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Dynamics of oxidized and reduced iron in a northern hardwood forest

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Abstract

Iron (Fe) is ubiquitous in forest ecosystems and its cycle is thought to influence the development of soil, particularly Spodosols (podsolization), and the biogeochemistry of macro-nutrients such as carbon (C), nitrogen (N), and phosphorus (P), as well as many trace metals. The cycle of Fe in northern hardwood forests remains poorly understood. To address some of these uncertainties, we constructed a biogeochemical budget of Fe for a small catchment at the Hubbard Brook Experimental Forest in the White Mountains of New Hampshire, USA. Horizonal, temporal, and elevational patterns of concentrations and fluxes of oxidized and reduced Fe species were assessed in leaf litter, soil, soil solution, and stream water. The chemistry of dissolved Fe was evaluated in the context of its relationship with dissolved organic carbon, pH, and dissolved oxygen. Soil solution fluxes of Fe were highest in the organic (Oa, 52.5 mol ha^{-1} yr^{-1}) horizon and decreased with depth in the mineral (Bh, 50.5 mol ha^{-1} yr^{-1}, and Bs, 19.7 mol ha^{-1} yr^{-1}) horizons, consistent with podsolization theories predicting immobilization of Fe following downward transport to mineral soils. The export of Fe in stream water (1.8 mol ha^{-1} yr^{-1}) was lower than precipitation input (3.5 mol ha^{-1} yr^{-1}). The low stream flux indicates most Fe in drainage waters was immobilized in the soil and retained in the watershed. The portion of total Fe as Fe(II) was approximately 10% to 60% in soil solutions, seemingly high for soils that are considered to be well-drained, oxidizing environments. Organic complexes likely stabilized Fe(II) in solution under oxidizing conditions that would otherwise promote considerably higher Fe(III)-to-Fe(II) ratios. Our study indicates that there are organic matter-derived sources of dissolved Fe(II) as well as substantial mobilization of Fe(II), possibly the result of the reduction of Fe-bearing soil minerals.

Introduction

Interest in iron (Fe) biogeochemistry stems from its role as a micronutrient and as an indicator of mineral weathering and soil development. Iron is relatively abundant in comparison to other trace metals. In soils and drainage waters, Fe transformations and fluxes are linked to the cycling and mobilization and immobilization of organic carbon (McDowell and Wood 1984; Ussiri and Johnson 2004; Gu et al. 1994), sulfur (Drobner et al. 1990; Harrison et al. 1989; Sollins et al. 1988), phosphorus (Yuan and Lavkulich 1994) and trace metals (Kabata-Pendias and Pendias 1984). Oxidation-reduction ("redox") transformations between ferric (Fe(III)) and ferrous (Fe(II)) iron can affect the mobilization and immobilization of Fe and compounds associated with Fe. The reduction of Fe(III) can significantly increase the concentration of available P that otherwise strongly sorbs to Fe oxide surfaces (Chacon et al. 2006; Peretyazhko and Sposito 2005). Redox reactions of Fe have also been proposed as a mechanism of abiotic nitrate immobilization in soils (Davidson et al. 2003).

In many northern ecosystems, soil development (podsolization) is closely coupled with iron cycling. The development of Spodosols involves the mobilization of Fe and Al to lower mineral soil by complexation with organic acids derived from foliar leaching and forest floor decomposition (e.g. Bloomfield 1953; de Coninck 1980; Dahlgren and Ugolini 1989). Podsolization is thought to result from the downward transport of organic-metal (Fe and Al) complexes until they co-precipitate or adsorb in the spodic (B) horizon due to decreasing carbon-metal ratios. Decreasing carbon-metal ratios are caused by the further complexation of Fe and Al (McKeague et al. 1978) and/or microbial breakdown of the organic carrier molecules (Boudot et al. 1989; Lundström et al. 2000).

Redox transformations involving Fe are often important in soils and sediments, especially in the presence of organic matter. Oxidation and reduction of Fe can be mediated by microbes (Weber et al. 2006) as well as by chemical constituents (Singer and Stumm 1970). Chemical and enhanced biological reduction of Fe has been shown to be mediated by natural organic matter under anoxic laboratory conditions (Chen et al. 2003). It has been proposed that humic substances can facilitate indirect reduction of Fe(III) by shuttling electrons from humic-reducing microorganisms to iron oxides (Lovley et al. 1996). Wet Spodosols, or Aquods, show redoximorphic features resulting from Fe reduction due to high water tables and saturated conditions with low dissolved oxygen concentrations (Buol et al. 2003).

Few input-output budgets of Fe have been constructed for forest ecosystems compared to those for major nutrients. Swanson and Johnson (1980) found that bulk precipitation input of Fe far exceeded output (deep seepage + streamflow) in a forested watershed in the New Jersey Pine Barrens. Heinrichs and Mayer (1977) reported Fe budgets for a 125-year-old beech forest and an 85-year-old spruce forest in central Germany’s Solling hill region. At both sites, bulk precipitation inputs of Fe exceeded deep seepage, indicating net retention of Fe. Fluxes from the humus layer suggested most retention occurs in the forest floor. However, in a 70-year-old spruce forest in southwestern Sweden, leaching of Fe from the A horizon exceeded input from precipitation (Tyler 1981). Jersak et al. (1995) used mass-balance modeling to quantify specific aspects of long-term Spodosol development, including Fe accumulation or loss. They found a net loss of Fe from two soils, and a small accumulation in a third. At the Hubbard Brook Experimental Forest (HBEF) in New Hampshire, the site of our study, Smith et al. (1986) found that stream output of Fe from a small leachwater catchment only slightly exceeded bulk precipitation input, indicating a small net loss of Fe.

The objective of this study was to develop a more comprehensive Fe budget for the HBEF and thereby provide a better understanding of Fe biogeochemistry in northern forest ecosystems. For example, to our knowledge there is no mass balance study in the literature that has considered the fluxes of Fe(II) and Fe(III). Moreover, in addition to input-output budgets, an evaluation of internal transformations and fluxes, including the relative distribution of Fe(II) and Fe(III), is critical to understanding the transfer and cycling of Fe in soil and plants in forest ecosystems. Comparison of fluxes with the Fe pool sizes in soil horizons provides further insight into the mobility and bioavailability of Fe. The results of this study of Fe budgets and transformations are also evaluated in the context of podsolization theory.

Site Description

The HBEF is located in the White Mountain National Forest in central New Hampshire, USA (43º56' N, 71º45' W). This study was conducted in and near Watershed 6, the HBEF biogeochemical reference watershed (13.2 ha, elevation 549-792 m, slope 16°), and Watershed 1 (11.8 ha, elevation 488-747 m, slope 19°), where wollastonite (calcium silicate) was applied in October 1998 as an experimental treatment to investigate the role of calcium supply in the structure and function of a forest ecosystem. Both Watershed 6 and Watershed 1 have southeasterly aspects. The climate at the HBEF is cool-temperate, humid-continental, with mean July and January temperatures of 19 and -9ºC respectively (at 450 m elevation). Annual precipitation averages ~140 cm and is distributed nearly evenly throughout the year. Approximately 30% of annual precipitation occurs as snow (Federer et al. 1989). The area is generally covered with glacial till derived from local bedrock with a depth ranging from zero along the ridge tops to several meters at the lower elevations (Palmer et al. 2004). The soils are well-drained Spodosols, mostly Haplorthods (Johnson et al. 2000), with a well-developed organic horizon (3-15 cm; Likens et al. 1977) and underlain by impervious bedrock (Littleton Formation, schist). Higher elevation soils tend to be shallowest and soil depth increases with decreasing elevation (Lawrence et al. 1986). The vegetation of both Watershed 6 and Watershed 1 is dominated by northern hardwood species, including American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.), and yellow birch (*Betula alleghaniensis* Britt.). At higher elevations, balsam fir (*Abies balsamea* (L.) Mill), red spruce (*Picea rubens* Sarg.), and white birch (*Betula papyrifera* var. *cordifolia* Marsh.) are prominent.

******FIGURE 1******

Methods

Sample Collection

To examine landscape patterns in Watershed 6, soil solution, stream water, throughfall and litterfall samples were collected by elevation zone. Tension-free lysimeters were installed immediately west of Watershed 6 in a low-elevation deciduous stand (600 m), a high-elevation deciduous stand (730 m), and in a coniferous stand (750 m) to collect soil solutions draining the Oa, Bh, and Bs horizons (Figure 1). The lysimeters were placed just outside of the Watershed 6 boundary to minimize soil disturbance within the watershed. Three replicate lysimeters are located in each of the three stands. Thirteen additional lysimeters were sampled in Watershed 1. A detailed description of lysimeter design and installation is provided by Driscoll et al. (1988a).

Soil water was collected from the lysimeters at approximately monthly intervals (March 2006-February 2007). In conjunction with the monthly collection of lysimeter samples, grab samples of stream water were collected from six sites arranged longitudinally in Watershed 6 and five sites in Watershed 1 (Figure 1). All lysimeter and stream samples were collected in 500 mL polyethylene or polypropylene bottles and stored at 4ºC prior to chemical analyses. Subsamples for Fe(II) analysis were taken shortly after collection and preserved with 1% hydrochloric acid (HCl) to minimize oxidation of Fe(II) to Fe(III) (Wilkin and Ptacek 2002). Throughfall collectors were installed immediately adjacent to each lysimeter plot in Watershed 6 (n = 9). These consisted of a wooden stand topped (~1.5 m above ground) with a 10-inch diameter polyethylene funnel connected with PVC tubing to a 1 L polypropylene bottle. Inserted in the base of the funnel was a plug of acid-washed polyester fibers to prevent large debris from washing into the sample containers. Throughfall samples were collected within 24 h following each of five precipitation events at the nine lysimeter sites in Watershed 6 during the summer of 2007.

Field measurements of dissolved oxygen (DO) were taken throughout the year during collection of soil solution samples from lysimeters,. Soil solution was pumped into a separate collection bottle separate from the sample intended for chemical analysis and the electrode of a portable HI 9142 dissolved oxygen meter (Hanna Instruments, Woonsockett, RI) was immediately placed in the water and gently (so as not to introduce excessive air) stirred until a stable value was reached. These measurements are considered qualitative because of the inherent difficulty of preventing introduction of atmospheric oxygen during the pumping of water from lysimeters. We assume that solution in the lysimeter reservoirs was in equilibrium with soil oxygen partial pressures.

Leaf litter samples for analysis of leachable Fe (including Fe(II) analysis) were collected from each of the vegetation zones at the conclusion of the leaf fall (late October to early November, 2007). Permanent litterfall traps (0.1 m^2 each) were placed approximately 1 m above the ground in the vicinity of the lysimeter plots to measure litterfall mass. To collect leaves immediately available for leachate Fe speciation analysis, the most recently fallen leaves were collected from the top of the forest floor adjacent to litter traps for chemical analysis. These samples were sorted into the dominant tree canopy species (sugar maple, American beech, yellow birch) prior to analysis. The leaves were bulked and homogenized to produce one sample per species per elevation zone.

Laboratory Analysis

Soil solution, throughfall, stream water, litter digests, and litter leachate were analyzed for total Fe and Fe(II). Total Fe was measured with a Perkin Elmer (Waltham, MA) Elan 6100 inductively coupled plasma mass spectrometer (ICP-MS). In preparation for this analysis, samples were preserved with 1% nitric acid. Ferrous iron concentration was measured using the 1,10-phenanthroline colorimetric method (Clesceri et al. 1998). This method includes acidification of the sample with hydrochloric acid to decouple Fe(II) ions from natural organic complexes. An addition of 1,10-phenanthroline, which has a very high affinity to form complexes with free Fe(II), produces a colored compound. A Thermo Scientific (Waltham, MA) Spectronic 20D+ spectrophotometer was used to measure absorbance at 510 nm. To account for interference from color due to dissolved organic matter, each sample was also measured for absorbance at the same wavelength without 1,10-phenanthroline. The resulting value was subtracted from the absorbance obtained with 1,10-phenanthroline to obtain a net absorbance for each sample. Ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$) was used as a standard for Fe(II) analysis calibration and quality control. Ferric iron concentration was calculated as the difference between total Fe and Fe(II) concentration.

The pH of the samples was measured with an Orion Ross Sureflow (Thermo Scientific, Waltham, MA) glass combination electrode connected to a Brinkman (Westbury, NY) Metrohm 716 DMS titration system. Samples were analyzed for DOC with a Teledyne Tekmar (Mason, OH) Phoenix 8000 TOC analyzer by infrared CO_2 detection following UV-enhanced persulfate oxidation. To prepare for DOC analysis, samples were filtered through 0.7 μm Whatman (Maidstone, England) AH 934 glass fiber filters into 40 mL glass vials.

Analysis of total Fe concentration was conducted on foliage samples representing the major tree species in each elevational vegetation zone using material from the Hubbard Brook sample archive. These samples were originally collected (by shotgun) in August, 2006 from the canopy near the Watershed 6 lysimeter sites as part of an ongoing yearly collection. The samples were subsequently dried and ground before archival. The samples were dry-ashed for 24 h at 400°C in a Thermo Scientific (Waltham, MA) Lindberg Blue muffle furnace. The ash was digested with 10N nitric acid and the resulting solution diluted with deionized water. Total Fe analysis was conducted with ICP-MS as described previously. Certified apple leaf samples (Standard Reference Material 1515, National Institute of Standards and Technology, Gaithersburg, MD) were used as a quality control check. Mean recovery of Fe in the certified apple leaves was 90 ± 5%.

Leaf litter was extracted for the determination of total Fe and Fe(II) concentration in leachates according to a method modified from Koseoglu and Acikgoz (1995). Litter was sorted by species and leaves were cut into small (~2x2 mm) squares using ceramic scissors and placed in 1N hydrochloric acid for 24 h. The leachate was analyzed for total Fe and Fe(II) as described above for the soil solution.

Computational Methods and Sources of Additional Data

Watershed fluxes and landscape patterns were evaluated based on data from Watershed 6 only. Additional data were used in this study from samples collected in Watershed 1. A comparison of data between Watershed 1 and Watershed 6 revealed no significant differences for Fe or DOC concentrations. Therefore, the data from the two watersheds were grouped for several of the analyses in this study, including horizonal and temporal patterns and relationships of Fe chemistry with DOC, pH, and dissolved oxygen. All analyses of vegetation zone patterns were conducted with Watershed 6 data only. Temporal analysis was based on seasonal mean concentrations of solutes (seasons defined as Spring = March, April, May; Summer = June, July, August; Fall = September, October, November; Winter = December, January, February).

Soil solution fluxes were calculated with a correction for transpiration with an estimate of evapotranspiration (ET = precipitation – stream flow) during the growing season (defined as 15 May-15 October, Dittman et al. (2007)). The ET was assumed to be distributed by soil depth according to the corresponding fine root mass of each horizon in each of the vegetation zones (Oa: 30-46%, Bh: 36-40%, Bs: 13-29%: T.J. Fahey, personal observation; Dittman et al. (2007)). Evapotranspiration was calculated for the watershed and this value was applied to each vegetation zone. Transpiration during the non-growing season was assumed to be zero. Flow draining each horizon was estimated as the difference between precipitation input and the calculated ET. Solute fluxes were calculated for each vegetation zone by multiplying the mean concentrations by the corresponding soil water fluxes for the growing and non-growing season. A whole-watershed flux was calculated by weighting the elevation zone fluxes by their respective areas (Spruce-Fir-Birch (SFB) = 20%, High Hardwood (HH) = 30%, and Low Hardwood (LH) = 50%).

Fluxes of stream water solutes were calculated by empirically modeling the concentration of dissolved Fe in as a function of stream discharge rate using the following equation:

$$[Fe]\left(\mu mol\ L^{-1}\right)=0.0885-0.0313\left[\log\left(L\ s^{-1}\right)\right]+0.0841\left[\log\left(L\ s^{-1}\right)\right]^{2} \quad \text{Equation 1}$$

This function was modeled using data collected in this study and from data collected between 1990 and 2000 (CE Johnson, unpublished data). Subcatchment Fe fluxes in stream water were calculated using stream flow rates prorated according to subcatchment area.

Throughfall flux was calculated by determining mean Fe quantities per mm of precipitation averaged from the five storm events sampled and scaling a subsequent weighted mean value to all precipitation during the growing season (May 15-Oct. 15). The throughfall flux for the non-growing season (Oct. 16-May 14) was assumed to be equal to the portion of bulk precipitation flux occurring during that time period. The throughfall water flux for each event was assumed to be equal to that of precipitation with a subtraction of 11% to correct for canopy interception (Aber and Federer 1992). Throughfall fluxes from each elevation zone were weighted in the same manner as described for soil solutions to obtain a whole watershed flux.

Annual leaf litterfall fluxes of Fe were estimated as equal to the total Fe content of foliage. The mean foliar Fe concentrations from the 2006 samples were multiplied by the total foliar biomass according to the 2002 Watershed 6 forest inventory survey for each species (TG Siccama, unpublished data), the most recent biomass survey data available at the time of our study. The values were weighted by tree species composition to obtain the total flux.

Values from other sources were used to provide a more complete Fe budget for Hubbard Brook. In particular, bulk precipitation input of Fe was reported by Smith et al. (1986) and updated to include more recent monitoring data. Petras (1996) estimated Fe fractions for soil horizons and soil pools at Hubbard Brook based on data from soil pits in Watershed 5.

One-way and two-way analyses of variance (ANOVA) were performed to determine whether differences and patterns for data groupings (e.g. soil horizons, elevational vegetation zones, seasons) were statistically significant. Paired t-tests were conducted to test for significant differences in soil water solute concentrations between specific seasons. Linear regressions were performed to analyze the correlation between data variables.

Results

Chemistry of Inputs to the Forest Floor: Throughfall and Litterfall

The volume-weighted average concentration of total dissolved Fe in throughfall in W6 was 0.44 μmol L^{-1} (LH = 0.45 μmol L^{-1}, HH = 0.43 μmol L^{-1}, SFB = 0.44 μmol L^{-1}; n=3 per vegetation zone per event). There were no significant differences in dissolved Fe concentrations between the elevation zones during any of the five precipitation events collected during the summer of 2007.

The concentration of total Fe in litterfall was estimated by analyzing foliage samples collected in August 2006. The mean species concentration of Fe in foliage was 42.9 μg g^{-1}. The lowest Fe concentration values were found in conifer needles (red spruce = 25.7 μg g^{-1}, balsam fir = 35.6 μg g^{-1}). Among hardwood species, the lowest concentration was found in the white birch sample (40.6 μg g^{-1}, collected at the spruce-fir-birch site). There were no significant differences between the mean Fe concentrations of sugar maple (49.2 μg g^{-1}) and American beech (48.1 μg g^{-1}; p=0.90). Sugar maple foliar Fe concentration also did not differ significantly from yellow birch (58.0 μg g^{-1}; p=0.27), but yellow birch had a higher foliar Fe concentration than beech at each sampling elevation (p=0.01).

******TABLE 1******

The readily leachable (1N HCl) Fe concentration in leaf litterfall was measured for the three major hardwood species: sugar maple, yellow birch, and American beech. Sugar maple had the lowest leachable Fe content, while yellow birch and beech showed higher values (Table 1). . Readily leachable Fe represented 23% of the total Fe content on average between the three species. Just over half of the readily leachable total Fe was in the reduced form (Fe(II)) for each of the three tree species (sugar maple = 53%, yellow birch = 53%, American beech = 61%).

Chemistry of Drainage Waters: Soil Solution and Stream Water

Patterns in the Soil Profile

In soil solutions of Watershed 6 and Watershed 1, Fe(II), Fe(III), DOC, and hydrogen ion all showed decreasing concentrations with increasing depth in the soil profile (Table 2). The decrease was significant across all soil depths for Fe(II) (Oa = 1.45 μmol L^{-1}, Bh = 0.82 μmol L^{-1}, Bs = 0.58 μmol L^{-1}, $p = 0.02$) and for DOC (Oa = 1530 μmol L^{-1}, Bh = 730 μmol L^{-1}, Bs = 510 μmol L^{-1}, $p < 0.01$). Although soil solution Fe(III) concentration showed decreasing values with depth (Oa = 2.58 μmol L^{-1}, Bh = 2.09 μmol L^{-1}, Bs = 1.52 μmol L^{-1}), the difference was only significant between the Oa horizon and the Bs horizon ($p = 0.02$). Across all vegetation zones the increase of pH (decrease of hydrogen ion concentration) with increasing depth was significant through all three soil horizons (Oa = 4.25, Bh = 4.59, Bs = 4.75, $p = 0.01$).

Elevational Patterns

Marked elevational landscape patterns were evident in the concentrations of dissolved Fe species, DOC and pH in soil solutions (Table 2) and stream water (Figure 2). For soil water draining each soil horizon and for stream water, Fe(II), Fe(III), DOC, and hydrogen ion concentrations were highest in the spruce-fir-birch subcatchment and generally decreased with decreasing elevation through the high-elevation hardwood and low-elevation hardwood zones of W6. This pattern was significant across all three elevation zones for Fe(II) and pH ($p \leq 0.01$). Significant differences were found for both Fe(III) and DOC concentrations between the spruce-fir-birch zone and the low-elevation hardwood zone. The spruce-fir-birch subcatchment had higher concentrations of Fe(III) and DOC than the low-elevation hardwood zone for soil solutions across all soil horizons ($p \leq 0.03$).

******TABLE 2******

******FIGURE 2******

No notable elevational vegetation zone patterns were evident in the distribution of Fe between the oxidized and reduced forms in the soil solutions. The percentage of total dissolved Fe as Fe(II) ranged from a low value of 16% in the soil water draining the Bh horizon in the low hardwood site to a high value of 44% in the solution draining the Oa horizon of the high hardwood zone.

The elevational patterns of Fe concentrations, as well as the soil horizonal patterns mentioned previously, have implications for the transport and retention of Fe (See Discussion section).

Seasonal Patterns

Generally, seasonal changes of soil solution Fe and DOC concentrations were found only in the Oa horizon leachates (Figure 3). The concentrations of Fe(II) and DOC in soil water draining the Oa horizon were both significantly lower in the spring and winter than in the summer and fall ($p \leq 0.01$). The concentrations of Fe(II) and DOC in the Oa horizon increased from the spring to summer to fall, and decreased from fall to winter. For DOC, but not for Fe(II), the increase from the summer to the fall was significant ($p < 0.01$). A similar pattern was observed in the Fe(III) concentrations of the Oa soil solutions, although the highest values were observed in the summer samples. Seasonal patterns for the Fe(III) concentration, however, were not significant ($p = 0.28$).

******FIGURE 3******

Paired t-test analysis revealed that the same patterns observed in the Oa leachate were also evident in the lower mineral soil horizons. The lowest concentrations occurred during the spring and winter, and the highest in the summer and fall. The relative proportion of Fe(II) and Fe(III) in soil solutions did not exhibit any significant ($p = 0.08$) seasonal pattern.

Relation of Iron Chemistry to Dissolved Organic Carbon and pH

Patterns in the concentration of dissolved Fe species was highly correlated with DOC and pH in soil solutions (Figure 4) and stream water (Figure 2). Within soil solutions, strong relationships existed for Fe(II) and Fe(III) with DOC. In each case the strength of the relationship increased with soil depth. For Fe(II) and DOC, the r^2 values were lowest for solution draining the Oa horizon and increased with drainage through mineral soil (Oa, $r^2 = 0.55$; Bh, $r^2 = 0.69$; Bs, $r^2 = 0.92$). The same pattern was observed for Fe(III) vs. DOC (Oa, $r^2 = 0.18$; Bh, $r^2 = 0.85$; Bs, $r^2 = 0.91$), with notably lower r^2 in the Oa horizon. The slopes of the Fe-DOC regression lines increase with soil depth for both Fe(II) and Fe(III). Concentrations of Fe were inversely correlated with pH of soil solutions and stream water (Figure 2). Note that DOC and soil solution pH are highly correlated (Fahey et al. 2005).

******FIGURE 4******

Discussion

Chemistry of Inputs to the Forest Floor: Deposition, Throughfall, Litterfall

No sampling of precipitation was undertaken for this study, but Fe inputs in bulk precipitation were available based on a 19-year record of precipitation chemistry at Hubbard Brook (1983-2001). The mean bulk deposition value during these years was 3.5 mol ha^{-1} yr^{-1} (CE Johnson, unpublished data). Smith et al. (1986) previously reported a mean flux of Fe in bulk precipitation of 8.7 mol ha^{-1} yr^{-1} for the period 1976-1985. This difference results from higher measured Fe concentrations in precipitation during the early years of that study, when Fe deposition was higher than in recent years.

Atmospheric deposition of Fe and other metals is a combination of both wet and dry deposition and is derived from a variety of natural and anthropogenic sources. Parekh and Husain (1981) characterized the anthropogenic sources of Fe and other metal deposition to rural areas of New York State, concluding that Fe deposition was largely associated with iron and steel industrial activity, as well as soil disturbance.

While the annual flux of Fe in bulk precipitation at Hubbard Brook may appear small (especially in comparison to soil pools; see below), it may serve as an important source of Fe to the canopy and forest floor. Additionally, deposition of metals in excess of natural historical levels could potentially alter soil chemistry, especially processes in the rhizosphere. Iron inputs in bulk precipitation represent about 7% of the value for soil solution draining the forest floor.

Precipitation passes through the forest canopy and is deposited on the forest floor as throughfall. The concentration of elements in throughfall compared to precipitation is determined by a series of complex processes, including incident wet deposition, evaporation, washoff of deposits in the canopy, foliar leaching, and uptake or sorption by foliage or epiphytic biota (Parker 1983). The flux of Fe in throughfall was 4.4 mol ha^{-1} yr^{-1}, about 25% higher than the flux in bulk precipitation. While the processes affecting throughfall Fe flux are complex, this difference suggests that washoff of dry deposition or foliar leaching are contributing to increased Fe as precipitation passes through the canopy.

Leaf litterfall is an important input of Fe to the forest floor. Unlike throughfall, litterfall represents Fe cycled through the ecosystem from root uptake. In the intrasystem cycle of forest ecosystems, litterfall is the dominant pathway for the return of nutrients to the soil (Schlesinger 1997).

The Fe content of leaf litterfall was estimated by measuring the concentration of Fe in fresh leaves. This value is an overestimate for litterfall if there is significant resorption of Fe during leaf senescence. Conversely, it is an underestimate if accretion of Fe in senescing leaves is taking place. Foliar Fe concentrations observed in our study were generally lower for each species than those reported by Gosz et al. (1972) for leaf litterfall at the HBEF. This difference in Fe concentration could be the result of interannual variation or indicative of accretion in senescing leaves. Killingbeck (1985) observed chinquapin oak in a gallery forest in Kansas resorbed 35% of its foliar Fe: however, he also observed that hackberry and red elm had significant accretion of Fe, while green ash and bur oak had neither significant resorption nor accretion. Tyler (2005) showed that most mineral elements, including Fe, increased in dry weight concentration during leaf senescence in European beech trees. For calculation and comparison purposes, we assumed that little change in foliar Fe content occurred during senescence.

The Fe concentrations measured in foliage for this study were similar across the species sampled (Table 1). There was no elevational pattern ($p = 0.30$) in Fe concentration for the major hardwood species. However, the lowest concentrations of Fe in foliage were found in the samples from conifers at the upper-elevation spruce-fir-birch site. Additionally, because conifer litterfall mass is lower than for deciduous forest (Fahey et al. 2005), we can infer that flux rates of Fe to soil from leaf litterfall are higher in the hardwood zones at Hubbard Brook.

Leaching of Fe(II) and Fe(III) from Leaf Litter

Following litterfall, some Fe from leaves can be leached and transported to deeper soil with percolating water. While autumnal litterfall represents a pulse flux of Fe to the forest floor, leaching from litter in the forest floor is a continual process of Fe transfer from the forest floor to the underlying soil horizons (Jones et al. 1994). Litter leachate is an initial source of dissolved Fe, as well as soluble organic compounds that can further mobilize Fe in the soil profile (Senesi et al. 1989; Senesi and Sposito 1989).

In order to obtain an estimate of the concentration of readily leachable Fe and its distribution as Fe(II) and Fe(III), litter samples were extracted with hydrochloric acid. This method was chosen because HCl can rapidly extract Fe from leaf litter, while at the same time it is not so aggressive that it would be expected to alter the ratio of Fe(II) to Fe(III). Total Fe(II) measurements of litter are impractical because complete digestion procedures would result in oxidation of Fe. The measurement of readily leachable Fe is ecologically relevant because it may approximate what can naturally be leached from fresh leaf litter.

The results of this experiment indicate that amounts of readily leachable Fe were relatively low when compared to the total Fe content of leaf litter (Table 1). The results also show that 50% or more of the Fe in litter leachate is in the reduced form (Fe(II)). Reduced Fe is the bioavailable form of Fe taken up by plants; ferric compounds are reduced prior to assimilation (Chaney et al. 1972). Consequently, it is not surprising to find large amounts of ferrous iron in vegetation. Within leaves Fe is a component of numerous enzymes and undergoes oxidation and reduction during the course of electron transport (Nason and McElroy 1963). This role may explain the nearly equal distribution between Fe(II) and Fe(III) in the leaf litter leachate.

Chemistry of Drainage Waters: Soil Solution and Stream Water

The concentrations of Fe(II), Fe(III), DOC, and hydrogen ion in soil solution decreased with depth in the soil profile at Hubbard Brook. The concentration of Fe species and DOC decreased further from the mineral soil to stream water. These results are consistent with theories of podsolization that predict translocation of Fe (and Al) from topsoil to subsoil as metal-organic complexes (e.g. de Coninck 1980; Dahlgren and Ugolini 1989). Petras (1996) quantified pools of soil Fe fractions by horizon at Hubbard Brook (Table 3). These data show that organically bound Fe pools increased with depth in the soil profile. Additionally, there was a large increase in the percentage of total Fe in organically bound forms from the E horizon to the Bh horizon (11.3% to 64.0%, Table 3). These data are consistent with long term accumulation of organically complexed Fe in the B horizons resulting from podsolization processes.

The mechanisms responsible for immobilization of Fe and Al-organic complexes are not completely understood. Numerous mechanisms for immobilization in the lower B horizons have been proposed. Sauer et al. (2007) summarized these immobilization hypotheses, many of which suggest that the downward transport of metal-organic complexes terminates when the complexes reach a condition of insolubility.

The ratios of mean DOC-to-Fe concentration decrease as solutions drain through the soil profile. This pattern holds for DOC-to-total Fe (Oa: 379, Bh: 251, Bs: 243), as well as both DOC-to-Fe(II) (Oa: 1050, Bh: 891, Bs: 874) and DOC-to-Fe(III) (Oa: 592, Bh: 349, Bs: 337). A decreasing carbon-to-metal ratio is indicative of decreasing solubility and increased immobilization in the mineral soils (McKeague et al. 1978; Schnitzer and Skinner 1963). Similarly, the slopes of the Fe-DOC regression lines (Figure 4) increase with depth in the soil profile, consistent with these podsolization theories.

******TABLE 3******

******TABLE 4******

While possible that multiple mechanisms of immobilization act concurrently, based on the data available from our study and other studies of Hubbard Brook soils, it seems likely that organic complexes gain additional Al and Fe during downward transport until precipitation is induced by the changing metal-to-carbon ratio (McKeague et al. 1978). This mechanism explains the depleted concentration of labile Fe pools in the E horizon (leaving mostly residual Fe; Table 3) and the high concentrations of organically bound Fe in the B horizons. Immobilization induced by the partial microbial breakdown of organic carrier molecules by microbes, as proposed by Boudot et al. (1989) and Lundström et al.(2000), could also result in the same horizonal patterns of reduced C:Fe in deeper soils, and the long-term accumulation of organic matter that is more recalcitrant and resistant to microbial breakdown.

Distinct landscape patterns in the concentration of Fe(II), Fe(III), DOC, and hydrogen ion were observed based on elevation (and vegetation zone) in the drainage waters of Watershed 6. The concentration of each solute was highest at the highest sampling locations (spruce-fir-birch zone) and decreased with decreasing elevation. Dissolved Fe concentrations were highly dependent on DOC concentrations. In the spruce-fir-birch zone, DOC concentrations were highest in part because of the recalcitrant nature of coniferous litter, cooler temperatures and greater soil moisture, which lead to reduced decomposition rates at higher elevation (Driscoll et al. 1988a). There is greater accumulation of organic matter with increasing elevation at Hubbard Brook, with the greatest amounts in the spruce-fir-birch zone (Gosz et al. 1976; Johnson et al. 2000). The depth of mineral soil is lowest in the spruce-fir-birch zone (Lawrence et al., 1986; Johnson et al., 2000) and consequently, there are a limited number of adsorption sites to facilitate the immobilization of DOC (and DOC-metal complexes) draining through the soil profile to stream waters (McDowell and Wood 1984; Fuller et al. 1985). The solubility of Fe was also greater in drainage waters of the spruce-fir-birch zone, due to lower pH and higher concentrations of organic acids (Driscoll et al. 1988b). The increase of soil solution and stream pH within the lower hardwood zone corresponds to an increase of base cation inputs due to percolation of soil water through deeper mineral soils at lower elevations, where neutralization occurs via weathering and cation exchange (and declining concentrations of DOC) (Johnson et al. 1981).

The seasonal patterns of Fe and DOC concentrations were most clearly expressed in the soil solution draining the Oa horizon. The highest Fe(II) and DOC concentrations were found during the summer and fall months, with lower values during the winter and spring. The observed seasonal pattern is likely due to enhanced decomposition of organic matter (and therefore DOC production) associated with higher temperatures and greater microbial activity during the summer months, as well as the inputs of fresh litter during the fall (Campbell et al. 2000; Dittman et al. 2007). The Fe(II) in soil solution likely exists as organic-Fe complexes and therefore would follow a similar seasonal pattern to DOC.

The patterns were less evident and not statistically significant in the mineral soil horizons perhaps because of the capacity of the mineral soil to "buffer" the concentration of DOC (McDowell and Wood 1984). The adsorption of DOC to mineral compounds modulates the concentration of solution transported through the deeper soil. The concentrations of Fe species in stream water were relatively low throughout the year and the lower reaches showed no discernable seasonal patterns, likely for the same reasons as mentioned above with regard to the mineral soil. The stream water chemistry from the upper reaches of the watershed exhibited a seasonal pattern similar to the soil solution in the spruce-fir-birch zone. These seasonal patterns support the contention that stream water in the upper elevation sites is derived from shallow flowpaths (Lawrence et al. 1986).

Relation of Iron Chemistry to Dissolved Organic Carbon, pH, and Dissolved Oxygen

The concentrations of Fe(II), Fe(III), and DOC all showed similar patterns in soil solution and stream water. These patterns suggest that dissolved Fe species exist primarily as organic-Fe complexes. It is unlikely that elevated concentrations of Fe species would occur in the absence of organic ligands. The solubility of Fe(III) is very low in the absence of organic ligands and Fe(II) is not stable under oxidizing conditions (Sunda 2000). Both oxidized and reduced Fe were strongly correlated with DOC in soil solution and the strength of the regression relationships increased with depth in the soil profile. This may be due to the higher variability of DOC concentrations in solution draining the Oa horizon compared to the Bh and Bs horizons, as well as an increasing availability of Fe for complexation with depth in mineral soils.

As with DOC, there was a strong relationship between the concentration of Fe species and pH which strengthened with depth in the soil profile. The patterns of pH and DOC were similar because much of the free acidity results from the dissociation of organic acids. It is not clear if the relationship of concentrations of Fe species with pH was a pH effect or a manifestation of the correlative relationship between pH and DOC.

Qualitative field measurements of dissolved oxygen in soil solutions were taken to determine whether oxygen concentrations were controlling oxidation-reduction chemistry and the distribution between Fe(II) and Fe(III) in soil solutions. These values ranged from nearly completely depleted (~0.1 mg L^{-1}) to completely saturated with oxygen (~9 mg L^{-1}). The lowest dissolved oxygen concentrations were observed during the summer and fall months, when microbial activity is highest (Groffman et al. 2001). The lowest concentrations were frequently found in the Oa horizon and increased with increasing depth in the soil profile. This pattern matches the negative correlation of dissolved oxygen concentrations with DOC in samples during the summer and fall months

Although dissolved oxygen concentrations in soil solutions were low at times, this condition did not appear to promote widespread reduction of soil Fe(III). Interestingly, we found that the Fe(II)-to-Fe(III) ratio did not fluctuate significantly with variations in DO concentrations. The soils of Hubbard Brook are generally considered to be well-drained and it might be expected that DO concentrations are consistently high. Yet we consistently found that a significant fraction of total Fe was in the reduced form, and this fraction was not related to the concentrations of DO. If microbial reduction of Fe was a significant process, concentrations of Fe(II) would be expected to be several orders of magnitude higher, as in wetland pore waters (Thompson et al. 2009). Highly elevated Fe(II) concentrations, indicating reducing conditions (accompanied by odors of reduced sulfur compounds and lower sulfate concentrations) were observed only in a few isolated instances during our study (e.g., W1 high hardwood Oa horizon during summer and fall months). While the water table level fluctuates temporally at Hubbard Brook, it may not be elevated for sufficiently long periods to promote high rates of Fe reduction. Additionally, oxygen depletion associated with elevated groundwater would need to coincide with conditions of high microbial activity, including warm temperatures and availability of labile carbon sources. Rochette and Cleary (2004) found evidence for Fe reduction in a New Hampshire Aquod (wet Spodosol) that was seasonally saturated (during the spring). It is possible that we underestimate the importance of Fe reduction due to the monthly sampling design.

The concentration of Fe species appears to be much more strongly influenced by DOC concentrations than by dissolved oxygen concentrations, suggesting that Fe(II) is stabilized in solution and is resistant to oxidation. The most likely mechanism for this pattern is stabilization as an organic-Fe(II) complex. Kieber et al. (2001) found that Fe(II) accounted for more than 80% of total dissolved Fe in rainwater collected in coastal areas of North Carolina and New Zealand. They suggested organic ligands stabilized Fe(II) against oxidation and found that this effect was eliminated when organic molecules were degraded upon exposure to high-intensity ultraviolet (UV) radiation. Willey et al. (2008) found a class of Fe(II)-binding ligands comparable in strength to the ferrozine complex in the hydrophobic fraction of dissolved organic matter of rainwater. These compounds stabilized Fe(II) in highly oxidizing marine surface waters for more than 4 hr. It seems likely that organic complexes in Hubbard Brook drainage waters can stabilize Fe(II), greatly attenuating oxidation kinetics.

Ecosystem Fluxes

Mass balance calculations for Fe at Hubbard Brook showed that the forest ecosystem exhibited net retention of Fe (stream export of Fe is lower than input from bulk precipitation; 1.8

and 3.5 mol ha^{-1} yr^{-1}, respectively). Moreover, Watershed 6 had relatively small fluxes of Fe to the forest floor, higher fluxes draining the forest floor through the soil profile, and lower fluxes again in stream water (Figure 5). Fluxes of Fe(II) and Fe(III) were calculated separately, except for bulk precipitation, throughfall, and total litterfall, for which the distribution between Fe(II) and Fe(III) was not available.

******FIGURE 5******

There was a substantial increase in Fe transport in soil solutions relative to bulk precipitation, throughfall, and litterfall. Bulk precipitation and litterfall fluxes were similarly small (3.5 and 3.4 mol ha^{-1} yr^{-1}, respectively). Throughfall flux (4.4 mol ha^{-1} yr^{-1}) was only marginally higher than these inputs. Net throughfall flux (total throughfall – bulk precipitation) was 0.9 mol ha^{-1} yr^{-1}.

The value for stream export of Fe reported here (1.8 mol ha^{-1} yr^{-1}) is lower than the dissolved Fe flux reported by Smith et al. (1986) (7.3 ± 4.0 mol ha^{-1} yr^{-1}, mean ± standard deviation). Smith et al. (1986) also found that an additional 3.2 ± 2.5 mol ha^{-1} yr^{-1} (mean ± standard deviation) of Fe was exported as course particulate matter rather than in dissolved form. Most of this elevated particulate flux is derived from the stream channel. We did not measure particulate matter for this study, and consequently, our Fe export should be considered an underestimate of total Fe export from the watershed.

The fluxes in soil solution were markedly higher than inputs to the forest floor and decreased with depth in the soil (Oa = 52.5 mol ha^{-1} yr^{-1}, Bh = 50.5 mol ha^{-1} yr^{-1}, Bs = 19.7 mol ha^{-1} yr^{-1}; Figure 5). The fluxes of Fe(II) and Fe(III) through the soil profile (Table 5) were similar to the horizonal patterns observed in Fe concentrations (Table 2). These fluxes are consistent with podsolization theory, which predicts translocation of Fe from the forest floor to mineral soil.

For both Fe(II) and Fe(III), the fluxes were highest draining the Oa horizon and decreased with depth in the mineral soil and stream water. The flux of Fe(II) in soil solution draining the Oa horizon (14.4 mol ha^{-1} yr^{-1}) was considerably larger than the total amount of Fe in litterfall (3.4 mol ha^{-1} yr^{-1}), and therefore is much larger than the annual flux of Fe(II) in litter leachate. This pattern indicates that the forest floor serves as a net source of Fe(II) to soil solution resulting from Fe(II) release during decomposition of additional organic matter and/or reduction of soil Fe(III) compounds. Fine root turnover provides a flux of 7.2 mol Fe ha^{-1} yr^{-1} (TJ Fahey, unpublished data). Reduction of Fe(III) is known to occur in the rhizosphere (Pinton et al. 2007; Fimmen et al. 2008). Decomposition of fine roots, as well as exudates from live roots could contribute to the reduction of soil Fe(III) and the supply of Fe(II) to soil solution. The abiotic reduction of Fe(III) (hydr)oxides by dissolved organic matter has been demonstrated with Spodosol organic horizon extracts (Buerge and Hug 1998), and with forest floor leachates of both hardwood and conifer forests (Chorover and Amistadi 2001). Chemical reduction of Fe(III) by dissolved organic matter could explain the portion of the Fe(II) flux in soil solution not accounted for by known sources of Fe(II), such as leaching of litter or decomposition of fine roots.

******TABLE 5******

The same general pattern of decreasing Fe fluxes with increasing soil depth occurred for each of the elevation zones with the exception of the high elevation hardwood zone (Table 5). In this subcatchment, the flux of Fe (especially Fe(III)) from the Oa horizon was markedly less than from the Bh horizon. The fluxes of Fe(II) and Fe(III) decreased with decreasing elevation also with the exception of the Oa horizon in the high elevation hardwood zone.

The fluxes of dissolved Fe through the soil profile are low when compared to the soil pools of total Fe or soluble + exchangeable Fe (Figure 5, Table 3). Based on the mean annual fluxes of Fe draining soil horizons, the average turnover time for soil Fe increases substantially with depth in the soil profile (for total soil Fe: Oa = 74.3 yr, E+Bh = 3010 yr, and Bs = 73,600 yr; for soluble + exchangeable: Oa = 0.84 yr, E+Bh = 12.9 yr, and Bs = 33.5 yr). The soluble + exchangeable Fe fractions in bulk soil represent much larger percentages of total soil Fe in the upper horizons (Oa: 1.1%, E+Bh: 0.43%, and Bs: 0.05%).

Conclusions

Several conclusions can be drawn from this study:

1. Iron dynamics were closely coupled with DOC and pH (as a result of organic acid dissociation) in soil solution and stream water. Iron concentrations follow the horizonal, elevational, and temporal patterns of DOC concentrations in the drainage waters of forested watersheds at Hubbard Brook. Concentrations were highest in solutions draining the organic soil horizons and decreased with depth in the soil profile. Higher concentrations were found in the upper reach of the watersheds in the spruce-fir-birch zone where temperatures are cooler and decomposition of organic matter is slower. Concentrations of Fe species decreased with decreasing elevation. Iron concentrations in Oa soil solutions were highest during the summer and fall months, when DOC concentrations were highest due to enhanced microbial activity and input from leaf litter.
2. The forest floor was a net source of Fe to the soil solution. Iron fluxes in solution draining the Oa horizon exceeded inputs (throughfall + litterfall) to the forest floor.

3. A large portion of total Fe fluxes in soils was in the form of Fe(II) relative to what may be expected in well-drained soils. The persistence of Fe(II) in solution, even when dissolved oxygen concentration were high, may be the result of stabilization as organic-Fe(II) complexes.
4. Ferrous iron was derived from decomposition and leaching leaf litter. Annual fluxes of Fe(II) from the Oa horizon exceeded the maximum possible contribution of litterfall. This indicates that Fe(II) was mobilized as soil Fe minerals were reduced (likely in the rhizosphere) and/or during decomposition of other organic materials.
5. Patterns of Fe dynamics in forest soil at Hubbard Brook are consistent with podsolization theories. Fe fluxes decreased with depth in the soil profile, indicating the translocation of Fe from the forest floor to mineral soil.

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Figure Captions

Figure 1. Hubbard Brook experimental watersheds with sampling sites indicated.

Figure 2. Elevational patterns of total Fe and DOC concentrations and pH for Watershed 6 stream water. Shown are mean values and standard errors. Vertical dotted lines indicate approximate vegetation zone transitions.

Figure 3. Seasonal mean concentrations of DOC, Fe(II), and Fe(III) in soil solution by soil horizon. Standard errors are represented by vertical bars.

Figure 4. Relationship of DOC with: a) Fe(II) and b) Fe(III) in soil solution by soil horizon.

Figure 5. Annual fluxes of dissolved Fe and soil Fe pools at Hubbard Brook. Flux calculations were based on Watershed 6 data. Soil pools are from Watershed 5 data (Petras 1996).

Table 1. Fe concentrations of litter (foliage) and litter leachate for the three major hardwood species.

	Total Fe ($\mu g\ g^{-1}$)	Leachable Fe ($\mu g\ g^{-1}$)	Leachable Fe (% of total Fe)	Leachable Fe(II) ($\mu g\ g^{-1}$)	Leachable Fe(III) ($\mu g\ g^{-1}$)
Sugar Maple	49.2	8.6	18	4.6	4.0
Yellow Birch	58.0	13.7	24	7.2	6.5
American Beech	48.0	12.2	25	7.1	5.0

Table 2. Mean concentrations of Fe(II), Fe(III), DOC and the pH for soil solutions of Watershed 6 by elevation zone and soil horizon. Values in parentheses represent standard deviations.

		Fe(II) ($\mu mol\ L^{-1}$)	Fe(III) ($\mu mol\ L^{-1}$)	Fe(II) (%)	DOC ($\mu mol\ L^{-1}$)	pH	n
Low Hardwood	Oa	0.9 (0.5)	2.9 (1.8)	23	860 (93)	4.34	21
	Bh	0.5 (0.2)	2.4 (1.8)	16	480 (220)	4.85	22
	Bs	0.1 (0.1)	0.2 (0.4)	39	220 (21)	4.91	23
High Hardwood	Oa	0.5 (0.1)	0.7 (0.2)	44	800 (270)	4.21	18
	Bh	0.9 (0.3)	4.8 (1.4)	16	1350 (54)	4.41	11
	Bs	0.3 (0.3)	1.2 (1.7)	22	390 (200)	4.64	16
Spruce-Fir-Birch	Oa	2.1 (0.5)	6.0 (4.7)	26	1640 (780)	4.09	19
	Bh	2.2 (0.8)	6.0 (1.0)	27	1360 (77)	4.23	18
	Bs	1.5 (0.5)	3.9 (2.5)	27	860 (190)	4.52	16

Table 3. Pools of soil Fe fractions at Hubbard Brook (modified from Petras (1996)).

Horizon	Fe fraction	Pool (mol ha^{-1})	Percent of total Fe
Oa	Soluble + exchangeable	44	1
	Inorganically bound	3	0
	Organically bound	1600	41
	Amorphous-oxide-bound	190	5
	Residual	2000	51
	Total	3900	100
E	Soluble + exchangeable	140	0
	Inorganically bound	38	0
	Organically bound	5900	11
	Amorphous-oxide-bound	200	0
	Residual	46,000	89
	Total	52,000	100
Bh	Soluble + exchangeable	510	1
	Inorganically bound	190	0
	Organically bound	64,000	64
	Amorphous-oxide-bound	1400	1
	Residual	37,000	37
	Total	100,000	100
Bs1	Soluble + exchangeable	480	0
	Inorganically bound	500	0
	Organically bound	76,000	51
	Amorphous-oxide-bound	15,000	10
	Residual	61,000	41
	Total	150,000	100
Bs2	Soluble + exchangeable	180	0
	Inorganically bound	560	0
	Organically bound	220,000	17
	Amorphous-oxide-bound	64,000	5
	Residual	1,000,000	77
	Total	1,300,000	100

Table 4. Summary of mean concentrations of DOC, Fe(total), Fe(II), and Fe(III). Standard deviations are indicated in parentheses.

Horizon	DOC (μmol C L^{-1})	Fe(total) (μmol L^{-1})	Fe(II) (μmol L^{-1})	Fe(III) (μmol L^{-1})
Oa	1530 (1200)	4.0 (3.6)	1.5 (1.1)	2.6 (2.7)
Bh	730 (530)	2.9 (2.7)	0.8 (0.7)	2.1 (2.3)
Bs	510 (650)	2.1 (4.2)	0.6 (1.0)	1.5 (3.2)

Table 5. Annual fluxes of Fe(II) and Fe(III) for drainage waters in Watershed 6.

Elevation zone	Horizon	Fe(II) flux (mol ha^{-1} yr^{-1})	Fe(III) flux (mol ha^{-1} yr^{-1})
Spruce-Fir-Birch	Oa	28.7	77.3
	Bh	27.8	56.2
	Bs	22.8	41.2
	Stream	20.5	44.0
High Hardwood	Oa	8.5	10.7
	Bh	12.4	59.7
	Bs	5.2	12.9
	Stream	4.0	3.8
Low Hardwood	Oa	12.3	38.8
	Bh	5.0	19.2
	Bs	1.6	1.3
	Stream	0.3	1.5
Watershed 6 Total	Oa	14.4	38.1
	Bh	11.8	38.8
	Bs	6.9	12.8
	Stream	0.3	1.5

Figure 1.

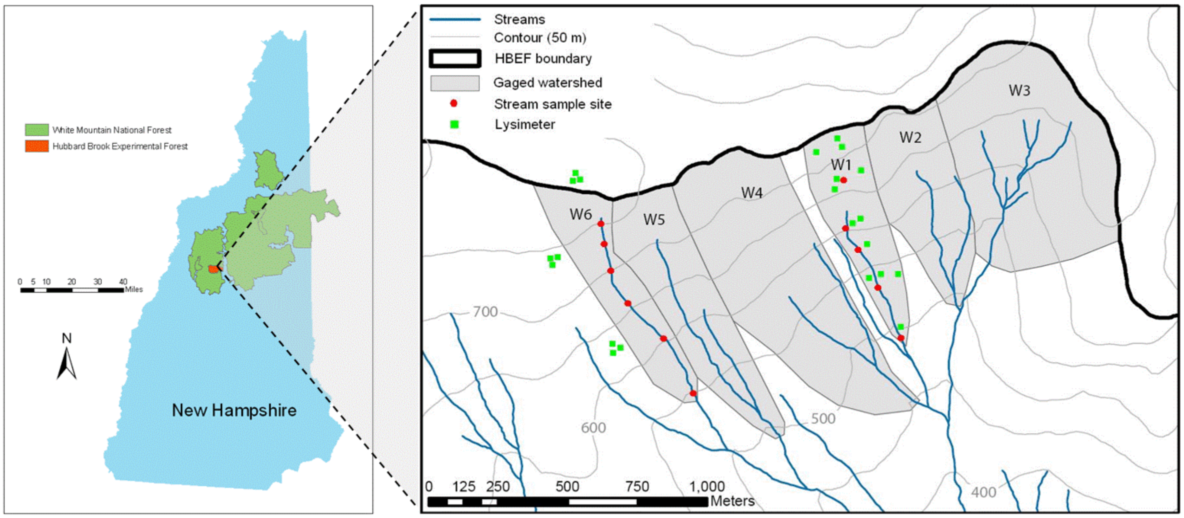

White Mountain National Forest
Hubbard Brook Experimental Forest
0 5 10 20 30 40 Miles
N
New Hampshire
Streams
Contour (50 m)
HBEF boundary
Gaged watershed
Stream sample site
Lysimeter
W1
W2
W3
W4
W5
W6
700
600
500
400
0 125 250 500 750 1,000 Meters

Figure 2.

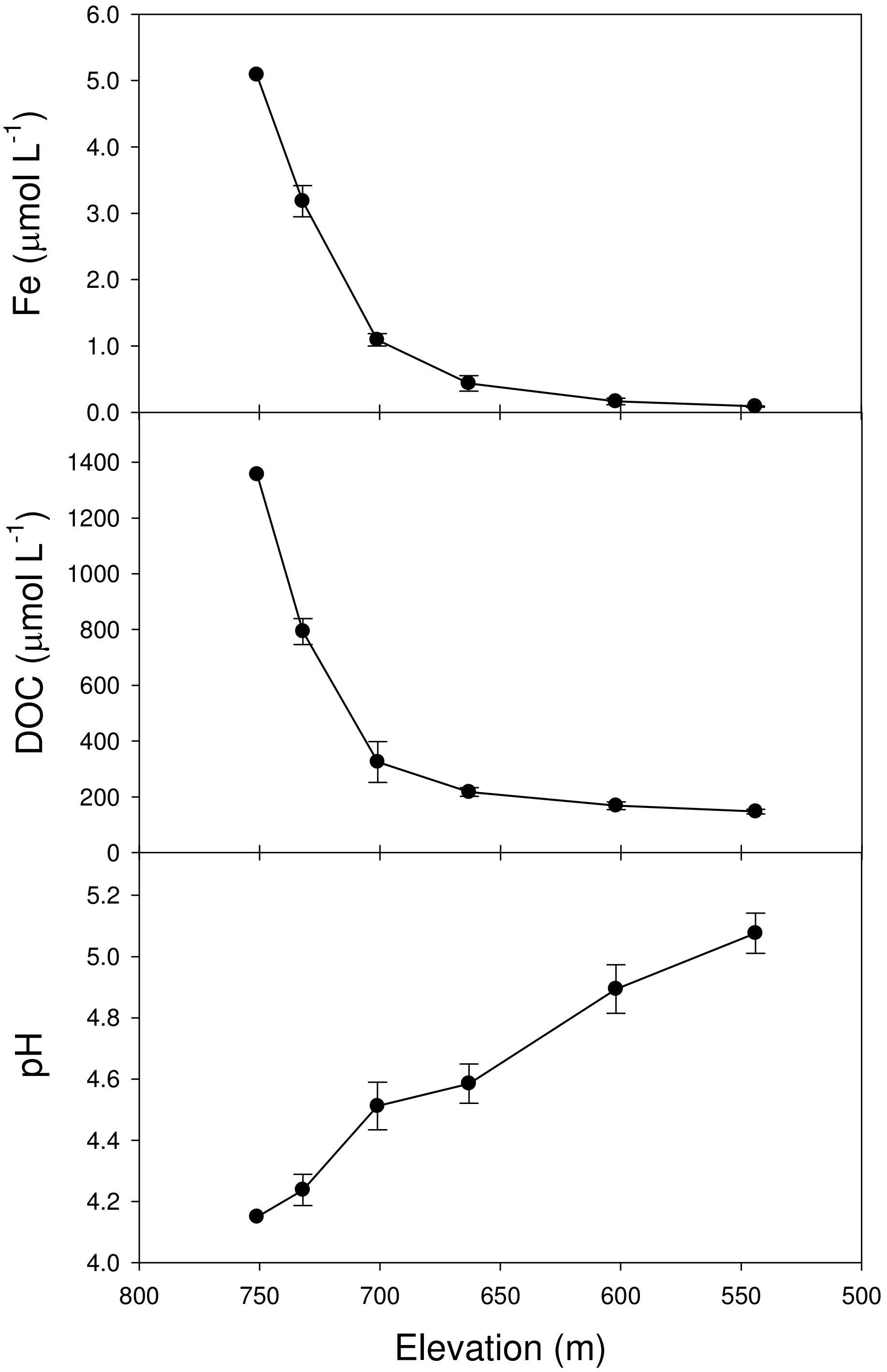

Fe (μmol L^{-1})
6.0
5.0
4.0
3.0
2.0
1.0
0.0
DOC (μmol L^{-1})
1400
1200
1000
800
600
400
200
0
pH
5.2
5.0
4.8
4.6
4.4
4.2
4.0
800
750
700
650
600
550
500
Elevation (m)

Figure 3.

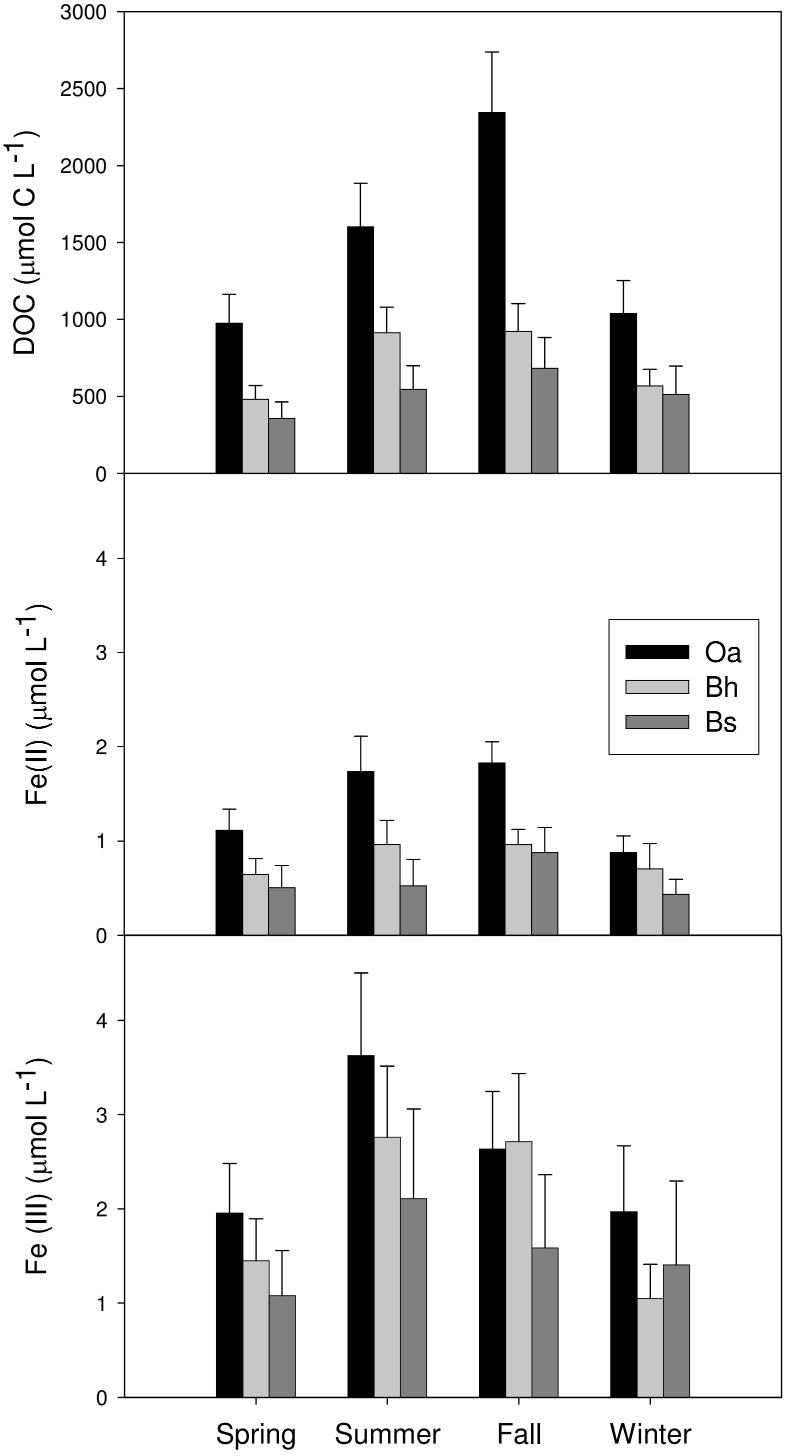

DOC (μmol C L-1)
3000
2500
2000
1500
1000
500
0
Fe(II) (μmol L-1)
4
3
2
1
0
Oa
Bh
Bs
Fe (III) (μmol L-1)
4
3
2
1
0
Spring
Summer
Fall
Winter

Figure 4.

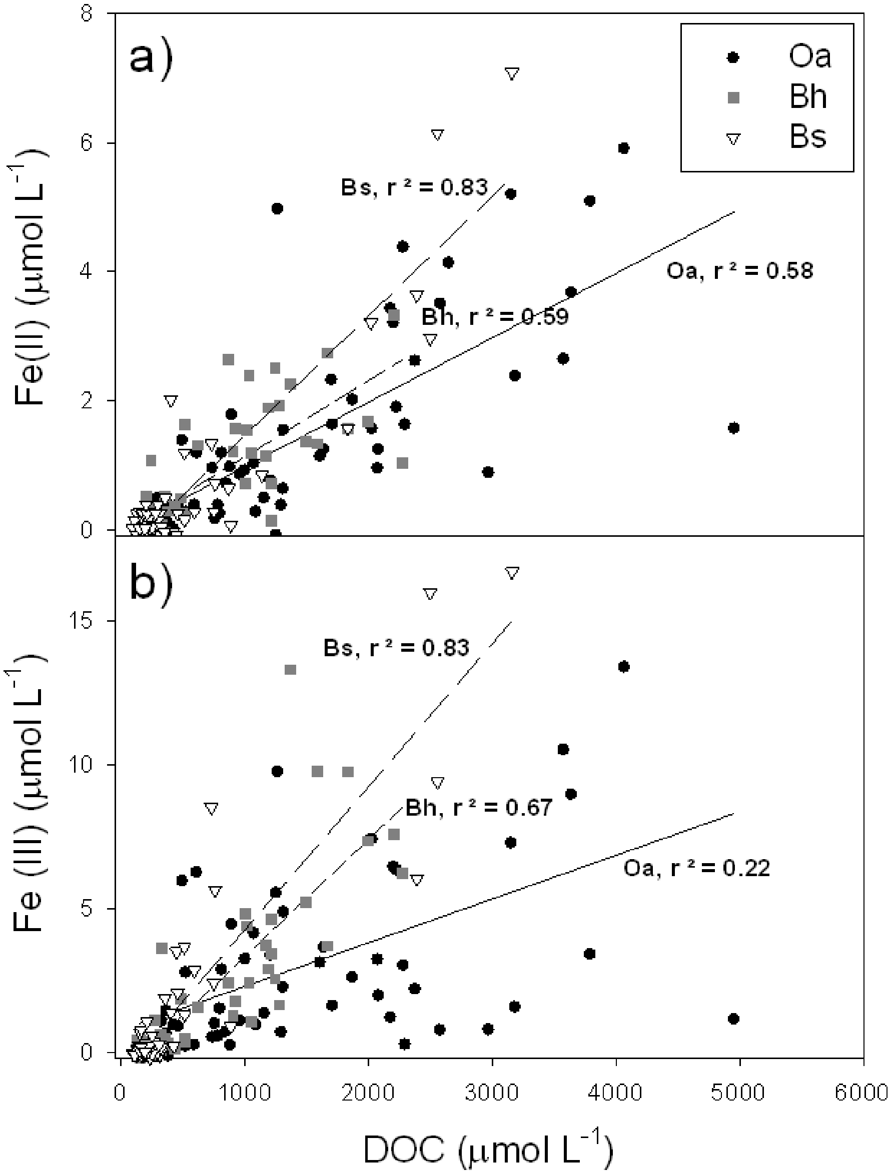
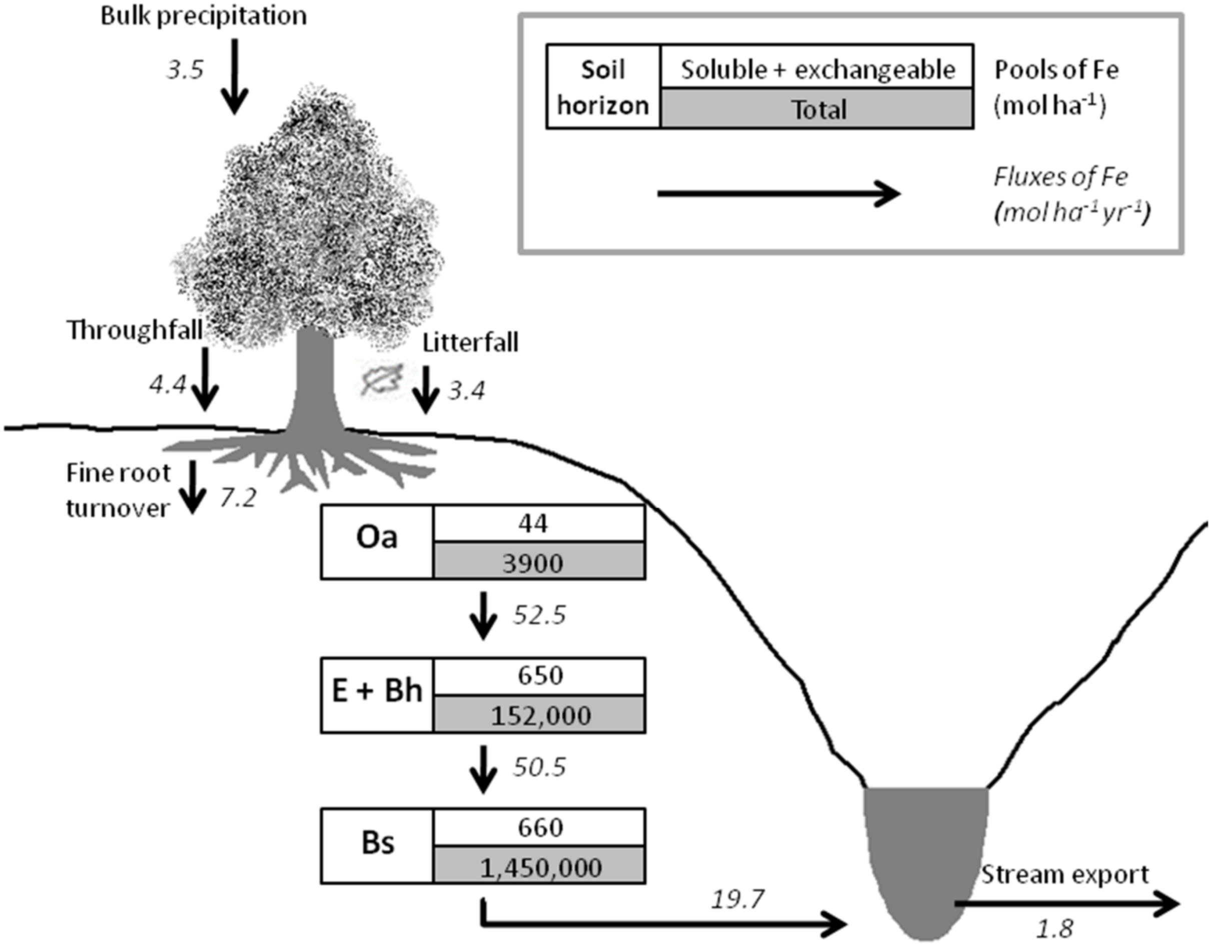

a)
b)
Oa
Bh
Bs
Bs, r² = 0.83
Bh, r² = 0.59
Oa, r² = 0.58
Bs, r² = 0.83
Bh, r² = 0.67
Oa, r² = 0.22
Fe(II) (µmol L⁻¹)
Fe (III) (µmol L⁻¹)
DOC (µmol L⁻¹)
0
2
4
6
8
0
5
10
15
0
1000
2000
3000
4000
5000
6000

Figure 5.


Bulk precipitation
3.5
Soil horizon
Soluble + exchangeable
Total
Pools of Fe (mol ha^{-1})
Fluxes of Fe (mol ha^{-1} yr^{-1})
Throughfall
4.4
Litterfall
3.4
Fine root turnover
7.2
Oa
44
3900
52.5
E + Bh
650
152,000
50.5
Bs
660
1,450,000
19.7
Stream export
1.8