

RESEARCH ARTICLE

10.1002/2015JG002992

Key Points:

- Shift from rock-derived to atmospheric sources of Sr with substrate age
- Plants acquire Sr from greater depths as ecosystem development progresses
- Demonstrates that similar ecosystem processes occur across climate types

Supporting Information:

- Supporting Information S1

Correspondence to:

A. A. Coble,
aacoble@mtu.edu

Citation:

Coble, A. A., S. C. Hart, M. E. Ketterer, G. S. Newman, and A. L. Kowler (2015), Strontium source and depth of uptake shifts with substrate age in semiarid ecosystems, *J. Geophys. Res. Biogeosci.*, *120*, 1069–1077, doi:10.1002/2015JG002992.

Received 17 MAR 2015

Accepted 12 MAY 2015

Accepted article online 19 MAY 2015

Published online 10 JUN 2015

Strontium source and depth of uptake shifts with substrate age in semiarid ecosystems

Ashley A. Coble^{1,2}, Stephen C. Hart³, Michael E. Ketterer^{4,5}, Gregory S. Newman⁶, and Andrew L. Kowler⁷

¹School of Forestry, Northern Arizona University, Flagstaff, Arizona, USA, ²Now at Department of Biological Sciences, Michigan Technological University, Houghton, Michigan, USA, ³Life and Environmental Sciences and Sierra Nevada Research Institute, University of California, Merced, California, USA, ⁴Department of Chemistry and Biochemistry, Northern Arizona University, Flagstaff, Arizona, USA, ⁵Now at Department of Chemistry, Metropolitan State University of Denver, Denver, Colorado, USA, ⁶The Natural History Museum of Denmark, University of Copenhagen, Copenhagen, Denmark, ⁷Department of Earth, Planetary, and Space Sciences, University of California, Los Angeles, California, USA

Abstract Without exogenous rock-derived nutrient sources, terrestrial ecosystems may eventually regress or reach a terminal steady state, but the degree to which exogenous nutrient sources buffer or slow to a theoretical terminal steady state remains unclear. We used strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) as a tracer and measured $^{87}\text{Sr}/^{86}\text{Sr}$ values in aeolian dust, soils, and vegetation across a well-constrained 3 Myr semiarid substrate age gradient to determine (1) whether the contribution of atmospheric sources of rock-derived nutrients to soil and vegetation pools varied with substrate age and (2) to determine if the depth of uptake varied with substrate age. We found that aeolian-derived nutrients became increasingly important, contributing as much as 71% to plant-available soil pools and tree (*Pinus edulis*) growth during the latter stages of ecosystem development in a semiarid climate. The depth of nutrient uptake increased on older substrates, demonstrating that trees in arid regions can acquire nutrients from greater depths as ecosystem development progresses presumably in response to nutrient depletion in the more weathered surface soils. Our results demonstrate that global and regional aeolian transport of nutrients to local ecosystems is a vital process for ecosystem development in arid regions. Furthermore, these aeolian nutrient inputs contribute to deep soil nutrient pools, which become increasingly important for maintaining plant productivity over long time scales.

1. Introduction

Rock-derived nutrients supplied by mineral weathering become depleted over time and without an additional nutrient source terrestrial ecosystems may eventually regress or reach a terminal steady state [Walker *et al.*, 2010; Walker and Syers, 1976]. Previous studies have demonstrated that aeolian dust provides a secondary source of essential plant nutrients in arid regions and contributes to soil development [Capo and Chadwick, 1999; Van der Hoven and Quade, 2002]. These exogenous nutrient sources may potentially buffer or slow terrestrial ecosystems from reaching a terminal steady state in arid regions.

Aeolian dust is recognized as an integral contributor to soil fertility and pedogenic processes, particularly in arid regions [Capo and Chadwick, 1999; Van der Hoven and Quade, 2002]. Rock-derived plant nutrients (i.e., phosphorus (P), potassium (K), calcium (Ca), and magnesium (Mg)) are predominately supplied by the parent material in residual soils, but atmospheric inputs can also contribute significant amounts [Chadwick *et al.*, 1999; Kennedy *et al.*, 1998; Reynolds *et al.*, 2001]. For instance, on the central Colorado Plateau, USA, aeolian dust is enriched relative to surface sediments in several different rock-derived nutrients [Reynolds *et al.*, 2001], contributing at least double the amounts of P, Mg, Ca, and molybdenum (Mo) to surface soils. However, it remains unclear how the relative contribution of aeolian dust and parent material to plant-available nutrient pools changes with ecosystem development in arid regions.

Substrate age gradients have been successfully used to investigate changes in biogeochemical processes in ecosystems over long time periods. In this space-for-time approach, a group of sites are selected with the same parent material but on land surfaces that have been exposed to weathering over different time periods. Additionally, sites are chosen to minimize differences in other soil forming factors, such as current climate, vegetation, and topography. Combining this approach with strontium (Sr) isotope analyses in wet

tropical forests in Hawai'i, researchers found that atmospheric nutrient sources, composed of Asian dust and marine aerosols, became increasingly important on highly weathered substrates [Chadwick *et al.*, 1999; Kennedy *et al.*, 1998].

Strontium isotopes have previously been used as an index of the relative contribution of in situ weathered versus atmospheric-derived nutrient sources in soils [Capo and Chadwick, 1999]. In the Hawaiian study, Sr uptake by vegetation shifted from primarily weathered sources of Sr on young substrates (0.3 kyr and 2.1 kyr) to atmospheric sources of Sr on older substrates (20 kyr, 1400 kyr, and 4100 kyr), suggesting that depleted rock-derived nutrients can be replenished by atmospheric sources [Kennedy *et al.*, 1998]. Dust fluxes in continental arid regions are of greater magnitude than near Hawai'i and potentially provide an important source of nutrients during ecosystem development. It remains uncertain whether there is a fundamental difference in the relative importance of aeolian dust inputs in dry versus wet climates during ecosystem development.

Plants typically have deep roots in arid ecosystems [Schenk and Jackson, 2002], and it has been generally assumed that the primary function of this deeper rooting pattern is to access a more seasonally consistent soil water source. However, previous research in arid ecosystems suggests that vertical root distribution is better correlated with nutrient acquisition than water uptake [McCulley *et al.*, 2004; Thomas, 2000]. Hence, increased plant uptake of limiting nutrients may be another important role of deep roots in dry ecosystems, particularly on older land surfaces where surface nutrient availability has declined [Selmants and Hart, 2008, 2010], N limitation shifts to P limitation [Newman and Hart, 2015], and soil depth increases [Perry *et al.*, 2008]; however, we know of no studies that have successfully evaluated this hypothesis.

A well-constrained, 3 Myr semiarid substrate age gradient that exhibits characteristic patterns of nutrient availability with substrate age [Selmants and Hart, 2008, 2010] provides an exceptional opportunity to address these hypotheses on the changing biogeochemical role of atmospheric nutrient inputs in arid environments. Specifically, we measured $^{87}\text{Sr}/^{86}\text{Sr}$ in soils, vegetation, and contemporary aeolian dust along a substrate age gradient in northern Arizona to evaluate (1) whether the relative proportion of atmospheric versus residual parent material sources of nutrients incorporated into vegetation and soil exchangeable pools varies with substrate age in semiarid ecosystems and (2) whether the soil depth of plant nutrient uptake and whether this depth varies with substrate age.

2. Methods

2.1. Field Methods and Sample Collection

Our study was conducted along a semiarid substrate age gradient (i.e., soil chronosequence) located within the San Francisco volcanic field in northern Arizona [Selmants and Hart, 2008]. This gradient consists of four sites that differ in parent material age but are similar in all other factors that influence soil and ecosystem development (in the sense of Jenny [1941]): Sunset Crater 1 kyr, O'Neill Crater 55 kyr, Red Mountain 750 kyr, and Cedar Mountain 3000 kyr. Weather stations were installed at each site in 2001, which were equipped to measure air temperature (Campbell Scientific, Logan, UT, USA), wind speed, and wind direction with an anemometer and wind vane (R. M. Young, Traverse City, MI, USA). Soils at each site developed on volcanic cinders that are composed primarily of microporphyrific basalt deposited on a pyroclastic sheet [Moore and Wolfe, 1987; Wolfe *et al.*, 1987]. All sites are at a similar elevation and experience similar current climates (mean annual precipitation ranges from 325 to 338 mm and mean annual air temperature ranges from 11 to 12°C [Selmants and Hart, 2008]). Each study site has minimal slope (<1%) and experiences prevailing southwesterly winds. There are two codominant vegetation types located across this substrate age gradient: piñon pine (*Pinus edulis*) and one-seed juniper (*Juniperus monosperma*). Vegetation samples for this study included only piñon pine because deep soil pits had previously been dug next to piñon pines for a companion study (Gregory Newman, The Natural History Museum of Denmark, unpublished data, 2005) allowing us to sample deeper soils and because of the difficulties in aging and obtaining juniper wood from tree increment cores.

In 2005, we dug five soil pits per site to a depth of 2 m using a backhoe. Each soil pit was located at the edge of the canopy dripline of isolated piñon pine trees (*Pinus edulis*; 25–30 cm basal diameter). The horizontal extent of the soil pits spanned 3–4 m, although soil sampling was constrained to the width of the tree

crown (1–2 m). The soil morphology and horizonation of each pit were described using terms and abbreviations from *Schoeneberger et al.* [2012]. Quantitative sampling of soil from each genetic horizon was made with the aid of a sampling frame inserted into the soil pit face adjacent to the tree. Soils were then returned to the laboratory, air dried, sieved (<2 mm mesh), and stored until analyzed. At the oldest site, soil samples taken from only four of the five soil profiles were used because one of the soil pits, upon detailed examination, exhibited a different pedogenic history than the other four pits at this site.

In January 2010, we collected two adjacent (vertically paired) increment cores of tree bole wood from each adjacent piñon ($n = 5$; $n = 4$ at the 3000 kyr site) perpendicular to the soil pit face using a 12 mm diameter increment borer inserted in trees approximately 45 cm above the ground surface. To obtain enough sample for isotopic analysis, we selected tree rings from the past 5 years (2005–2009) of tree growth, which provided a time-integrated isotopic value over this period. One core of the pair was mounted, sanded, and then used to measure the growth increment over the past 5 years; this length was then used to guide the removal of wood from the paired, unprocessed core for isotopic analysis. At the end of the growing season in fall 2009, we collected current-year piñon needles from each of the cardinal directions around the upper third of each tree canopy to form a single foliar composite. These tree wood and foliar samples were then air dried in the laboratory and stored until analysis.

At each site, we installed three dust collectors in intercanopy spaces (>10 m diameter). Each collector was placed in an inconspicuous location at a distance of more than 60 m from minor roads and consisted of an aluminum angel food cake pan with silicone polyester coating placed on a pole 2 m above the ground (similar to previously used design [Reheis, 2006]). The cross-section surface area of each pan was 0.066 m². The 2 m height prevented inputs of saltating sand-sized particles and collected only the vertical component of dry deposition. Inside the pan, stainless steel mesh rested 4 cm below the rim of the pan, and glass marbles rested on top of the mesh to reduce removal of dust by wind after deposition. We collected dust samples 3 times over a 1 year period: summer: 7–8 May 2009 to 17–18 August 2009, fall: 17–18 August 2009 to 30–31 October 2009, and winter/spring: 30–31 October 2009 to 6–7 May 2010. Sampling dates were chosen to reflect the four seasons; however, we were unable to collect samples during the winter because heavy snow limited access to some sites. At the time of collection, all collector components were rinsed with deionized water, and the solution was poured into acid-washed 2 L polyethylene bottles for transport. In the laboratory, the sample was placed in an oven at 30°C to evaporate water from the sample, and large (>0.5 mm) organic detritus was separated from inorganic sediment using forceps and a dissecting microscope.

2.2. Strontium Isotope Analysis and Mixing Model

We analyzed soil, dust, and vegetation samples for Sr isotopes and elemental concentrations. We determined $^{87}\text{Sr}/^{86}\text{Sr}$ values and Sr concentrations of both total and exchangeable pools for soil samples, $^{87}\text{Sr}/^{86}\text{Sr}$ values of total pools for dust samples (because the limited amounts of dust sample prevented additional measurements of exchangeable pools), and $^{87}\text{Sr}/^{86}\text{Sr}$ of total pools from vegetation samples to reflect the Sr taken up and assimilated by the vegetation. Only summer and fall dust collections were used for isotopic analysis because sample contamination occurred in the pans during the first winter/spring collection period. Winter/spring dust was collected the following year in order to estimate seasonal and annual dust fluxes.

Soil exchangeable pools were determined by extracting with 1 M ammonium acetate adjusted to a pH of 7.0 (1 g soil in 10 mL NH₄OAc [Carter, 1993]). Extracts were then filtered (0.45 μm polyvinylidene fluoride), evaporated, and dissolved in 2 M nitric acid (HNO₃). The total Sr pool in soil was determined by grinding the <2 mm fraction with a ball mill to <200 mesh (75 μm). Samples were dry ashed and digested with a mixture of HNO₃ and hydrofluoric acid, and then boric acid was added. This procedure results in an essentially complete dissolution of the entire sample. Control samples (U.S. Geological Survey AGV-2 and G-2) with known Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ values were also digested and analyzed alongside unknown samples and served as internal standards. Dust samples were prepared in the same manner as the total Sr soil pool, except the samples were not ground. Vegetation samples (both bole wood and foliage) were ground in a Wiley mill through a 40 mesh (425 μm) screen (A. Thomas Co., Philadelphia, PA, USA). Then, samples were ashed and digested in HNO₃.

For all isotopic measurements, samples were passed through solid-phase extraction columns containing Sr-specific resin (Eichrom, Lisle, IL, USA). The columns were rinsed with 8 M HNO₃, and Sr was eluted with deionized water [Horwitz *et al.*, 1992]. Strontium isotopic compositions were analyzed with a VG Axiom multiple collector inductively coupled plasma–mass spectrometer (MC ICP-MS; VG Instruments, Winsford, Cheshire, UK) and Sr concentrations with a Thermo X Series II quadrupole ICP-MS (Thermo Scientific, West Palm Beach, FL, USA). Isotopic values were normalized to measured values of National Institute of Standards and Technology 987. Analytical uncertainties for isotopic analysis of the total Sr soil pool, dust, and vegetation were ± 0.00009 as were most uncertainties for Sr isotopic ratios of the exchangeable Sr soil pool. This uncertainty estimate is based upon the measured precision of replicates as well as the values found for AGV-2 and G-2 controls. However, given the low recovery of exchangeable Sr, particularly in C horizons where there is little exchangeable Sr present, some uncertainties were as high as ± 0.00070 .

We used a mixing model to determine the relative contributions of atmospheric and weathering sources to soils and vegetation using measured values of both atmospheric and parent material end-members. Dust sources and dust deposition rates can vary over time and space [e.g., Reynolds *et al.*, 2001; Lawrence and Neff, 2009]; thus, for the atmospheric end-member, we applied a single dust $^{87}\text{Sr}/^{86}\text{Sr}$ value to all four sites. This value (0.70891) was calculated from the mean $^{87}\text{Sr}/^{86}\text{Sr}$ value of dust collected from three of the four sites (1 kyr site 0.70867, 750 kyr site 0.70934, and 3000 kyr site 0.70873) and was within the range of regional $^{87}\text{Sr}/^{86}\text{Sr}$ values reported for dust in New Mexico: 0.7087 to 0.7096 [Capo *et al.*, 1998; Van der Hoven and Quade, 2002]. Dust $^{87}\text{Sr}/^{86}\text{Sr}$ values from the 55 kyr site (mean $^{87}\text{Sr}/^{86}\text{Sr}$ = 0.70684) were excluded from this calculation because these values were below the range of previously reported regional values [Capo *et al.*, 1998; Van der Hoven and Quade, 2002]. We speculate that greater human activity and associated soil disturbance near the 55 kyr site may have resulted in a more locally derived dust signature compared to the other sites along the gradient, and thus, we excluded this value from our calculation of the atmospheric end-member value. To determine the parent material end-member, we calculated the mean $^{87}\text{Sr}/^{86}\text{Sr}$ value of the total Sr pool of C horizons from all sites and used a single parent material end-member value for all sites because (1) at the oldest site (3000 kyr site), we did not have any samples from the C horizon, as it was not exposed within the profile, and (2) Sr isotopic composition of basalt in the San Francisco volcanic field is fairly well constrained, ranging from 0.70260 to 0.70420 [Brookins and Moore, 1975; Pushkar and Stoesser, 1975]. This parent material end-member value (0.70386 ± 0.00032) was within the range of known local basalt values [Brookins and Moore, 1975; Pushkar and Stoesser, 1975].

We used the following two-component mixing equation to estimate the percentage of atmospheric contribution to Sr contained in the total Sr vegetation and exchangeable Sr soil pool [Kennedy *et al.*, 1998]: $^{87}\text{Sr}/^{86}\text{Sr}_{\text{sample}} = X_{\text{atm}} \times ^{87}\text{Sr}/^{86}\text{Sr}_{\text{atm}} + (1 - X_{\text{atm}}) \times ^{87}\text{Sr}/^{86}\text{Sr}_{\text{pm}}$, where X_{atm} is the proportion of atmospheric (dust) contribution to the sample mixture, $^{87}\text{Sr}/^{86}\text{Sr}_{\text{pm}}$ is the Sr isotope ratio of the residual parent material, and $^{87}\text{Sr}/^{86}\text{Sr}_{\text{atm}}$ is the Sr isotope ratio of the atmospheric (dust) contribution. This mixing model was also used to estimate the atmospheric contribution to the total soil pool, except when the total soil $^{87}\text{Sr}/^{86}\text{Sr}$ value was higher than the atmospheric end-member.

We determined the depth-weighted means of soil exchangeable and total $^{87}\text{Sr}/^{86}\text{Sr}$ values to integrate the Sr isotope values of all genetic horizons with depth. The use of depth-weighted means assumes a constant bulk density. Mean bulk density in the soil horizons across all soil pits at the three oldest sites ranged from 0.89 to 1.36 with a standard error of ± 0.04 –0.18. We do not have bulk density measurements from the youngest (1 kyr) site, because the loose consistence of soil throughout the profile made it difficult to determine. Annual dust flux calculations ($\text{g m}^{-2} \text{yr}^{-1}$) for each collector were determined based on the area of dust collectors (area 660.9 cm^2).

2.3. Depth of Nutrient Uptake

To estimate the depth of nutrient uptake by *Pinus edulis*, we graphically compared the bole wood $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic values with the exchangeable soil $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic values and matched the isotopic ratios of the vegetation with the exchangeable soil isotopic ratios. When isotopic ratios of vegetation were lower than measured isotopic values in the soil, it was assumed that uptake occurred at a greater depth than our measurements because we assumed that the observed decline in $^{87}\text{Sr}/^{86}\text{Sr}$ with depth continued at depths that exceeded our sampling limits. This method is similar to approaches used previously [Berger *et al.*, 2006;

Table 1. Depth-Weighted Mean (DWM) Soil Total, Soil Exchangeable, and *Pinus edulis* Bole Wood and Foliage $^{87}\text{Sr}/^{86}\text{Sr}$ Values With 95% Confidence Intervals in Parentheses^a Along a 3 Myr Old Substrate Age Gradient in a Semiarid Climate

Substrate Age (kyr)	DWM Soil Total $^{87}\text{Sr}/^{86}\text{Sr}$	DWM Soil Exchangeable $^{87}\text{Sr}/^{86}\text{Sr}$	Atmospheric Contribution to DWM Soil Total Pools (%)	Atmospheric Contribution to DWM Soil Exchangeable Pools (%)	<i>Pinus edulis</i> Bole Wood $^{87}\text{Sr}/^{86}\text{Sr}$	<i>Pinus edulis</i> Foliage $^{87}\text{Sr}/^{86}\text{Sr}$	Atmospheric Contribution to Bole Wood (%)	Atmospheric Contribution to Foliage (%)
1	0.70384 (0.00011)	0.70551 (0.00027)	2 (3)	33 (5)	0.70535 (0.00015)	0.70543 (0.00013)	29 (3)	31 (3)
55	0.70509 (0.00037)	0.70506 (0.00004)	24 (7)	24 (1)	0.70525 (0.00005)	0.70525 (0.00018)	27 (1)	28 (3)
750	0.70661 (0.00144)	0.70632 (0.00046)	54 (29)	49 (9)	0.70640 (0.00019)	0.70661 (0.00031)	50 (4)	54 (6)
3000	0.71058 (0.00053)	0.70740 (0.00061)	>100 (0)	70 (12)	0.70725 (0.00052)	0.70743 (0.00058)	67 (10)	71 (11)

^aFor 95% confidence intervals, $n = 5$ for the 1 kyr, 55 kyr, and 750 kyr sites and $n = 4$ for the 3000 kyr site, except DWM of soil total pool $n = 4$ for the 750 kyr site and $n = 2$ for the 3000 kyr site. Atmospheric contributions (%) to soil and vegetation Sr pools were calculated using a two end-member mixing model using a mean dust $^{87}\text{Sr}/^{86}\text{Sr}$ value (0.70891) and the mean C horizon $^{87}\text{Sr}/^{86}\text{Sr}$ value across all sites (0.70386). The atmospheric contributions to DWM soil total pools at the 3000 kyr site were outside the range of the assumed end-member values.

[Jackson et al., 2002; McCulley et al., 2004]. This approach provided a mean depth of uptake that can be used for relative comparisons among sites, although uptake likely occurs above and below the estimated depth [McCulley et al., 2004]. We estimated depth of uptake for each soil pit individually because compositing data was difficult as the depth of horizon, type of horizon, and their respective $^{87}\text{Sr}/^{86}\text{Sr}$ values varied among soil pits within a site. For a variety of reasons, not all soil pits were used for these analyses. All soil pits at the 1 kyr site were excluded from this analysis because of high analytical errors (C horizon exchangeable $^{87}\text{Sr}/^{86}\text{Sr}$) or multiple horizons with similar values. One soil pit at the 55 kyr site was excluded from analysis because multiple horizons had similar $^{87}\text{Sr}/^{86}\text{Sr}$ values, one soil pit at the 750 kyr site was excluded because of high analytical errors, and one soil pit at the 3000 kyr site was excluded because $^{87}\text{Sr}/^{86}\text{Sr}$ values of horizons were missing from depths greater than 50 cm.

3. Results

3.1. Atmospheric Contribution to Vegetation and Soil Pools

Annual dust fluxes across the substrate age gradient were relatively similar among sites ($5.1 \text{ g m}^{-2} \text{ yr}^{-1}$ at the 1 kyr site, $11.8 \text{ g m}^{-2} \text{ yr}^{-1}$ at the 55 kyr site, $5.3 \text{ g m}^{-2} \text{ yr}^{-1}$ at the 750 kyr site, and $8.1 \text{ g m}^{-2} \text{ yr}^{-1}$ at the 3000 kyr site). Similarly, mean wind velocity and wind direction data collected from all sites across the substrate age gradient were also consistent across seasons (data not shown).

Atmospheric end-member $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.70891) at our study sites were higher than parent material end-member $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.70386), which were consistent with known local basalt $^{87}\text{Sr}/^{86}\text{Sr}$ values [Brookins and Moore, 1975; Pushkar and Stoesser, 1975]. The contribution of atmospheric Sr to soil exchangeable pools, soil total pools, and *P. edulis* biomass increased with substrate age, yet were similar at the two youngest sites (Table 1). Although the atmospheric contribution to soil exchangeable and vegetation pools was greater at the 1 kyr site than the 55 kyr site, 95% confidence intervals suggest that these contributions were similar at the two youngest sites. Soil and vegetation pools were equally composed of atmospheric and weathering Sr sources at the 750 kyr site and only on the oldest substrate were soil and vegetation pools dominated by atmospheric Sr sources. Based on 95% confidence intervals, soil depth-weighted means of $^{87}\text{Sr}/^{86}\text{Sr}$ were generally different between total and exchangeable pools at the youngest and oldest sites but were similar at the intermediate-aged sites (Table 1). *Pinus edulis* needles and bole wood had similar $^{87}\text{Sr}/^{86}\text{Sr}$ values and thus comparable atmospheric Sr contributions. Furthermore, needle $^{87}\text{Sr}/^{86}\text{Sr}$ values were significantly and positively correlated with bole wood $^{87}\text{Sr}/^{86}\text{Sr}$ values across trees from all sites ($r^2 = 0.96$; $n = 19$, $P < 0.0001$). The $^{87}\text{Sr}/^{86}\text{Sr}$ values of vegetation also closely matched the isotopic values of the exchangeable soil pool (Table 1).

Soil exchangeable $^{87}\text{Sr}/^{86}\text{Sr}$ values generally decreased with depth (Figure 1). Where this did not occur was the result of horizons that contained a pedogenic carbonate (designated by a "k" subscript, e.g., B_k, Bt_k, or C_k) subordinate horizon that had greater $^{87}\text{Sr}/^{86}\text{Sr}$ values relative to surrounding soil layers (Table S1 in the

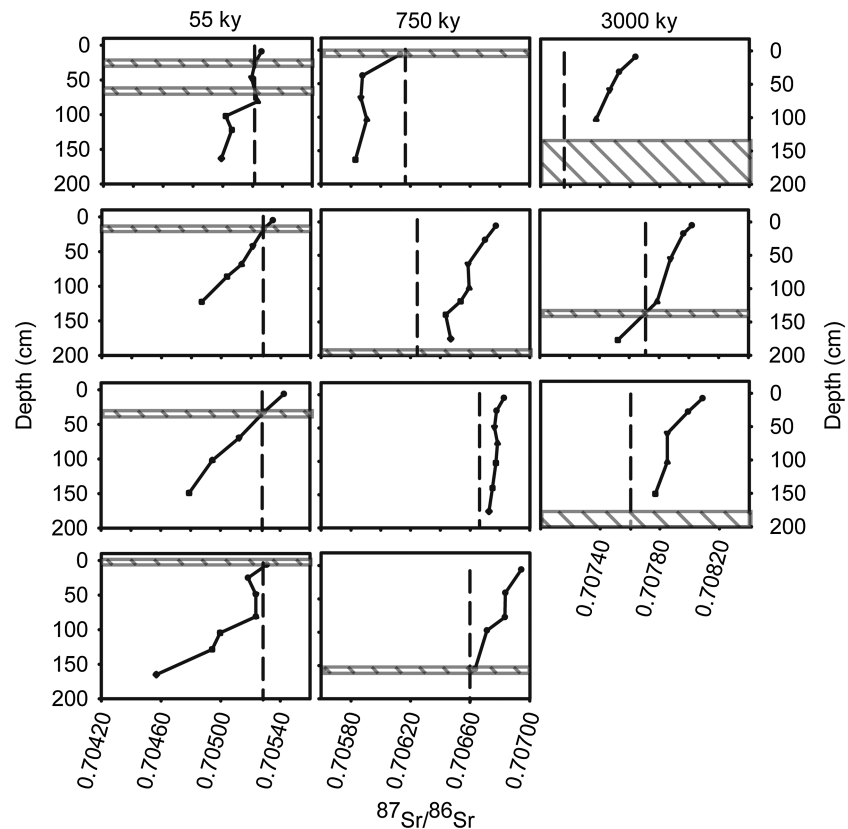


Figure 1. Depth of nutrient uptake by *Pinus edulis* along a well-constrained, 3 Myr old substrate age gradient in a semiarid climate. The depth of uptake was estimated as the depth at which bole wood $^{87}\text{Sr}/^{86}\text{Sr}$ values (dashed vertical line) match the soil exchangeable $^{87}\text{Sr}/^{86}\text{Sr}$ values (filled circles) for each paired *Pinus edulis* and soil pit. Soil exchangeable $^{87}\text{Sr}/^{86}\text{Sr}$ values were placed at the mean depth of each soil horizon sampled. Estimated mean depth of uptake for each *Pinus edulis* and paired soil pit is indicated by hatch marks, but actual depth of uptake likely occurs above and below these estimates. Absence of hatch marks in one soil profile at the 750 kyr site indicates that depth of uptake exceeded the 200 cm depth.

supporting information). Dust is a major contributor to carbonate minerals in pedogenic carbonate layers from arid regions, and $^{87}\text{Sr}/^{86}\text{Sr}$ values are higher and more variable in pedogenic carbonate layers relative to basalt [Van der Hoven and Quade, 2002]. Most soil exchangeable $^{87}\text{Sr}/^{86}\text{Sr}$ values fell in between end-member $^{87}\text{Sr}/^{86}\text{Sr}$ values with two exceptions: at the 1 kyr site, underlying parent material from previous eruptions resulted in Sr isotope values at depths that were greater than the parent material end-member, and at the 750 kyr site, one Bw horizon had a higher $^{87}\text{Sr}/^{86}\text{Sr}$ value than the atmospheric end-member.

3.2. Depth of Nutrient Uptake

Using bole wood $^{87}\text{Sr}/^{86}\text{Sr}$ values, we found that the depth of Sr uptake increased with substrate age. At the 55 kyr site, Sr uptake occurred from shallow (0 to 32 cm or to 66 cm) surface soils (Figure 1); however, in one of the four soil pits examined, there were two possible depths of uptake (26 or 66 cm). At the 750 kyr site, Sr uptake occurred both in shallow surface soils (0 cm) and from deep soil pools (below 190 cm; Figure 1). At the 3000 kyr site, Sr uptake by *P. edulis* occurred from soil depths below 133 cm in the three soil profiles examined (Figure 1). The ranges in $^{87}\text{Sr}/^{86}\text{Sr}$ values in the soil profiles did not overlap among sites. The lowest $^{87}\text{Sr}/^{86}\text{Sr}$ values occurred in soil profiles from the youngest (55 kyr) site evaluated, and the greatest $^{87}\text{Sr}/^{86}\text{Sr}$ values occurred at the oldest (750 kyr) site (Figure 1). When vegetation $^{87}\text{Sr}/^{86}\text{Sr}$ values were lower than measured $^{87}\text{Sr}/^{86}\text{Sr}$ of exchangeable soil horizons, we assumed that uptake occurred at a greater depth than the depth at which our samples were collected (limited to 2 m). The lack of a consistent decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ gradient with soil depth prevented us from clearly identifying the depth of Sr uptake by *P. edulis* at the youngest site (1 kyr).

4. Discussion

Our results are the first to demonstrate that Sr sources incorporated into soil and vegetation pools shift from parent material to atmospheric sources of Sr as ecosystem development progresses in semiarid ecosystems. Using a shorter (120 kyr) basalt soil chronosequence in a semiarid region of New Mexico, *Reynolds et al.* [2012] did not observe this pattern, but our results and others [*Selmants and Hart*, 2010] suggest that a much longer time span is required before weathering rates begin to deplete parent material sources of rock-derived nutrients and before vegetation and soil pools shift from parent material sources to atmospheric sources of Sr in semiarid ecosystems. In Hawai'i, atmospheric sources of Sr begin to dominate vegetation- and basalt-derived soils within 20 kyr of soil development [*Kennedy et al.*, 1998], whereas across the semiarid substrate age gradient used in our study, this dominance was first observed at 3000 kyr of soil development. *Selmants and Hart* [2010] estimated that weathering rates along this semiarid substrate age gradient are reduced by at least 2 orders of magnitude relative to mesic soil chronosequences. In both of these contrasting environments, ecosystem productivity in latter stages of ecosystem development is maintained apparently by inputs of nutrients from outside the ecosystem (such as aeolian dust) as internal sources of nutrients become less available [*Selmants and Hart*, 2010]. Additionally, our results suggest that increased rooting depth and depth of nutrient uptake by the vegetation may be an additional mechanism of semiarid ecosystems for maintaining productivity as rock-derived nutrients are depleted from surface soils.

By using contemporary aeolian $^{87}\text{Sr}/^{86}\text{Sr}$ values, our estimates of the atmospheric contributions to soil and vegetation pools assume that the aeolian Sr isotopic value has not changed over time. However, aeolian sources and Sr isotopic values likely have varied over millennia across these study sites. For example, measurements from ice cores and marine sediments reveal that aeolian deposition rates can be much higher during glacial than interglacial periods [e.g., *Rea*, 1994]. Contemporary dust fluxes at our study sites ($5.1\text{--}11.8\text{ g m}^{-2}\text{ yr}^{-1}$) were comparable to previously reported contemporary dust fluxes in arid environments of the southwestern U.S. ($10\text{--}60\text{ g m}^{-2}\text{ yr}^{-1}$ in south central New Mexico [*Gile and Grossman*, 1979], $12\text{ g m}^{-2}\text{ yr}^{-1}$ in west and central Texas [*Rabenhorst et al.*, 1984], $4.3\text{--}15.7\text{ g m}^{-2}\text{ yr}^{-1}$ in southern Nevada and southeast California [*Reheis*, 1995], $2\text{--}20\text{ g m}^{-2}\text{ yr}^{-1}$ in southern Nevada and California [*Reheis*, 2006], and $10.4\text{ g m}^{-2}\text{ yr}^{-1}$ in Canyonlands National Park [*Reheis*, 2003]), but it is uncertain how dust fluxes or the Sr isotopic signature may have varied over time. For example, total soil $^{87}\text{Sr}/^{86}\text{Sr}$ values in most profiles at the oldest site exceeded the range of contemporary aeolian $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.7087 to 0.7096) from this and previous studies [*Capo et al.*, 1998; *Van der Hoven and Quade*, 2002], suggesting that aeolian $^{87}\text{Sr}/^{86}\text{Sr}$ values may have been higher at some time in the past. Without an understanding of historical variability in aeolian sources and Sr at each of the four sites, we cannot adequately determine how this may have affected our estimates of atmospheric inputs. Nevertheless, our methods are similar to those previously utilized in arid environments [e.g., *Reynolds et al.*, 2012] and reveal an increase in atmospheric Sr contributions to soil and vegetation pools over time.

In contrast to continental ecosystems, coastal ecosystems may receive atmospheric inputs in the form of marine aerosols in addition to aeolian dust inputs [*Chadwick et al.*, 2009]. For example, on land surfaces of Hawaiian substrates, plants acquired the majority of their atmospheric Ca, Mg, K, and Sr from marine aerosols and the majority of their atmospheric P from aeolian dust [*Chadwick et al.*, 2009]. By comparison, contemporary dust fluxes ($5.1\text{--}11.9\text{ g m}^{-2}\text{ yr}^{-1}$) across our semiarid substrate age gradient are a factor of 4 to 40 greater than estimates of dust inputs to the Pacific Ocean near the Hawaiian Islands during the Holocene and earlier glacial periods [*Rea*, 1994]. The relatively high aeolian dust fluxes received in continental arid regions, coupled with our finding that atmospheric Sr is increasingly incorporated into soil and vegetation pools with substrate age, suggest a potentially important source of nutrients to ecosystem development and plant growth over long time scales in these climates.

Using a novel combination of a long, well-constrained substrate age gradient in a semiarid climate and Sr isotope analyses, our data suggest that plants acquire nutrients from greater depths as ecosystem development progresses. The pattern of increasing depth of Sr uptake with increasing substrate age is consistent with solum formation [*Perry et al.*, 2008] and deepening fine root concentration patterns across this substrate age gradient (Gregory Newman, The Natural History Museum of Denmark, unpublished data, 2005). Our previous research along this gradient has shown that surface soil water availability increases with ecosystem development [*Selmants and Hart*, 2008], while surface soil P availability decreases

[Selmants and Hart, 2010]. These previous findings, combined with the results reported here, support the hypothesis that deep plant roots are important for both increasing nutrient acquisition and water uptake in semiarid woodlands as well as grasslands [Jackson *et al.*, 2002; McCulley *et al.*, 2004].

The decreasing soil exchangeable $^{87}\text{Sr}/^{86}\text{Sr}$ values observed with depth across this substrate age gradient demonstrate that atmospheric Sr sources are concentrated near the soil surface and decrease deeper in the soil profile. Furthermore, the soil $^{87}\text{Sr}/^{86}\text{Sr}$ values become more radiogenic with substrate age. For example, at the oldest site, the $^{87}\text{Sr}/^{86}\text{Sr}$ values found at depth were more radiogenic than the $^{87}\text{Sr}/^{86}\text{Sr}$ values found at the surface at the younger sites (e.g., a lack of overlap in $^{87}\text{Sr}/^{86}\text{Sr}$ values in the soil profiles among the three substrates; Figure 1), resulting in the presence of aeolian contributions at greater depths in older soils. As a result, aeolian sources of Sr, although less radiogenic than Sr found at the surface, remained dominant deep within the soil profile at the oldest site. This can be explained by translocation and/or vertical mixing of atmospheric Sr in the soil profile on millennial time scales, allowing plants to extract aeolian Sr from greater depths at the older sites—despite the higher concentration of dust-derived Sr near the surface. Alternatively, the observed thickening of aeolian contributions across this substrate age gradient may be due to progressive aggradation of aeolian material on top of the local substrate, creating cumelic soils that become thicker with time [McFadden *et al.*, 1986]. Regardless of the mechanisms responsible for the distribution of atmospherically derived Sr, our results indicate that a greater depth of uptake by *P. edulis* occurs with increasing substrate age.

5. Conclusions

In this study, we used Sr isotopes as a tracer and measured $^{87}\text{Sr}/^{86}\text{Sr}$ values in soil, vegetation, and dust across a well-constrained 3 Myr substrate age gradient to evaluate two previous hypotheses, for which there was little supporting data. We found that atmospheric contributions of Sr increased with substrate age in semiarid ecosystems, consistent with previous observations in mesic ecosystems. Furthermore, our results suggest that the depth of uptake by *P. edulis* also increased with substrate age. However, variability in local pedology resulting in the lack of a consistent decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ gradient with soil depth prevented us from evaluating this hypothesis across all sites and all soil pits and demonstrates the limitations of using $^{87}\text{Sr}/^{86}\text{Sr}$ to identify the depth of uptake in these semiarid ecosystems. Our findings have helped unify biogeochemical theory by demonstrating that similarities in patterns and processes occur across vegetation types within semiarid climates and across climate types.

Acknowledgments

This research was funded by the Mission Research Program at the Northern Arizona University School of Forestry (McIntire-Stennis/AZ Bureau of Forestry). The VG Axiom MC ICP-MS was obtained through the NSF MRI Program (CHE-0118604 to M.E.K.) and the X Series II instrument was obtained through funds from the Arizona Technology Research and Innovation Fund. We thank Ben Sullivan, Stephanie Jackson, and Adam Coble for their field and laboratory assistance. Data supporting Figure 1 are available in Table S1 in the supporting information.

References

- Berger, T. W., S. Swoboda, T. Prohaska, and G. Glatzel (2006), The role of calcium uptake from deep soils for spruce (*Picea abies*) and beech (*Fagus sylvatica*), *For. Ecol. Manage.*, 229(1–3), 234–246, doi:10.1016/j.foreco.2006.04.004.
- Brookings, D. H., and R. B. Moore (1975), Strontium isotope initial ratios from the San Francisco volcanic field, *Isochron West*, 12, 1–2.
- Capo, R. C., and O. A. Chadwick (1999), Sources of strontium and calcium in desert soil and calcrete, *Earth Planet. Sci. Lett.*, 170(1–2), 61–72, doi:10.1016/S0012-821x(99)00090-4.
- Capo, R. C., B. W. Stewart, and O. A. Chadwick (1998), Strontium isotopes as tracers of ecosystem processes: Theory and methods, *Geoderma*, 82(1–3), 197–225, doi:10.1016/S0016-7061(97)00102-X.
- Carter, M. R. (1993), *Soil Sampling and Methods of Analysis*, Lewis Publishers, Boca Raton, Fla.
- Chadwick, O. A., L. A. Derry, P. M. Vitousek, B. J. Huebert, and L. O. Hedin (1999), Changing sources of nutrients during four million years of ecosystem development, *Nature*, 397(6719), 491–497, doi:10.1038/17276.
- Chadwick, O. A., L. A. Derry, C. R. Bern, and P. M. Vitousek (2009), Changing sources of strontium to soils and ecosystems across the Hawaiian Islands, *Chem. Geol.*, 267(1–2), 64–76, doi:10.1016/j.chemgeo.2009.01.009.
- Gile, L. H., and R. B. Grossman (1979), *The Desert Project Soil Monograph*, Government Printing Office, Washington, D. C.
- Horwitz, E. P., R. Chiarizia, and M. L. Dietz (1992), A novel strontium-selective extraction chromatographic resin, *Solvent Extr. Ion Exch.*, 10(2), 313–336, doi:10.1080/07366299208918107.
- Jackson, R. B., J. L. Banner, E. G. Jobbagy, W. T. Pockman, and D. H. Wall (2002), Ecosystem carbon loss with woody plant invasion of grasslands, *Nature*, 418(6898), 623–626, doi:10.1038/nature00910.
- Jenny, H. (1941), *Factors of Soil Formation: A System of Quantitative Pedology*, McGraw-Hill, New York.
- Kennedy, M. J., O. A. Chadwick, P. M. Vitousek, L. A. Derry, and D. M. Hendricks (1998), Changing sources of base cations during ecosystem development, Hawaiian Islands, *Geology*, 26(11), 1015–1018, doi:10.1130/0091-7613(1998)026<1015:Csobcd>2.3.Co;2.
- Lawrence, C. R., and J. C. Neff (2009), The contemporary physical and chemical flux of aeolian dust: A synthesis of direct measurements of dust deposition, *Chem. Geol.*, 267, 46–63, doi:10.1016/j.chemgeo.2009.02.005.
- McCulley, R. L., E. G. Jobbagy, W. T. Pockman, and R. B. Jackson (2004), Nutrient uptake as a contributing explanation for deep rooting in arid and semi-arid ecosystems, *Oecologia*, 141, 620–628.
- McFadden, L. D., S. G. Wells, and J. C. Dohrenwend (1986), Influences of quaternary climatic changes on processes of soil development on desert loess deposits of the Cima volcanic field, California, *Catena*, 13, 361–389.

- Moore, R. B., and E. W. Wolfe (1987), Geologic map of the east part of the San Francisco volcanic field, north-central Arizona, Map MF-1960, Dep. of the Interior, U.S. Geol. Surv., Washington, D. C.
- Newman, G. S., and S. C. Hart (2015), Shifting soil resource limitations and ecosystem retrogression across a three million year semi-arid substrate age gradient, *Biogeochemistry*, doi:10.1007/s10533-015-0090-7.
- Perry, D. A., R. Oren, and S. C. Hart (2008), *Forest Ecosystems*, 2nd ed., The Johns Hopkins Univ. Press, Baltimore, Md.
- Pushkar, P., and D. B. Stoesser (1975), $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in some volcanic rocks and some semifused inclusions of the San Francisco volcanic field, *Geology*, 3, 669–671.
- Rabenhorst, M. C., L. P. Wilding, and C. L. Girdner (1984), Airborne dusts in the Edwards Plateau region of Texas, *Soil Sci. Soc. Am. J.*, 48(3), 621–627.
- Rea, D. K. (1994), The paleoclimatic record provided by eolian deposition in the deep sea: The geologic history of wind, *Rev. Geophys.*, 2, 159–195, doi:10.1029/93RG03257.
- Reheis, M. C. (1995), Dust deposition in southern Nevada and California, 1984–1989: Relations to climate, source area, and lithology, *J. Geophys. Res.*, 100, 8893–8913, doi:10.1029/94JD03245.
- Reheis, M. C. (2003), *Dust Deposition in Nevada, California, and Utah: 1984–2002*, Dep. of the Interior, U.S. Geol. Surv. Open File Rep. 03-138, 11 pp. [Available at <http://pubs.usgs.gov/of/2003/ofr-03-138/>.]
- Reheis, M. C. (2006), A 16-year record of eolian dust in southern Nevada and California, USA: Controls on dust generation and accumulation, *J. Arid Environ.*, 67, 487–520.
- Reynolds, A. C., J. Quade, and J. L. Betancourt (2012), Strontium isotopes and nutrient sourcing in a semi-arid woodland, *Geoderma*, 189, 574–584, doi:10.1016/j.geoderma.2012.06.029.
- Reynolds, R., J. Belnap, M. Reheis, P. Lamothe, and F. Luiszer (2001), Aeolian dust in Colorado Plateau soils: Nutrient inputs and recent change in source, *Proc. Natl. Acad. Sci. U.S.A.*, 98(13), 7123–7127, doi:10.1073/pnas.121094298.
- Schenk, H. J., and R. B. Jackson (2002), Rooting depths, lateral root spreads, and belowground/aboveground allometries of plants in water-limited environments, *J. Ecol.*, 90, 480–494.
- Schoeneberger, P. J., D. A. Wysocki, E. C. Benham, and Soil Survey Staff (2012), Field book for describing and sampling soils, version 3.0, Natural Resources Conservation Service (U.S. Department of Agriculture), National Soil Survey Center, Lincoln, Nebr.
- 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.
- Selmants, P. C., and S. C. Hart (2010), Phosphorus and soil development: Does the Walker and Syers model apply to semiarid ecosystems?, *Ecology*, 91, 474–484.
- Thomas, F. M. (2000), Vertical rooting patterns of mature *Quercus* trees growing on different soil types in northern Germany, *Plant Ecol.*, 147, 95–103.
- Van der Hoven, S. J., and J. Quade (2002), Tracing spatial and temporal variations in the sources of calcium in pedogenic carbonates in a semiarid environment, *Geoderma*, 108, 259–276.
- Walker, L. R., D. A. Wardle, R. D. Bardgett, and B. D. Clarkson (2010), The use of chronosequences in studies of ecological succession and soil development, *J. Ecol.*, 98(4), 725–736, doi:10.1111/j.1365-2745.2010.01664.x.
- Walker, T. W., and J. K. Syers (1976), The fate of phosphorus during pedogenesis, *Geoderma*, 15, 1–19.
- Wolfe, E. W., G. E. Ulrich, and C. G. Newhall (1987), Geologic map of the northwest part of the San Francisco volcanic field, north-central Arizona, Map MF-1957, Dep. of the Interior, U.S. Geol. Surv., Washington, D. C.