Substrate age and tree islands influence carbon and nitrogen dynamics across a retrogressive semiarid chronosequence

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Received 15 July 2007; revised 17 October 2007; accepted 5 November 2007; published 1 March 2008.

[1] The long-term dynamics of carbon (C) and nitrogen (N) in semiarid ecosystems remain poorly understood. We measured pools and fluxes of surface soil C and N, as well as other soil properties, under tree canopies and in intercanopy spaces at four sites that form a volcanic substrate age gradient in semiarid piñon-juniper woodlands of northern Arizona, United States. Clay content and soil water-holding capacity increased consistently with substrate age, but both soil organic C and N increased only up to the 750,000 year site and then declined at the oldest (3,000,000 year) site. Measures of soil C and N flux displayed a similar pattern to total C and N pools. Pools and fluxes of C and N among the three canopy types became more homogeneous with substrate age up to the 750,000 year site, but disparity between tree and intercanopy microsites widened again at the oldest site. The δ^{15}N of both tree leaves and surface soils became progressively more enriched across the substrate age gradient, consistent with a N cycle increasingly dominated by isotope fractionating losses. Our results point to consistencies in patterns of ecosystem development between semiarid and more humid ecosystems and suggest that pedogenic development may be an important factor controlling the spatial distribution of soil resources in semiarid ecosystems. These data should help both unify and broaden current theory of terrestrial ecosystem development.

Citation: Selmants, P. C., and S. C. Hart (2008), Substrate age and tree islands influence carbon and nitrogen dynamics across a retrogressive semiarid chronosequence, *Global Biogeochem. Cycles*, *22*, GB1021, doi:10.1029/2007GB003062.

1. Introduction

[2] A general pattern during the long-term development of humid ecosystems is a progressive increase in pool sizes and flux rates of soil organic carbon (C) and nitrogen (N) during early to midstages of pedogenesis. This progressive phase is often followed by a decline or regressive phase, characterized by significant reductions in storage and cycling rates of ecosystem C and N on older, more highly weathered substrates [*Stevens and Walker*, 1970; *Syers et al.*, 1970; *Westman*, 1975; *Robertson and Vitousek*, 1981; *Sollins et al.*, 1983; *Chapin et al.*, 1994; *Hobbie et al.*, 1998; *Crews et al.*, 1995; *Riley and Vitousek*, 1995; *Torn et al.*, 1997; *Lilienfein et al.*, 2003]. Although this transition from progressive to decline phase during pedogenesis appears to be fairly robust in humid ecosystems [*Wardle et al.*, 2004], the long-term dynamics of soil organic C and N in more water-limited systems are less well understood [*Austin et al.*, 2004].

[3] Precipitation and evapotranspiration are critical determinants of the rate and trajectory of pedogenesis [*Chadwick and Chorover*, 2001]. Thus the factors controlling C and N dynamics during long-term soil and ecosystem development in arid and semiarid climates may be fundamentally different than those in more humid climates. For example, weathering of coarse fragments into finer, clay-sized particles during pedogenesis in semiarid climates should increase water-holding capacity and plant-available water storage [*Hook and Burke*, 2000], leading to concomitant increases in net primary productivity and rates of soil C and N cycling [*Foster*, 1988; *Austin et al.*, 2004]. Such increases in soil water availability are relatively less important during the development of humid ecosystems, where precipitation exceeds potential evapotranspiration during most of the year [*Waring and Running*, 2007]. Patchy distribution of vegetation may also be an important factor regulating the development of arid and semiarid ecosystems. Soil organic C and N tend to be concentrated under large shrub or tree canopies in more arid ecosystems, resulting in the well-documented ''islands of fertility'' [*Charley and West*, 1975; *Burke*, 1989; *Schlesinger et al.*, 1996; *Aguiar and Sala*, 1999]. In contrast, humid ecosystems have more continuous vegetation cover and a relatively homogeneous distribution of soil organic matter and nutrients [*Waring and Running*, 2007]. What remains unclear is whether long-term pedogenic change might drive a systematic shift in the degree of soil resource heterogeneity in semiarid ecosystems, such that younger, poorly developed soils might have a more discontinuous distribution of soil organic C and N than older, more highly weathered soils.

[4] It has been suggested that a shift from N to phosphorus (P) limitation initiates the decline phase common to

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0886-6236/08/2007GB003062

Table 1. Age, Location, Elevation, Climate, and Soil Classification of the Four Sites Along the San Francisco Volcanic Field (SFVF) Substrate Age Gradient, Northern Arizona, United States

Site	Age,[a] 10^3 years	Location, Latitude, Longitude	Elevation, m	MAP,[b] mm	MAT,[b] °C	PET,[b] mm a^{-1}	USDA Soil Classification[c]
Sunset Crater	1	35.394°N, 111.424°W	1905	328 (42)	12 (0.2)	1325 (30)	Typic Ustorthent
O'Neill Crater	55	35.246°N, 111.459°W	1941	352 (39)	11 (0.3)	1328 (25)	Typic Durustand
Red Mountain	750	35.538°N, 111.867°W	2073	325 (42)	11 (0.2)	1334 (27)	Typic Argiustoll
Cedar Mountain	3,000	35.391°N, 112.141°W	2003	338 (40)	11 (0.2)	1324 (30)	Typic Haplustalf

[a]From *Moore and Wolfe* [1987] and *Wolfe et al.* [1987].
[b]Mean with standard error in parentheses, 2002–2005, data from *Selmants* [2007]. MAP = mean annual precipitation, MAT = mean annual air temperature, and PET = potential evapotranspiration.
[c]Soil taxonomic subgroups; from *Miller et al.* [1995].

humid ecosystems in the latter stages of pedogenesis [*Walker and Syers*, 1976; *Vitousek and Farrington*, 1997; *Richardson et al.*, 2004]. If so, N should behave as an excess nutrient late in ecosystem development, leading to greater losses of N from the system. Moreover, N loss during the decline phase should predominately be in the form of leached nitrate and trace gas fluxes driven by nitrification and denitrification, pathways that leave N remaining within the system enriched in ^{15}N [*Martinelli et al.*, 1999]. Pulse precipitation events and frequent drying-rewetting cycles in semiarid ecosystems make it difficult to estimate rates of N cycling and loss on decadal or even annual timescales [*Austin et al.*, 2004]. However, the N stable isotopic composition of plant foliage and soil organic matter can be used as time-integrated measures of controls on N storage and loss [*Robinson*, 2001; *Amundson et al.*, 2003]. If N shifts from a limiting to an excess nutrient during the long-term development of semiarid ecosystems, both tree foliage and surface soils should become more enriched in ^{15}N as the N cycle becomes increasingly dominated by isotope fractionating losses [*Martinelli et al.*, 1999; *Brenner et al.*, 2001; *Amundson et al.*, 2003].

[5] Here we report patterns of surface soil C and N dynamics in four semiarid woodland sites with soils derived from basaltic cinders ranging in age from 930 to ~3,000,000 years. By controlling for the effects of parent material, current climate, topography, and dominant vegetation [*Jenny*, 1941], we used this substrate age gradient as a model system to isolate the influence of substrate age on C and N dynamics under semiarid conditions. Specifically, our study was designed to address three fundamental research questions: (1) Do pools and fluxes of surface soil C and N follow the pattern of an initial progressive phase followed by a decline common to the development of humid ecosystems? (2) How do tree islands influence surface soil C and N dynamics at different stages of soil development? and (3) Are there fundamental shifts in how N cycles through these semiarid woodlands at different stages of soil development as indicated by $\delta^{15}N$ signatures of surface soils and tree foliage?

2. Methods

2.1. Study Sites

[6] This study was conducted within the San Francisco Volcanic Field (SFVF), which covers an area of ~5000 km^2 along the southwestern edge of the Colorado Plateau in northern Arizona, United States [*Duffield*, 1997; *Priest et al.*, 2001]. Since its formation during the late Miocene, volcanic activity within the SFVF has migrated in a generally east-northeast direction at a rate of ~2 cm a^{-1} due to the westward movement of the North American Plate over a stationary magma source [*Tanaka et al.*, 1986; *Priest et al.*, 2002]. This migration of volcanism has resulted in >600 volcanic vents, most of which are monogenetic basaltic cinder cones, ranging in age from ~6,000,000 years at the southwestern edge of the field to <1,000 years along the northeastern edge [*Tanaka et al.*, 1986; *Priest et al.*, 2001].

[7] We selected four sites within the SFVF that differ markedly in the age of their underlying substrate, from 930, through to 55,000, 750,000, and 3,000,000 years (Table 1 and Figure 1). Dates for the older three sites are derived from extensive K-Ar dating and paleomagnetic surveys within the SFVF [*Moore and Wolfe*, 1987; *Wolfe et al.*, 1987]. The youngest site has been dated through a combination of dendrochronological and paleomagnetic data [*Holm*, 1987]. The four sites are all within 60 km of each other (Figure 1) and are similar in elevation and current climate (Table 1). Mean annual temperature is ~11°C, and annual precipitation is ~340 mm, half of which falls as snow and the other half as rain during sporadic convective thunderstorms in late summer [*Sheppard et al.*, 2002]. The substrate (i.e., parent material) is volcanic cinders, consisting primarily of microporphyritic basalt deposited as a pyroclastic sheet [*Moore and Wolfe*, 1987; *Wolfe et al.*, 1987]. In an attempt to minimize the influence of erosion and deposition, all four sites are on stable topographic positions with minimal slope (<1%). The 930 year site and the 750,000 year site are on flat portions of gently sloping ridges, while the 55,000 and 3,000,000 year sites are on flat lowlands. All sites are fully exposed to prevailing southwesterly winds. Each site is characterized by an open woodland vegetation type with two codominant tree species: piñon pine (*Pinus edulis*) and one-seed juniper (*Juniperus monosperma*). Intercanopy vegetation at the three older sites is dominated by the C_4 grass species *Bouteloua gracilis*. Intercanopy spaces at the youngest site, Sunset Crater, are sparsely vegetated with woody shrubs (primarily *Fallugia paradoxa* and *Rhus trilobata*), but graminoids are largely absent. Aside from rare individuals in the genera *Oxytropis* and *Lupinus* present at the two oldest sites, plant species capable of forming symbioses with N-fixing bacteria are absent from the four substrate age gradient sites.

[8] Within an approximately 1.5 ha area at each of the four sites we selected eight piñon pines, eight one-seed junipers, and eight intercanopy spaces to assess the influence of tree

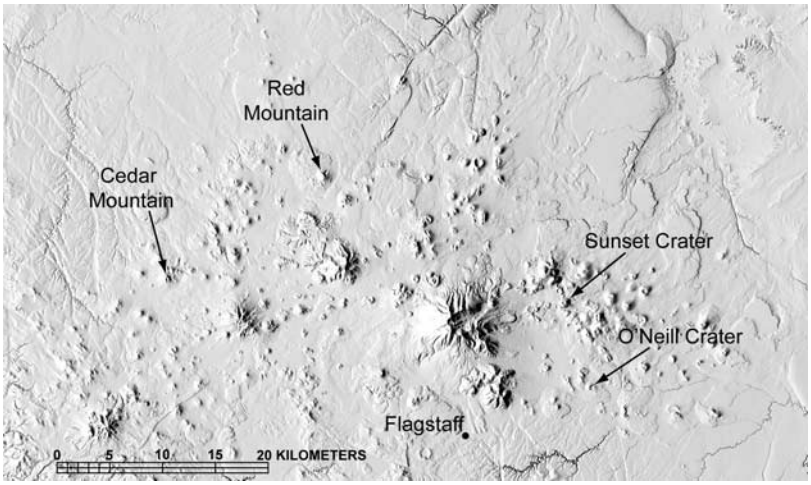

Figure 1. Location of the four study sites within the San Francisco volcanic field (SFVF) in northern Arizona, United States. Image courtesy of the United States Geological Survey, Flagstaff, Arizona, United States.

islands on surface soil C and N dynamics at different stages of soil development. We selected study trees of similar size at all four sites: between 4.5 and 5.0 m tall, a canopy diameter of ~5 m and basal stem diameter ranging from 25 to 35 cm. We selected intercanopy spaces at each site that were a minimum of 10 m in diameter.

[9] We do not assume that soils at each site have developed under identical conditions. Like any soil chronosequence, older sites have been subjected to wider climatic variations and have been occupied by a broader array of plant communities through time [*Chadwick et al.*, 1999; *Wardle et al.*, 2004]. Nevertheless, a common substrate has been exposed to environmental and biological influences for substantially different lengths of time across this natural substrate age gradient. Our study seeks only to relate C and N dynamics under the present climatic regime in soils at different stages of development.

2.2. Surface Soil Organic C, N, and δ^{15}N

[10] Surface (0–15 cm) mineral soil samples collected in August 2004 from the three canopy microsites (piñon pine, one-seed juniper, and intercanopy spaces) at each of the four sites were analyzed for soil organic C, soil total N, and δ^{15}N. Each individual soil sample was a composite of six subsamples collected with a 2-cm diameter Oakfield soil sampler (Oakfield Apparatus, Incorporated, Oakfield, Wisconsin, United States) taken from around the circumference of each study tree (midway between the trunk and the dripline) or around the plot center of each intercanopy space. All soil samples were sieved to <2 mm and allowed to air dry. A portion of each sample was then oven dried at 105°C for 48 h, finely ground, and analyzed for C and N concentration and ^{15}N enrichment at the Colorado Plateau Stable Isotope Laboratory (http://www.mpcer.nau.edu/isotopelab). We did not pretreat samples with acid to remove inorganic C because, although pedogenic carbonate is present at depth (>30 cm), there is no inorganic C in surface (0–15 cm) soils at any of the four sites [*Cheevers*, 1982; *Holzschuh*, 2004]. We confirmed this by testing a portion of each surface soil sample ($n = 96$) for the presence of pedogenic carbonate with 6 M HCl as described by *Nelson and Sommers* [1982]. Results were negative in all cases, so we are confident that total C in our soil samples is equivalent to organic C.

2.3. Laboratory Incubations of Soil C and N Transformations

[11] Surface soil samples collected in August 2004 were also analyzed for net N mineralization and microbial respiration during a 28-d laboratory incubation conducted under aerobic conditions. Two ~10 g (oven-dry equivalent) subsamples from each composite soil sample were adjusted to −33 kPa matric potential as described by *Haubensak et al.* [2002]. Immediately following adjustment of water content, one set of subsamples was extracted with 50 mL of 2 M KCl, shaken for 1 h on a mechanical reciprocating shaker, and filtered through Whatman no. 1 filter paper that was preleached with deionized water. The filtered extracts were frozen for later analysis of initial NH_4^+ and NO_3^- pools. The second set of subsamples was placed in 120 mL specimen containers and incubated for 28 d in 0.95 L Mason jars sealed with a lid containing a butyl rubber septum. Each jar had 30 mL of deionized water in the bottom to minimize soil water loss during the incubation period, and incubation took place inside a dark growth chamber at 23 ± 1°C. Carbon dioxide concentrations in the headspace of each jar were determined after 7, 14, and 28 d by taking a sample of the headspace with a syringe and injecting it into a Shimadzu GC8-A gas chromatograph equipped with a thermal conductivity detector (Shimadzu Scientific Instruments, Columbia, Maryland, United States). The headspace of each jar was flushed with ambient air immediately after each sampling period. After 28 d the incubated soil samples were extracted with 2 M KCl as described above and, along with the initial samples, analyzed for NH_4^+ and NO_3^- concentrations using a Lachat Instruments QuickChem 8000 Flow Injection Autoanalyzer (Lachat Instruments, Loveland, Col-

orado, United States). In addition to absolute rates, we also calculated the amount of C respired relative to total soil organic C and the net amount of N mineralized relative to total soil N as indices of substrate quality across the four sites [*Powers*, 1990; *Schweitzer et al.*, 2004].

2.4. Gross Rates of N Transformation

[12] The ^{15}N isotope dilution method [*Hart et al.*, 1994] was used to measure gross N transformation rates on surface (0–15 cm) mineral soil samples under field conditions over a 1-d incubation period. We conducted measurements under six piñon pines, six one-seed junipers, and in six intercanopy spaces at each of the four sites from 2 through 7 September 2003. We chose these dates because soils at each site were warm and moist and we expected gross N transformation rates to be highest at this time. At each canopy microsite we took two adjacent mineral soil cores using a 4.8 cm inner diameter polycarbonate tube inside an AMS Core Sampler (AMS, Incorporated, American Falls, Idaho, United States). Soil from each core was sieved to <4 mm in the field, composited together, and an ~20 g field-moist subsample was extracted in 75 mL of 2 M KCl for later determination of initial NH_4^+ and NO_3^- pool sizes. Two other ~75 g field-moist subsamples were placed into individual polyethylene bags (wall thickness = 100 μm) and each labeled with 1 mL of a 200 mg N L^{-1} solution at 99% ^{15}N enrichment in the form of either $(^{15}NH_4)_2SO_4$ or $K^{15}NO_3$. An ~20 g field-moist subsample from each of the two polyethylene bags was extracted in 75 mL of 2 M KCl immediately after labeling (t_0 sample). The remaining soil was left in the bag and buried in one of the two holes left by the coring device, where it was allowed to incubate for 24 h with adequate air in the headspace of the closed bag to allow for aerobic conditions. After 24 h, bags were removed from the soil, and an ~20 g field-moist subsample from each of the two polyethylene bags was extracted in 75 mL of 2 M KCl (t_{24} sample).

[13] Gross N mineralization and gross nitrification rates were calculated using $^{14+15}N$ and ^{15}N in t_0 and t_{24} samples, NH_4^+ and NO_3^- pool sizes of labeled pools, and the equations of *Kirkham and Bartholomew* [1954]. Our ^{15}N diffusion procedure followed that of *Stark and Hart* [1996]. Pool sizes of NH_4^+ and NO_3^- were determined using a Lachat Autoanalyzer as described earlier, and ^{15}N enrichment of t_0 and t_{24} samples were determined by continuous-flow direct combustion and mass spectrometry at the Utah State University Stable Isotope Laboratory (http://www.biology.usu.edu/labsites/isotope).

2.5. Microbial C and N and Nitrification Potentials

[14] Unlabeled soils from the cores taken during the ^{15}N isotope dilution incubation were also analyzed for microbial C, microbial N, and nitrification potential. Microbial C and N were determined using the chloroform fumigation extraction method [*Brookes et al.*, 1985; *Vance et al.*, 1987] as modified by *Haubensak et al.* [2002]. Briefly, ~60 g of field-moist soil from each core was divided into unfumigated and fumigated subsamples. Unfumigated subsamples were extracted immediately with 100 mL of 0.5 M K_2SO_4 and frozen for later analysis of initial dissolved organic C and N pools. Fumigated subsamples were exposed to $CHCl_3$ in glass desiccators under vacuum for 5 d [*Haubensak et al.*, 2002] and then extracted with 0.5 M K_2SO_4. Total organic C in fumigated and unfumigated subsamples was determined using a Dohrmann DC-80 Carbon Analyzer (Tekmar-Dohrmann, Cincinnati, Ohio, United States). Total N in each extract was determined by modified micro-Kjeldahl digestion [*Haubensak et al.*, 2002] followed by colorimetric analysis for NH_4^+-N using a Lachat Autoanalyzer. We calculated C and N flush due to fumigation by subtracting organic C or N in unfumigated subsamples from the respective fumigated subsamples. Microbial C and N values were not corrected for extraction efficiency [*Fierer and Schimel*, 2002]; results are expressed as mg of $CHCl_3$-labile C or N kg^{-1} of oven-dried soil. We also expressed microbial C and N as proportions of total soil organic C and N, respectively; these ratios have been found to be useful indicators of substrate quality [*Anderson and Domsch*, 1989; *Zak et al.*, 1994; *Williamson et al.*, 2005].

[15] Nitrification potentials were determined on unlabeled soil samples from the ^{15}N isotope dilution cores using the shaken soil-slurry method as described by *Hart et al.* [1994]. In this method, soil samples are incubated aerobically under laboratory conditions with optimum water, NH_4^+-N, and PO_4^{3-}-P availability. These conditions allow for the assessment of maximum nitrification rates (V_{max}), and the results can be used as an index of the size of the active NH_4^+ oxidizer community [*Hart et al.*, 1994]. We combined ~15 g of field-moist soil with 100 mL of a solution containing 1.5 mM NH_4^+-N and 1 mM PO_4^{3-}-P into 250 mL Erlenmeyer flasks capped with vented rubber stoppers. Flasks were placed on an orbital shaker at 180 rpm for 24 h. Each flask was sampled four times by removing 10 mL of slurry and pipetting it into a 15 mL centrifuge tube. Samples were subsequently spun at 8000 g for 8 min, and supernatant was transferred to polypropylene culture tubes. Solutions were analyzed for NO_3^- -N with a Lachat Autoanalyzer. The rate of NO_3^- production was calculated by linear regression of solution concentration versus time [*Hart et al.*, 1994].

2.6. Foliar N and $\delta^{15}N$

[16] We measured the N concentration and $\delta^{15}N$ of foliage from the two dominant tree species across the substrate age gradient. At each of the four sites we collected sunlit, canopy foliage from piñon pine and one-seed juniper study trees (n = 8 for each species per site) in November 2003. Foliage was collected with a pole pruner from each of the four cardinal directions and composited into one sample per tree. We analyzed only needles from current year's foliage for piñon pine and only 2-cm length shoot tip samples from one-seed juniper, as it is not possible to determine annual cohorts in this species [*Lajtha and Getz*, 1993; *Williams and Ehleringer*, 1996]. Foliar samples were dried at 70°C for 24 h, finely ground, weighed into tin capsules, and analyzed for N concentration and $\delta^{15}N$ by continuous-flow direct combustion and mass spectrometry at the Colorado Plateau Stable Isotope Laboratory.

2.7. Soil pH, Particle Size, and Water Content

[17] We measured pH and particle size distribution of surface (0–15 cm) mineral soil samples collected from each

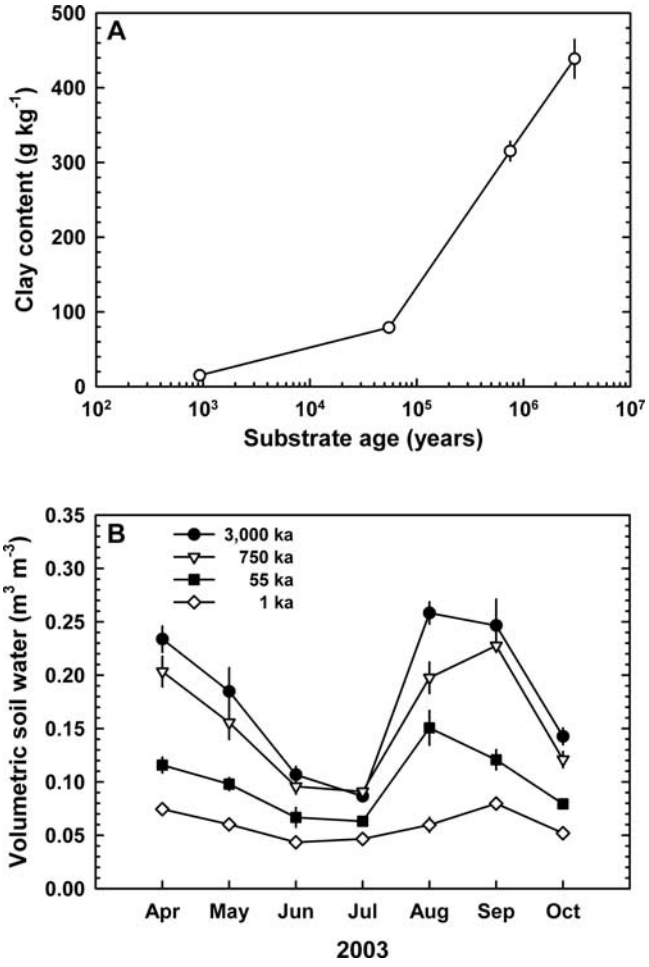

Figure 2. (a) Surface mineral soil (0–15 cm) clay content and (b) volumetric water content from April to October 2003 across the San Francisco volcanic field (SFVF) substrate age gradient, northern Arizona, United States. Data are means, and vertical bars represent ±1 SE.

site in 2002, and measured volumetric water content of surface (0–15 cm) soils in intercanopy spaces throughout the growing season in 2003. Soils from piñon pine, one-seed juniper, and intercanopy microsites (n = 8 per microsite) at each of the four sites were sieved to <2 mm, and pH was determined in 1:2 suspensions of air-dry soil to 0.01 M $CaCl_2$ solution [*Hendershot et al.*, 1993] using an Orion 720A pH meter (Allometrics, Incorporated, Baton Rouge, Louisiana, United States). Particle size analysis was conducted on five intercanopy surface soil samples (sieved to <2 mm) from each site using a standard hydrometer method as described by *Gee and Bauder* [1986]. Volumetric water content of soil was measured in intercanopy spaces at each site (n = 5 per site) in 2003 using a portable Trase Systems Time Domain Reflectometry unit (Soilmoisture Corporation, Santa Barbara, California, United States). Time domain reflectometry probes were permanently installed, and measurements were taken every 2 weeks from April to October 2003.

2.8. Statistical Analyses

[18] Our study design is not replicated at the site level because only one basaltic scoria deposit was available at the young end of the substrate age gradient, and also because of logistical constraints on locating and sampling replicate sites at each developmental stage. Thus we confined our use of inferential statistics to within-site comparisons of canopy microsites (i.e., surface soils under piñon pine canopies, one-seed juniper canopies, and from intercanopy spaces). We used one-factor analysis of variance (ANOVA) to test for differences in surface soil C and N pools and fluxes among the three canopy microsites within each of the four sites along the SFVF substrate age gradient. Posthoc all pairwise comparisons were conducted as mean separation tests, with the alpha level adjusted for the number of tests using the Dunn-Sidak method [*Sokal and Rohlf*, 1995]. We used two-tailed t-tests for within-site comparisons of piñon pine and one-seed juniper foliar N concentration and $\delta^{15}N$ values. Statistical analyses were conducted using the SAS JMP IN 5.1 software package (SAS Institute, Incorporated, Cary, North Carolina). We used $\alpha = 0.10$ for all statistical tests on all variables, primarily because of the high variability associated with measuring gross rates of N flux under field conditions.

3. Results

3.1. Soil Particle Size, Water Content, and pH

[19] Clay content increased substantially with substrate age, from ~15 g kg^{-1} at the youngest site to >400 g kg^{-1} at the oldest site (Figure 2a), along with a concomitant >90% decrease in sand-sized (0.05–2.0 mm) particles from ~930 g kg^{-1} at the youngest site to ~110 g kg^{-1} at the oldest site (data not shown). The increase in the proportion of clay-sized particles is reflected in the pattern of surface soil volumetric water content across the SFVF substrate age gradient. Throughout the 2003 growing season (April to October), older sites with higher clay content had consistently higher surface soil moisture than younger sites with lower clay content (Figure 2b). Surface soil pH was highest at the youngest site and lowest at the oldest site (Table 2). Within sites, soils under one-seed juniper generally had higher pH than soils under piñon pine, with intercanopy soils intermediate between piñon and juniper microsites. The exception to this pattern was the 55,000 year site, where there was no significant difference in pH among canopy microsites (Table 2).

3.2. Soil Organic C and N Pools

[20] In general, both soil organic C and N pools increased from the youngest to the 750,000 year site and then declined to the oldest site (Figure 3). However, C and N pools under one-seed juniper canopies at the two youngest sites were a notable exception to this pattern. Soil organic C under one-seed juniper canopies was higher at the youngest site than at the next oldest site, O'Neill Crater, and soil total N was roughly equivalent under juniper canopies at these two sites (Figure 3).

[21] The pattern of within-site canopy microsite differences in surface soil C and N pools shifted with substrate

Table 2. Surface Mineral Soil (0–15 cm) pH, Carbon to Nitrogen (C/N) Mass Ratio, and Microbial C and N (Expressed as Chloroform-Labile C or N) Across the San Francisco Volcanic Field (SFVF) Substrate Age Gradient in Northern Arizona, United States[a]

Site	pH	C/N	Microbial C, mg kg^{-1}	Microbial N, mg kg^{-1}
Sunset Crater (0.93 ka)				
Intercanopy	6.74 (0.15)ab	14.1 (0.45)a	15.65 (3.89)a	4.22 (0.42)a
Piñon pine	6.57 (0.08)a	18.4 (0.68)b	37.15 (3.32)b	8.09 (0.88)b
One-seed juniper	7.08 (0.11)b	18.9 (0.41)b	41.26 (3.99)b	8.34 (1.35)b
O'Neill Crater (55 ka)				
Intercanopy	6.56 (0.04)a	10.4 (0.11)a	85.16 (3.08)a	15.80 (1.02)ab
Piñon pine	6.40 (0.08)a	11.6 (0.18)b	86.27 (7.21)a	13.15 (1.48)a
One-seed juniper	6.51 (0.07)a	11.2 (0.18)b	67.26 (8.36)a	18.29 (1.28)b
Red Mountain (750 ka)				
Intercanopy	6.70 (0.13)ab	12.2 (0.10)a	581.71 (73.76)a	36.09 (5.12)a
Piñon pine	6.39 (0.09)a	13.9 (0.20)b	649.38 (42.23)a	25.67 (5.16)a
One-seed juniper	6.82 (0.13)b	13.6 (0.32)b	678.60 (93.11)a	28.14 (5.94)a
Cedar Mountain (3000 ka)				
Intercanopy	6.17 (0.06)ab	10.9 (0.15)a	335.31 (79.44)a	19.21 (1.97)a
Piñon pine	6.00 (0.09)a	12.5 (0.26)b	358.59 (19.70)a	31.16 (2.53)b
One-seed juniper	6.38 (0.08)b	12.1 (0.28)b	471.82 (44.91)a	30.52 (4.43)b

[a]Data are means with standard errors in parentheses; different letters indicate significant differences ($p < 0.10$) among tree and intercanopy microsites within a site.

age (Figure 3). At the youngest site both soil organic C and total soil N were substantially higher under junipers than in either piñon or intercanopy microsites ($F = 10.09$, $p < 0.01$ and $F = 9.26$, $p < 0.01$, respectively). Soils under tree canopies at O'Neill Crater (55,000 years) had significantly higher organic C ($F = 5.99$, $p < 0.01$) and total N ($F = 3.45$, $p = 0.03$) than soils in intercanopy spaces, but there was no difference between piñon and juniper microsites in either C or N soil pools (Figure 3). At the 750,000 year site there was again no difference in surface soil C and N under tree canopies, but piñon pine microsites had significantly higher organic C than intercanopy soils ($F = 3.16$, $p = 0.06$); there was no difference among the three canopy microsites in surface soil total N ($F = 0.58$, $p = 0.57$). At the oldest site both organic C and total N were higher in soils under tree canopies than in intercanopy soils ($F = 8.23$, $p < 0.01$ and $F = 4.51$, $p = 0.02$, respectively).

[22] There was no consistent trend in surface soil C to N (C/N) mass ratio with substrate age. The C/N ratio was highest at the youngest site (14–19), lowest at the next oldest site, O'Neill Crater (10–12), and intermediate between these two extremes at the two oldest sites (Table 2). There was a consistent trend in tree canopy versus intercanopy microsite differences in surface soil C/N ratio across the substrate age gradient; no significant difference was found between piñon and juniper microsites, but C/N ratios were significantly lower in intercanopy soils than soils under tree canopies at Sunset Crater ($F = 23.81$, $p < 0.01$), O'Neill Crater ($F = 11.48$, $p < 0.01$), Red Mountain ($F = 16.14$, $p < 0.01$), and Cedar Mountain ($F = 10.85$, $p < 0.01$).

3.3. Microbial C and N

[23] Microbial C (expressed as $CHCl_3$-labile C) across the substrate age gradient largely reflected the pattern of soil organic C pools, with a substantial increase up to the 750,000 year site and subsequent decline at the oldest site (Table 2). Soil microbial C was significantly higher under tree canopies than in intercanopy soils ($F = 4.95$, $p = 0.02$) at the youngest site, Sunset Crater. However, there was no difference in soil microbial C among canopy microsites at the three older sites (O'Neill Crater: $F = 2.6$, $p = 0.11$; Red Mountain: $F = 0.47$, $p = 0.63$; Cedar Mountain: $F = 1.84$, $p = 0.19$; Table 2). Soil microbial N (expressed as $CHCl_3$-labile N) also increased from the youngest site to the 750,000 year site but, rather than declining, microbial N was roughly equivalent at the two oldest sites (Table 2). The pattern of canopy microsite differences was similar at the youngest site and the oldest site, with soil microbial N significantly higher under tree canopies than intercanopy soils at both Sunset Crater ($F = 5.77$, $p = 0.01$) and Cedar Mountain ($F = 4.53$, $p = 0.03$). At O'Neill Crater (55,000 years), soil microbial N was higher under juniper canopies than under piñon canopies, with intercanopy soils similar to both tree microsites ($F = 3.89$, $p = 0.04$). There was no difference in soil microbial N among the three canopy microsites at the 750,000 year site ($F = 1.01$, $p = 0.39$; Table 2).

[24] The proportion of soil organic C present as microbial C increased consistently with substrate age up to the 750,000 year site, with the oldest site maintaining these peak values rather than declining (Table 3). At both Sunset Crater and O'Neill Crater, the two youngest sites, intercanopy soils had the highest percentage of soil organic C as microbial C, followed by piñon soils and then juniper soils ($F = 43.19$, $p < 0.01$; $F = 34.09$, $p < 0.01$, respectively). There was no difference among canopy microsites in the ratio of microbial to total organic C at either Red Mountain ($F = 0.85$, $p = 0.45$) or Cedar Mountain ($F = 0.54$, $p = 0.6$; Table 3). Microbial N as a proportion of total N displayed a less consistent overall pattern with substrate age, but was generally lowest at the younger two sites and highest at the oldest site (Table 3). Intercanopy and piñon soils had significantly higher proportions of total N in the form of microbial N than did juniper soils at the youngest site ($F =$

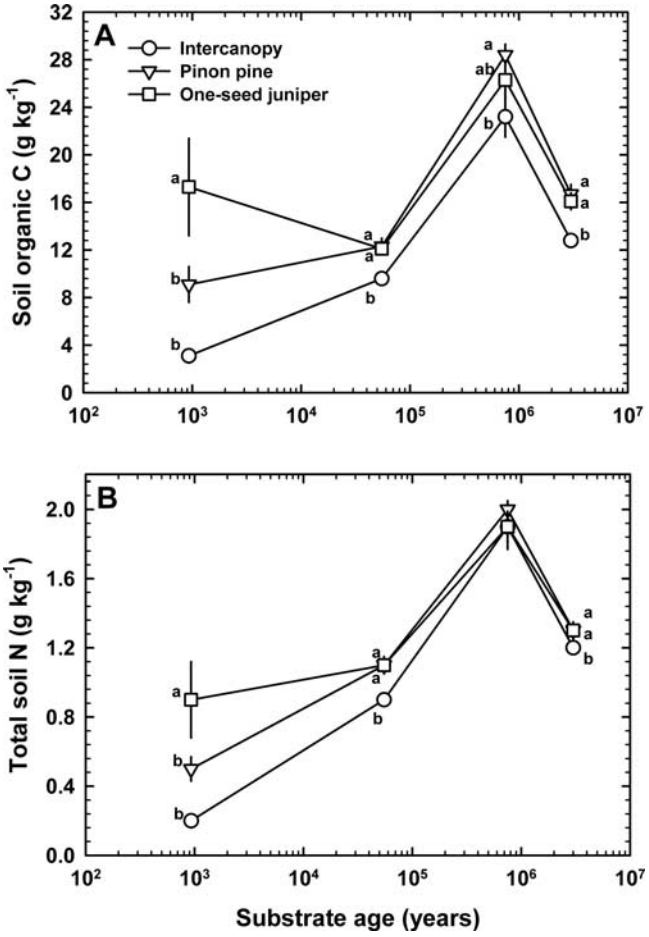

Figure 3. (a) Surface mineral soil (0–15 cm) organic carbon and (b) total nitrogen across the San Francisco volcanic field (SFVF) substrate age gradient in northern Arizona, United States. Data are means, and vertical bars represent ±1 SE. Different letters indicate significant differences ($p < 0.10$) among tree and intercanopy microsites within a site.

19.33, $p < 0.01$). The ratio of microbial N to total N was highest under piñon canopies at the 55,000 year site ($F = 20.94$, $p < 0.01$), and there was no difference among canopy microsites at the 750,000 year site ($F = 2.15$, $p = 0.15$). At the oldest site, piñon soils had a significantly greater proportion of total N as microbial N than intercanopy soils, with juniper soils intermediate between these two ($F = 4.68$, $p = 0.03$; Table 3).

3.4. Microbial Respiration and Net N Mineralization

[25] Microbial respiration and net N mineralization during the laboratory incubation reflected trends in total C and N pools across the substrate age gradient, with an increase in both CO_2 production and net N mineralization from the youngest to the 750,000 year site and a subsequent decline at the oldest site (Figure 4). Also similar to the trend for total C pools, microbial respiration in juniper soils from Sunset Crater was higher than that in juniper soils from the next oldest site, O'Neill Crater (Figure 4a). At both the 930 year and the 55,000 year sites, microbial respiration was significantly higher under tree canopies than intercanopy soils ($F = 10.97$, $p < 0.01$ and $F = 6.01$, $p = 0.01$, respectively; Figure 4a). In contrast, respiration was highest in soils under piñon pine at both the 750,000 year site ($F = 6.83$, $p < 0.01$) and at the oldest site ($F = 6.81$, $p < 0.01$), but CO_2 flux from juniper soils at the oldest site was no different from either intercanopy or piñon pine soils (Figure 4a). Similar to microbial respiration, net N mineralization was also significantly higher in soils from under tree canopies at the youngest site ($F = 6.47$, $p < 0.01$; Figure 4b). However, there was no difference in net N mineralization among soils from the three canopy microsites at O'Neill Crater ($F = 0.84$, $p = 0.45$), and both Red Mountain and Cedar Mountain had significantly higher net N mineralization rates from soils under piñon pine canopies than either intercanopy or juniper soils ($F = 6.15$, $p = 0.01$ and $F = 3.30$, p = 0.06, respectively; Figure 4b).

[26] The proportion of total soil organic C respired during the laboratory incubation remained remarkably consistent across the substrate age gradient at ~2.5% (Table 3). There was no difference among canopy microsites in the relative amount of C respired at any of the four sites (Sunset Crater: $F = 1.27$, $p = 0.31$; O'Neill Crater: $F = 1.01$, $p = 0.39$; Red Mountain: $F = 1.50$, p = 0.25; Cedar Mountain: $F = 1.25$, $p = 0.32$). Relative net N mineralization, expressed as a percentage of total soil N, increased with substrate age up to the 750,000 year site, with similar peak values maintained at the oldest site (Table 3). Within the youngest site, intercanopy soils had the lowest proportion of total N mineralized and piñon soils the highest, with juniper soils intermediate ($F = 4.18$, $p = 0.04$; Table 3). There was no difference among canopy microsites at O'Neill Crater ($F = 0.43$, $p = 0.66$). Relative net N mineralization at the two oldest sites was highest under piñon canopies, lowest under juniper canopies, and intermediate in intercanopy soils ($F = 5.14$, $p = 0.02$ and $F = 5.04$, $p = 0.02$, respectively; Table 3).

3.5. Gross N Transformation Rates and Potential Nitrification

[27] Rates of gross N mineralization measured under field conditions generally increased up to the 750,000 year site and then declined to the oldest site, although this trend was more muted for rates under tree canopies than in intercanopy spaces across the substrate age gradient (Figure 5a). Similar to patterns of microbial respiration and total soil C and N pools, however, gross N mineralization was higher under juniper canopies at Sunset Crater, the youngest site, than at the next older site, O'Neill Crater (Figure 5a). Within sites, gross rates of N mineralization were significantly higher under tree canopies than in intercanopy spaces at the youngest site ($F = 8.81$, $p < 0.01$), highest under piñon pine canopies at the 55,000 year site ($F = 3.42$, $p = 0.06$), and similar among the three canopy microsites at the 750,000 year site ($F = 0.47$, $p = 0.63$), where rates of gross N mineralization tended to be at their highest across the substrate age gradient (Figure 5a). Gross N mineralization rates in soils under tree canopies were significantly higher

Table 3. Proportions of Organic C and Total N Present as Microbial (Chloroform-Labile) C and N, As Well As Relative Microbial Respiration and Relative Net N Mineralization in Surface Mineral Soils (0–15 cm) Across the San Francisco Volcanic Field (SFVF) Substrate Age Gradient in Northern Arizona, United States[a]

Site	Microbial C as % of Organic C	Microbial N as % of Total N	Respired C as % of Organic C	N Mineralized (Net) as % of Total N
Sunset Crater (0.93 ka)				
Intercanopy	0.61 (0.04)a	1.98 (0.20)a	2.08 (0.26)a	−0.17 (0.40)a
Piñon pine	0.37 (0.03)b	1.52 (0.09)a	2.41 (0.20)a	0.77 (0.06)b
One-seed juniper	0.21 (0.02)c	0.83 (0.07)b	2.79 (0.43)a	0.59 (0.12)ab
O'Neill Crater (55 ka)				
Intercanopy	0.92 (0.02)a	1.66 (0.07)a	1.97 (0.38)a	1.40 (0.13)a
Piñon pine	0.69 (0.03)b	1.22 (0.06)b	2.38 (0.12)a	1.37 (0.16)a
One-seed juniper	0.57 (0.04)c	1.69 (0.05)a	2.42 (0.10)a	1.25 (0.06)a
Red Mountain (750 ka)				
Intercanopy	2.43 (0.16)a	1.44 (0.04)a	2.21 (0.12)a	1.38 (0.11)ab
Piñon pine	2.41 (0.12)a	1.43 (0.13)a	2.45 (0.17)a	1.89 (0.26)a
One-seed juniper	2.66 (0.15)a	1.73 (0.15)a	2.05 (0.19)a	1.12 (0.08)b
Cedar Mountain (3000 ka)				
Intercanopy	2.47 (0.54)a	1.63 (0.14)a	2.51 (0.05)a	1.53 (0.06)ab
Piñon pine	2.34 (0.20)a	2.31 (0.09)b	2.84 (0.08)a	1.78 (0.12)a
One-seed juniper	2.82 (0.15)a	2.25 (0.25)ab	2.69 (0.18)a	1.33 (0.11)b

[a]Data are means with standard errors in parentheses; different letters indicate significant differences ($p < 0.10$) among tree and intercanopy microsites within a site.

than in intercanopy spaces at the oldest site ($F = 4.40$, $p = 0.03$), a similar pattern to that within the youngest site (Figure 5a).

[28] Gross rates of nitrification in all three canopy microsites increased consistently from the youngest site to the 750,000 year site and then declined to the oldest site (Figure 5b); a similar but more pronounced trend than the pattern for gross N mineralization. Gross rates of nitrification were highest under juniper canopies at the youngest site, with rates under piñon pine intermediate between intercanopy and juniper soils ($F = 2.74$, $p = 0.09$; Figure 5b). There was no difference in gross nitrification among canopy microsites at either O'Neill Crater ($F = 0.39$, p = 0.68) or Red Mountain ($F = 0.81$, $p = 0.46$; Figure 5b). At the oldest site, Cedar Mountain, gross nitrification was significantly lower under piñon pine canopies compared to either intercanopy or juniper soils ($F = 10.02$, $p < 0.01$).

[29] Results from the potential nitrification assay revealed an even more pronounced trend of increasing nitrification in all three canopy microsites up to the 750,000 year site and a subsequent decline to the oldest site (Figure 5c). Also, the apparent trend of reduced nitrification in piñon soils as shown by the gross rate field assay was much more dramatic (and statistically significant) in the potential nitrification assay, especially at the three older sites (Figure 5c). At the youngest site, potential nitrification was significantly lower in both intercanopy spaces and under piñon pine canopies than under juniper canopies ($F = 6.56$, $p < 0.01$). Potential nitrification at O'Neill Crater was highest in soils from intercanopy spaces, lowest in piñon soils, and intermediate in juniper soils ($F = 7.98$, $p < 0.01$). Despite higher overall rates of potential nitrification at Red Mountain than at Cedar Mountain, the two oldest sites had a similar pattern of microsite differences (Figure 5c). Within each of these sites, the highest rate of potential nitrification was in intercanopy soils, followed by juniper soils, and the lowest rates were in soils from under piñon pine canopies (Red Mountain: $F = 14.77$, $p < 0.01$; Cedar Mountain: $F = 31.99$, $p < 0.01$; Figure 5c).

3.6. Foliar N Concentrations

[30] Despite an apparently large increase in N availability across the SFVF substrate age gradient, foliar N concentrations of piñon pine trees were remarkably similar at each of the four sites at about 14 g kg^{-1} (Table 4). Foliar N concentrations of one-seed juniper appear to be more plastic, with the lowest concentrations at the youngest site, increasing to their highest level by the 55,000 year site, and then declining to between 13.5 and 14 g kg^{-1} at the oldest two sites (Table 4). Foliar N concentrations between the two tree species were significantly different at the youngest site, where piñon pine trees had higher concentrations of N in their foliage than one-seed juniper trees ($t = 3.97$, $p < 0.01$). However, there was no difference in foliar N concentrations between piñon pines and one-seed junipers at the three older sites (O'Neill Crater: $t = 1.19$, $p = 0.86$; Red Mountain: $t = 0.57$, $p = 0.71$; Cedar Mountain: $t = 0.75$, $p = 0.23$).

3.7. Soil and Foliar $\delta^{15}N$

[31] The $\delta^{15}N$ of surface soils, piñon foliage, and juniper foliage all increased substantially with substrate age (Figure 6). Surface soils under one-seed juniper trees were significantly more depleted in ^{15}N than soils under piñon pine or in intercanopy spaces at the youngest site ($F = 7.31$, $p < 0.01$), but there were no differences among soil microsites at O'Neill Crater ($F = 0.32$, $p = 0.73$), Red Mountain ($F = 1.67$, $p = 0.21$), or Cedar Mountain ($F = 0.13$, $p = 0.87$; Figure 6a). Within-site differences between foliar $\delta^{15}N$ values of piñon pine and one-seed juniper displayed a similar pattern, with piñon pine foliage significantly more enriched in ^{15}N at Sunset Crater ($t = 2.32$, $p = 0.02$), but no

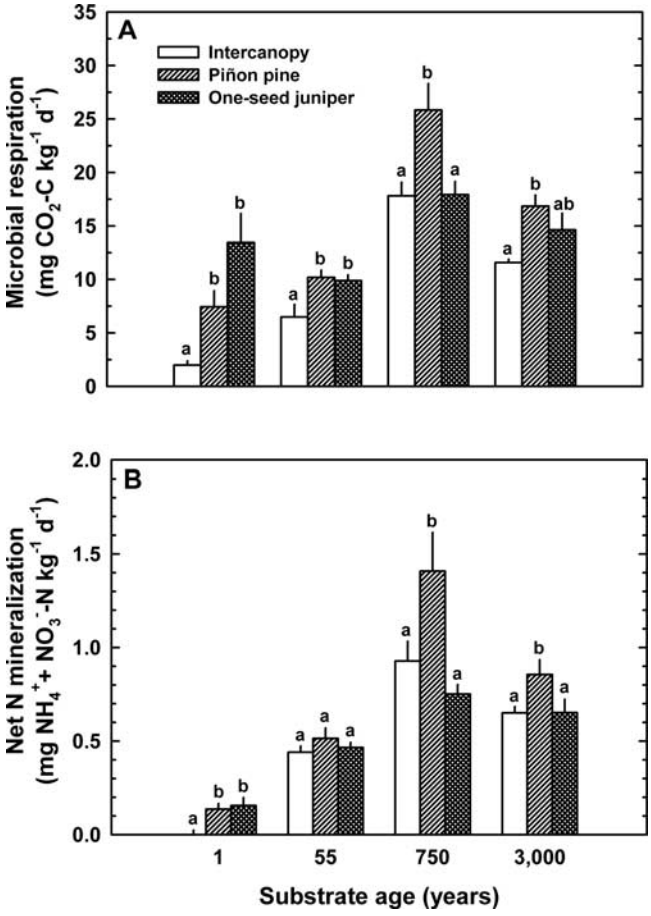

Figure 4. (a) Microbial respiration and (b) net N mineralization during a 28 d laboratory incubation of surface soils from each of four sites across the San Francisco volcanic field (SFVF) substrate age gradient, northern Arizona, United States. Data are means, and vertical bars represent 1 SE. Different letters indicate significant differences ($p < 0.10$) among tree and intercanopy microsites within a site.

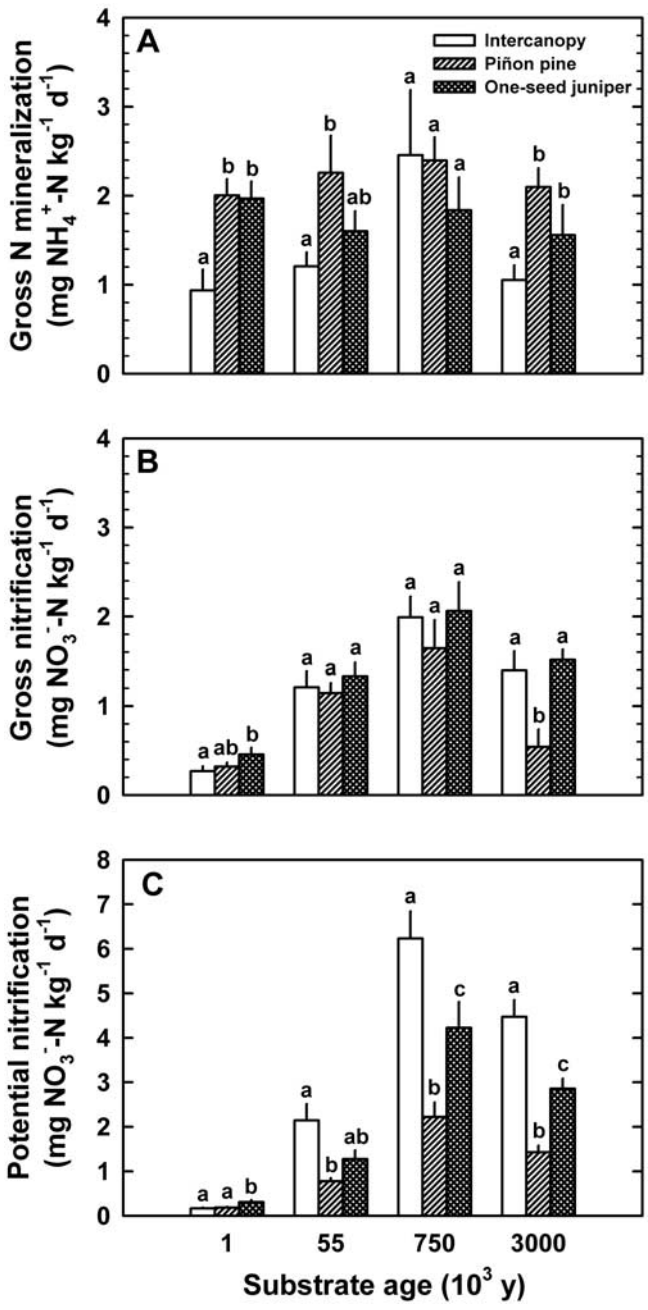

Figure 5. (a) Gross N mineralization, (b) gross nitrification, and (c) potential nitrification in surface soils from across the San Francisco volcanic field (SFVF) substrate age gradient, northern Arizona, United States. Gross N mineralization and gross nitrification were measured in situ under field conditions, potential nitrification was measured under laboratory conditions using unlabeled soil from the gross rate assay. Data are means, and vertical bars represent 1 SE. Different letters indicate significant differences ($p < 0.10$) among tree and intercanopy microsites within a site.

difference between tree species at O'Neill Crater ($t = 0.51$, $p = 0.68$), Red Mountain ($t = 0.55$, $p = 0.70$), or Cedar Mountain ($t = 1.13$, $p = 0.14$; Figure 6b).

4. Discussion

4.1. C and N Dynamics With Substrate Age

[32] A broadly consistent pattern during the long-term development of humid ecosystems is a progressive increase in pools and fluxes of C and N early in pedogenesis followed by a decline in older, more highly weathered soils [*Odum*, 1969; *Westman*, 1975; *Walker et al.*, 1981; *Crews et al.*, 1995; *Torn et al.*, 1997; *Richardson et al.*, 2004; *Wardle et al.*, 2004]. Our results demonstrate that this pattern common to humid systems also holds across the semiarid SFVF substrate age gradient. One striking difference between our results and those from more humid ecosystems is the time-span over which these changes in C and N dynamics occur. The decline phase in humid ecosystems usually becomes apparent within a few thousand years of soil development [*Wardle et al.*, 2004], whereas pools and fluxes of soil C and N along the semiarid SFVF substrate age gradient are maximized much later at ~750,000 years.

Table 4. Foliar N Concentrations of Piñon Pine and One-Seed Juniper Across the San Francisco Volcanic Field (SFVF) Substrate Age Gradient, Northern Arizona, United States[a]

Tree Species	Sunset Crater	O'Neill Crater	Red Mountain	Cedar Mountain
Piñon pine	14.29 (0.43)*	14.42 (0.69)	13.57 (0.53)	14.06 (0.76)
One-seed juniper	12.08 (0.35)	15.97 (0.71)	13.94 (0.57)	13.54 (0.45)

[a]Units for foliar N concentrations are g kg^{-1}. Data are means with standard errors in parentheses; an asterisk indicates a significant difference ($p < 0.10$) between piñon pine and one-seed juniper foliar N concentrations within a site.

This delay likely reflects slower weathering rates and reduced biological activity in more arid ecosystems, where evapotranspiration exceeds precipitation for much of the year [*Chadwick and Chorover*, 2001].

[33] Disproportionately large C and N pools and fluxes under one-seed juniper canopies at the youngest (930 year) site are notable exceptions to the pattern of increase and then decline with substrate age. This may stem from an interaction of small leaf area and coarse-textured soil. One-seed juniper leaves are ~2 mm by 1.5 mm, whereas surface soils at the 930 year site are dominated by sand and gravel-sized cinders (0.5 to >2 mm diameter). We suggest that litter from one-seed juniper trees is readily incorporated into the poorly developed soil at this site, allowing it to decompose more rapidly than litter from other, larger-leaved plant species which remains on the surface.

[34] Recent research focusing on the decline phase in humid systems suggests that soil organic matter quality declines during ecosystem retrogression, which then feeds back to reduce both decomposition and plant productivity [*Wardle et al.*, 2004; *Williamson et al.*, 2005]. This does not appear to be the case along our substrate age gradient, as substrate quality remains similar or increases slightly between the two sites where C and N pools and fluxes are maximal and where they decline. Carbon and N fluxes and microbial biomass (which regulates these fluxes) appear to decline at the oldest site along the SFVF substrate age gradient because of the overall reduction in soil organic matter, not because of reduced substrate quality. We suggest the oldest site along our substrate age gradient has reached a new, stable equilibrium state caused by reduced inputs of C and energy to the soil subsystem.

[35] There is some evidence to suggest that P limitation to productivity may be at least partially responsible for the apparent decline in C and energy inputs at the oldest site. Surface soils at the oldest site have the lowest concentrations of total and labile (i.e., plant-available) P and the highest phosphatase enzyme activity, suggesting a possible P limitation to biological activity [*Selmants*, 2007]. In addition, preliminary results from water and nutrient addition trials indicate that aboveground net primary productivity (NPP) of intercanopy vegetation at the oldest site is limited by P but not water or N (G. S. Newman, K. Hess, and S. C. Hart, unpublished data, 2007). Increased P limitation of NPP may explain why pools and fluxes of surface soil C and N decline at the 3,000,000 year site, but substrate quality and relative cycling rates of C and N remain similar to the 750,000 year site where pools and fluxes of C and N are maximized.

4.2. Islands of Fertility Effect

[36] In general, spatial variation in pools and fluxes of C and N among canopy microsites followed a trend of increasing homogeneity up to the 750,000 year site, but a slight reversal of this trend at the 3,000,000 year site. This mirrors the pattern of increase and then decline in overall C and N storage and cycling rates with substrate age, suggesting that the stage of soil and ecosystem development may exert some control over the "islands of fertility" effect in arid and semiarid ecosystems. Our results support the idea that spatial heterogeneity of soil organic C and N is most pronounced in semiarid ecosystems still in the early stages of primary succession, when patches of poorly developed soil largely devoid of C and N remain uncolonized by plants. As pedogenesis proceeds, soil organic C and N

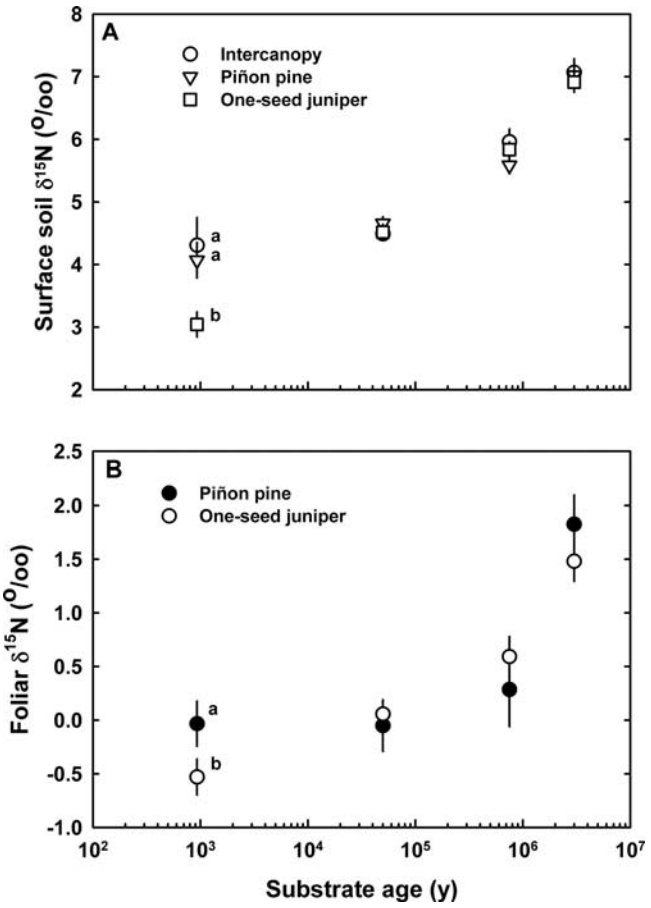

Figure 6. The $\delta^{15}N$ values of (a) surface soils and (b) tree foliage across the San Francisco volcanic field (SFVF) substrate age gradient, northern Arizona, United States. Data are means, and vertical bars represent 1SE. Different letters indicate significant differences ($p < 0.10$) among tree and intercanopy microsites within a site.

become more homogenously distributed across the landscape because the majority of surface soil has been occupied by plants at some point, and increased clay content leads to a greater capacity of soils to stabilize organic matter [*Gregorich et al.*, 1990; *Baldock and Skjemstad*, 2000; *Kaye and Burke*, 2002]. However, this trend toward increased homogeneity with substrate age breaks down at the oldest site, which may be the result of a threshold response to increasing clay content.

[37] At ~430 g kg^{-1}, the oldest site has very high clay content, which should reduce the infiltration rate and increase surface runoff and erosion of soil organic matter in response to precipitation events [*Laio et al.*, 2001; *Austin et al.*, 2004]. Soils under piñon and juniper canopies are somewhat protected from wind and water erosion by low branches and thick O horizons [*Vinton and Burke*, 1995] and may become depositional areas for sediment eroded from intercanopy spaces. Hence wind and water redistribution of surface soil material may account for the increased difference between tree islands and intercanopy microsites at the 3,000,000 year site compared to the 750,000 year site.

[38] Not all measurements of surface soil C and N dynamics followed the trend of increasing homogeneity among microsites up to the 750,000 year site and then a reversal at the 3,000,000 year site. The pattern of surface soil pH and C/N ratio among canopy microsites remained relatively consistent within each of the four sites, even though both of these factors experienced large site-level changes. The chemistry of litter inputs is likely similar across the sequence because the same two tree species dominate each site. Hence relatively short-term tree species influences on soil pH and C/N ratio take place against a background of large, pedogenically driven changes in the physicochemical properties of the soil in which they are rooted. These long-term pedogenic processes likely set limits on plant species effects on soil chemistry.

[39] Potential nitrification rates also do not follow a trend of increasing homogeneity among microsites with substrate age. Although the overall trend is one of increase and then decline to the oldest site, nitrifier populations under piñon canopies at the three oldest sites appear to become increasingly suppressed relative to those in intercanopy spaces and, to a lesser extent, under juniper canopies. This pattern may reflect competition for NH_4^+ between plants/mycorrhizae and nitrifying prokaryotes. Piñons form associations with ectomycorrhizal fungi [*Gehring et al.*, 1998], while the remaining plant species that occur across the age gradient, including one-seed juniper, are colonized by arbuscular mycorrhizal (AM) fungi [*Gehring and Whitham*, 1992]. Piñon roots and their ectomycorrhizal fungi may compete more successfully against nitrifiers for NH_4^+ than roots colonized by AM fungi [*Kaye and Hart*, 1997; *Klopatek and Klopatek*, 1997]. Nitrifiers may thus be limited by NH_4^+ availability under piñon canopies despite high rates of N mineralization in piñon soils at the three older sites.

4.3. Foliar N Concentrations

[40] Variation in foliar N concentrations of both piñon pine and one-seed juniper with substrate age are extremely limited along our semiarid soil chronosequence. This result is in stark contrast to large increases in foliar N early in ecosystem development in both New Zealand and Hawai'i, followed by significant declines at later stages [*Crews et al.*, 1995; *Richardson et al.*, 2004]. We suggest that low plasticity in foliar N concentrations is indicative of the conservative life history strategy of the two dominant tree species across this semiarid substrate age gradient, rather than a lack of variation in soil N availability [*Drenovsky and Richards*, 2004; *Neff et al.*, 2006]. Piñon pine and one-seed juniper may be physiologically constrained from varying their foliar N concentrations in response to variations in soil nutrient content. Instead, these two species may simply increase foliar production when resources are plentiful, a strategy consistent with adaptation to water-limited, low-nutrient environments [*Chapin*, 1980; *Bloom et al.*, 1985].

4.4. ^{15}N of Tree Foliage and Surface Soil

[41] The overall trend in soil and foliar $\delta^{15}N$ across the substrate age gradient supports the idea that young, coarse-textured soils of low N status and low water-holding capacity lose N primarily in the form of either NH_4^+ or dissolved organic N. In contrast, losses in the form of either leached NO_3^- or N containing trace gases driven by nitrification and denitrification predominate in older, finer-textured soils of higher N status and greater water-holding capacity. The enrichment in ^{15}N of foliage and surface soils at older sites occurs because the pathways of loss are more fractionating, and losses by fractionating pathways leave the remaining N enriched [*Högberg*, 1997]. This pattern is consistent with those along very long substrate age gradients in both humid Hawai'ian montane rainforest and California semiarid grassland ecosystems [*Martinelli et al.*, 1999; *Brenner et al.*, 2001]. In our study, significant differences in $\delta^{15}N$ among soil microsites or between piñon and juniper foliage were only found at the youngest site, a similar pattern to that of foliar N concentrations. We suggest that this may reflect differences in N acquisition strategy between one-seed juniper and piñon pine in young soils where N is in extremely short supply, but that these differences are ameliorated in older, more developed soils where N is more available.

[42] Relatively high rates of nitrification during wet periods at the older two sites can lead to accumulation of NO_3^- as soils dry out because diffusion is restricted and biological sinks are limited [*Austin et al.*, 2004]. When these dry soils are rewetted after a precipitation event, accumulated NO_3^- can be lost via leaching or denitrification. Denitrification in particular can proceed at high rates during brief windows of high water, C, and NO_3^- availability and appears to be accentuated by frequent wetting-drying cycles [*Groffman and Tiedje*, 1988]. Our data show an overall decline in both gross and potential rates of nitrification from the 750,000 to the 3,000,000 year old site, yet both surface soil and foliar $\delta^{15}N$ become more enriched over the same time-span. Higher clay content and greater water-holding capacity at the 3,000,000 year site may allow nitrifiers to remain active for longer periods, resulting in greater annual production of NO_3^- and potentially higher rates of denitrification compared to the 750,000 year site. In addition, although all four sites likely experience a similar number of

drying-rewetting events in a given year, the 3,000,000 year site experiences the widest range of water availability ($\sim$0.15 m^3 m^{-3} from April to October 2003), suggesting individual wet-dry cycles are more extreme at this site compared to younger sites with more coarse-textured soil. This could exacerbate N losses induced by wet-dry cycles compared to younger sites with lower variability in soil water content [*Peterjohn and Schlesinger*, 1990].

5. Conclusions

[43] Our results have several important implications for both unifying and broadening current terrestrial ecosystem development theory. First, they suggest that long-term controls over C and N dynamics during ecosystem development are broadly similar in both semiarid and more humid climates. These changes in C and N dynamics may simply occur more rapidly in humid ecosystems because inputs of water, energy, and acidity are much greater per unit time than in more arid ecosystems. Second, the apparent relationship between substrate age and the magnitude of the ''islands of fertility'' effect suggests that the stage of soil and ecosystem development could be an important driver of spatial heterogeneity in ecosystem C and N across semiarid landscapes. Finally, the pattern of ^{15}N enrichment with substrate age provides a time-integrated line of evidence that, similar to humid ecosystems, N behaves as an excess nutrient at later stages of ecosystem development, suggesting broad consistencies in patterns of N cycling and loss during long-term development of semiarid and humid ecosystems.

[44] **Acknowledgments.** We thank Kyle Christie, Dan Guido, Jen Schweitzer, Dylan Fischer, Carrie LeRoy, Dave Baumley, Morgan Luce, Ann Roberts, Greg Newman, and Brittany Johnson for assistance in the field and in the laboratory. This research was funded by EPA-STAR Graduate Fellowship U-916251, a Merriam-Powell Center for Environmental Research Graduate Fellowship, a scholarship from the Achievement Rewards for College Scientists (ARCS) Foundation of Arizona, and by McIntire-Stennis appropriations to NAU and the State of Arizona. Thanks to D. Wardle and an anonymous reviewer for comments that greatly improved the quality of this manuscript.

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