O horizons, atmospheric deposition, deep root uptake, mineral weathering and dissolution, and hydrologic leaching. This study clearly indicated that Fe cycles at rates that can be characterized as a major chemical element rather than a trace- or micro-element. Overall, we hypothesize that the secondary forest's continuous organic additions to mineral soils substantially transformed soil Fe-oxides, which may be significantly altering the bioavailability and retention of macro- and micro-nutrients, chemical contaminants, and organic matter itself. The ecosystem cycling of all essential nutrients, macro- and micro-nutrients alike, are in great need of research, especially with respect to changing bioavailability and disposition in soil on time scales of decades.

ACKNOWLEDGEMENTS

The research was partly funded by the NSF LTREB Program, DEB-01-20698, and by Duke University's Graduate School and Nicholas School of the Environment and Earth Sciences. We acknowledge field and laboratory assistance of Michael Hofmockel, Ryan Fimmen, Meg Mobley, Brian Roberts, Jason Jackson, and Peter Cada.

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TABLE 1. General physical and chemical properties of the Ultisols from the long-term soil experiment at the Calhoun Experiment Forest, SC USA. Soil data are from 1990 samplings (Richter et al., 2006).

					Exchangeable/extractable†				Total		
Horizon	Depth	pHs*	SOC	Clay	BC	ECEC	SO_4	Fe	Fe	Mn	Cu
	(m)		---- % ----		---- mmolc kg^{-1} ----			---- g kg^{-1} ----		-- mg kg^{-1} --	
A	0-0.075	3.8	0.67	10.0	1.1	11.9	0.2	1.73	7.1	217	4
E	0.075-0.15	4.2	0.41	13.0	0.9	7.7	0.2	2.48	7.1	217	4
EB	0.15-0.35	4.4	0.31	18.0	3.5	10.0	1.1	7.30	10.7	216	6
BE	0.35-0.6	4.4	0.33	39.3	14.5	23.7	7.8	20.85	28.2	172	15
Bt	0.6-1.0	4.0	0.23	48.5	13.0	29.2	10.2	30.94	44.5	152	22
Bt	1.0-1.5	4.0	0.23	42.9	5.8	26.6	10.1	28.64	42.8	164	22
BC	2.0-2.5	4.0	0.07	37.7	1.7	32.7	8.3	16.37	34.6	210	23
CB	2.5-3.0	4.0	0.08	28.5	2.1	36.2	-	11.32	-	-	-

* pHs is soil pH in 0.01 M $CaCl_2$.

† Exchangeable BC is the sum of NH_4-acetate exchangeable Ca, Mg, and K; ECEC is effective cation exchange capacity, BC plus KCl-acidity; extractable SO_4 is NH_4VO_3-extractable; and extractable Fe is dithionite-citrate-bicarbonate extractable Fe (Richter et al. 1994, Markewitz et al. 1998, Richter et al. 2006).

TABLE 2. Summary of elemental accretions in tree biomass and forest floor (1957 to mid-1990s), mineral-soil depletions (1962 to 1997), and ecosystem fluxes of canopy litterfall, canopy throughfall, and net soil leaching at Calhoun long-term soil experiment, South Carolina, USA.

	Soil Trace Elements (kg ha^{-1})				
Components, fluxes	B	Mn	Zn	Cu	Fe
35-yr removals*					
Plant biomass	2.1	24.7	2. 5	0.34	28.7
O horizon	0.8	24.9	2.3	0.56	472.6
Net soil leaching†	NA	-2.3	0.7	<0.001	2.1
Total	2.9	47.3	5.5	0.90	503.4
Annual internal flux					
Litterfall	0.04	3.49	0.13	0.01	0.19
Throughfall	NA	1.39	0.86	0.01	0.11
Total	NA	4.88	0.99	0.02	0.30
35-yr Soil Changes					
HCl-extractable ‡	-2.5	-20.2	-0.3	+0.2	+9.6
*(*1 SE*)*	(*0.05*)	(*0.5*)	(*0.01*)	(*0.01*)	(*0.23*)
AAO-extractable ‡	-4.1	-57.7	0.0	+0.8	+275.8
*(*1 SE*)*	(*0.2*)	(*2.9*)	(*0.02*)	(*0.06*)	(*19.6*)

* denotes nutrient content of all vegetation components including stemwood, stembark, foliage, live and dead branches, and roots.

† denotes net leaching estimates which represent differences of total leaching output minus atmospheric input. Soil leaching is the estimated leaching at 60-cm soil depth assuming a median 30-cm runoff annually.

‡ denotes changes which were only estimated when trace element concentrations were significantly different between 1962 and 1997 (see Table 3).

TABLE 3. HCl- and AAO-extractable trace elements in 1962 and 1997 in Calhoun soils.

(a)

Soil layer (m)	HCl-Extractable Trace Elements				
	B	Mn	Zn	Cu	Fe
	1962 sample concentrations (ug/g)				
0-0.075	0.304	16.15	0.372	0.188	14.36
0.075-0.15	0.260	11.72	0.201	0.140	8.23
0.15-0.35	0.311	8.21	0.096	0.179	5.53
0.35-0.60	0.402	2.47	0.060	0.140	6.71
	1997 sample concentrations (ug/g)				
0-0.075	0.032****	2.79****	0.206****	0.259	19.36*
0.075-0.15	0.030****	7.40****	0.151****	0.238*	11.68**
0.15-0.35	0.043****	7.78	0.087	0.222	5.26
0.35-0.60	0.096****	1.95	0.039***	0.238*	5.93
	Change in contents 1997-1962 (kg/ha)				
0-0.075	-0.31	-15.23	-0.19	NS	+5.69
0.075-0.15	-0.26	-4.92	-0.06	+0.08	+3.93
0.15-0.35	-0.82	NS	NS	NS	NS
0.35-0.60	-1.10	NS	-0.07	+0.07	NS
0-0.60	-2.5	-20.2	-0.3	+0.16	+9.6

(b)

Soil layer (m)	AAO-Extractable Trace Elements				
	B	Mn	Zn	Cu	Fe
	1962 sample concentrations (ug/g)				
0-0.075	0.700	63.47	0.960	0.584	186.4
0.075-0.15	0.612	68.32	0.537	0.616	202.4
0.15-0.35	0.659	40.29	0.315	0.493	185.9
0.35-0.60	0.310	15.42	0.293	0.443	333.5
	1997 sample concentrations (ug/g)				
0-0.075	0.225****	40.49****	0.771	0.577	248.7****
0.075-0.15	0.226****	58.40**	0.491	0.597	255.6****
0.15-0.35	0.100****	50.40	0.375	0.656	233.4***
0.35-0.60	0.000****	11.14	0.225	0.650****	330.4
	Change in contents 1997-1962 (kg/ha)				
0-0.075	-0.54	-37.73	NS	NS	+70.9
0.075-0.15	-0.44	-19.98	NS	NS	+60.6
0.15-0.35	-1.97	NS	NS	NS	+144.3
0.35-0.60	-1.10	NS	NS	+0.79	NS
0-0.60	-4.1	-57.7	0.0	+0.79	+275.8

*, **, ***, **** means significant at the 0.05, 0.01, 0.001 and 0.0001 probability levels, respectively, for obtaining a greater F for contrasts between 1962 and 1997.

“NS” indicates a nonsignificant difference.

TABLE 4. Mean concentration and distribution of Fe, Mn, Zn and Cu throughout aquatic continuum from April 2004 to April 2006 at Calhoun Forest, South Carolina, USA.

Depth	Hydrologic flux	Concentration				Flux			
		Cu	Zn	Mn	Fe	Cu	Zn	Mn	Fe
	cm yr^{-1}	ug/L		mg/L			kg ha^{-1} yr^{-1}		
Bulk precipitation	123	0.45	0.008	0.007	0.004	0.006	0.09	0.08	0.05
Wet-only precipitation	123	0.48	0.016	0.003	0.004	0.006	0.20	0.04	0.05
Canopy throughfall	105	0.89	0.080	0.129	0.010	0.009	0.84	1.35	0.11
O horizon soil solution	101	2.37	0.022	0.296	0.079	0.024	0.22	2.99	0.80
0.075 m soil solution	97	9.49	0.048	0.160	0.183	0.092	0.46	1.55	1.78
0.6 m soil solution	71	1.77	0.038	0.005	0.001	0.013	0.27	0.04	0.01
2 m soil solution	39	3.75	0.032	0.008	0.002	0.015	0.13	0.03	0.01
Seep		2.62	0.003	0.034	0.111	-	-	-	-
Stream		1.68	0.006	0.087	0.144	-	-	-	-

Note: Hydrologic flux estimates are taken from a similar study at Calhoun in 1992 to 1994 (Markewitz and Richter, 1998).

TABLE 5. Mineral soil elemental cycling patterns over decades among forest and soil ecosystems at Calhoun Experimental Forest, South Carolina, USA.

40-year pattern	Major elements	Trace elements
Depletion	Total N, Exchangeable Ca & Mg, Ca-associated P	HCl- & AAO-Mn, B
Resupply	Exchangeable K, Labile P	HCl- & AAO-Zn, Cu
Accumulation	Total C, Exchangeable & AAO-Al	HCl- & AAO-Fe

Note: Citation for N (Richter et al. 2000); Ca, Mg and K (Richter et al. 1994; Markewitz et al. 1998; Markewitz and Richter, 2000); P (Richter et al. 2006), C (Richter et al. 1999), Al (Richter et al. 1994; Markewitz and Richter, 1998).

TABLE 6. Comparisons of components and annual fluxes of trace elements at Calhoun ecosystem. Although decadal changes in trace elements in the mineral soils can be grouped into three patterns, ecosystem cycling patterns range widely among the five elements.

Indices of cycling	B	Mn	Zn	Cu	Fe
Wet deposition / Throughfall	--	0.03	0.22	0.60	0.36
Plant Biomass / O horizon	2.50	1.00	1.11	0.53	0.06
Plant Biomass / Litterfall	52.5	7.1	19.2	30.0	151
O horizon / Litterfall	20	7.1	17.7	60	2487
O horizon / (Litterfall+Throughfall)	--	5.1	2.3	30	1575
Oi horizon / Litterfall	2.4	3.1	4.2	7.8	69.7
(Oea horizons) / Oi horizon	7.5	1.3	3.3	6.1	34.7

TABLE 7. Trace elements concentrations and contents of litterfall and O horizons of the Calhoun forest (1997 collections). CV% for concentrations is in parentheses.

	Concentrations (mg kg^{-1})					Contents (kg ha^{-1})					
Horizon	B	Cu	Zn	Mn	Fe	OM	B	Cu	Zn	Mn	Fe
Litterfall	8.1	1.6	27.4	713	39.3	4900	0.04	0.008	0.134	3.49	0.19
	(41)	(43)	(8)	(11)	(6)						
Oi	4.95	4.05	28	560.7	683	19399	0.095	0.078	0.54	10.74	13.2
	(14)	(14)	(9)	(32)	(25)						
Oe	7.15	3.7	17.5	150.5	4755	51726	0.65	0.329	1.553	13.15	426.5
	(31)	(18)	(16)	(38)	(13)						
Oa	9.32	21.7	31.2	156.4	4955	4540	0.061	0.151	0.208	1.04	32.9
	(23)	(31)	(8)	(40)	(10)						
Total O hr	-	-	-	-	-	115710	0.806	0.558	2.301	24.93	472.6

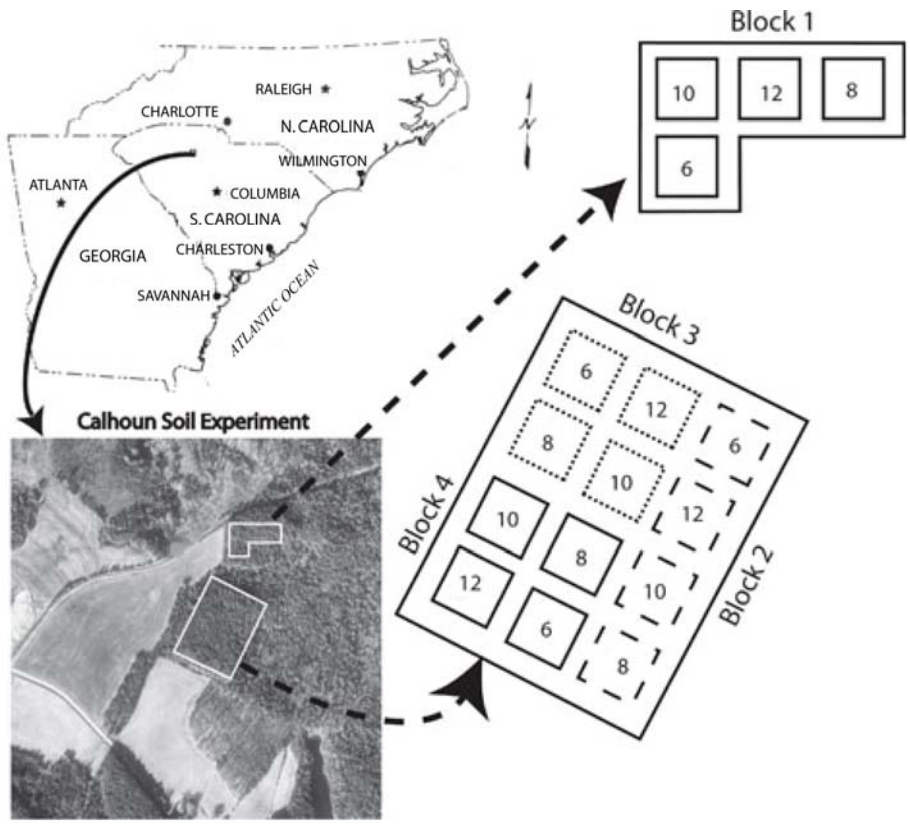
Note: n=16 plots for organic matter (OM), B, Cu, Zn and Mn at each depth, and n=4 block composite for Fe. Total means the sum of Oi, Oe and Oa, and other materials collected in the O horizon samples.

Figure Legends

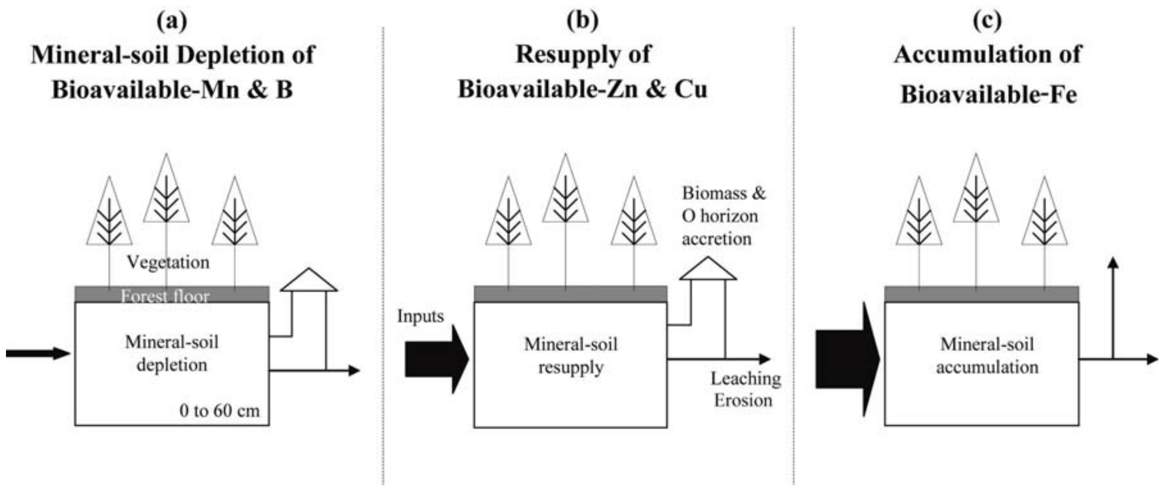
FIG. 1. Location of the randomized complete block design of the Calhoun Experimental Forest, SC, USA. The original experiment in 1957 involved planting loblolly pine seedlings at one of four spacings, 6 x 6 ft, 8 x 8 ft, 10 x 10 ft, and 12 x 12 ft, thus the plot codes of 6, 8, 10, and 12 in each of four blocks.

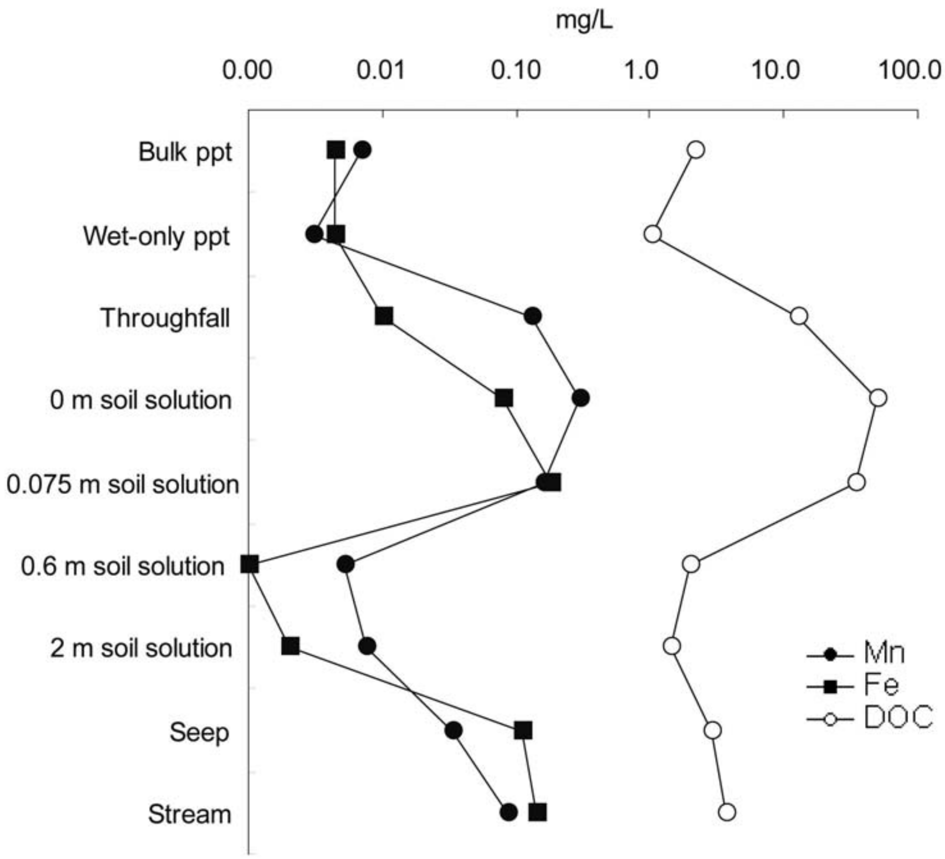
FIG. 2. Conceptual diagram of trace element cycling patterns in mineral soils over decades at Calhoun Experiment Forest, SC, USA. As mineral soil supports the growth of a forest, its bioavailable nutrients on a net basis are depleted, resupplied, or accumulated depending on a balance of inputs, recycling and removals. The biogeochemical processes of input and recycling include atmospheric deposition, mineral dissolution, deep root uptake, proton inputs (eg, Al), and net sequestration (eg. C). The processes of removal include plant uptake and accumulation in tree biomass and forest floor, hydrologic leaching, and erosion.

FIG. 3. Volume-weighted mean annual concentrations of total Fe and Mn and dissolved organic carbon (DOC) in solutions from the Calhoun Experimental Forest, South Carolina for the period April 2004 to April 2006.



Block 1
10
12
8
6
RALEIGH
CHARLOTTE
N. CAROLINA
WILMINGTON
ATLANTA
COLUMBIA
S. CAROLINA
GEORGIA
CHARLESTON
SAVANNAH
ATLANTIC OCEAN
N
Block 3
6
12
8
10
6
12
Block 4
10
8
12
10
6
8
Block 2
Calhoun Soil Experiment


(a)
Mineral-soil Depletion of
Bioavailable-Mn & B
Vegetation
Forest floor
Mineral-soil
depletion
0 to 60 cm
(b)
Resupply of
Bioavailable-Zn & Cu
Biomass &
O horizon
accretion
Inputs
Mineral-soil
resupply
Leaching
Erosion
(c)
Accumulation of
Bioavailable-Fe
Mineral-soil
accumulation


mg/L
0.00
0.01
0.10
1.0
10.0
100.0
Bulk ppt
Wet-only ppt
Throughfall
0 m soil solution
0.075 m soil solution
0.6 m soil solution
2 m soil solution
Seep
Stream
Mn
Fe
DOC