

Global patterns of the isotopic composition of soil and plant nitrogen

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[1] We compiled new and published data on the natural abundance N isotope composition ($\delta^{15}\text{N}$ values) of soil and plant organic matter from around the world. Across a broad range of climate and ecosystem types, we found that soil and plant $\delta^{15}\text{N}$ values systematically decreased with increasing mean annual precipitation (MAP) and decreasing mean annual temperature (MAT). Because most undisturbed soils are near N steady state, the observations suggest that an increasing fraction of ecosystem N losses are ^{15}N -depleted forms (NO_3 , N_2O , etc.) with decreasing MAP and increasing MAT. Wetter and colder ecosystems appear to be more efficient in conserving and recycling mineral N. Globally, plant $\delta^{15}\text{N}$ values are more negative than soils, but the difference ($\delta^{15}\text{N}_{\text{plant}} - \delta^{15}\text{N}_{\text{soil}}$) increases with decreasing MAT (and secondarily increasing MAP), suggesting a systematic change in the source of plant-available N (organic/ NH_4^+ versus NO_3^-) with climate. Nitrogen isotopes reflect time integrated measures of the controls on N storage that are critical for predictions of how these ecosystems will respond to human-mediated disturbances of the global N cycle. *INDEX TERMS:* 1040 Geochemistry: Isotopic composition/chemistry; 1615 Global Change: Biogeochemical processes (4805); 1866 Hydrology: Soil moisture; 3322 Meteorology and Atmospheric Dynamics: Land/atmosphere interactions; *KEYWORDS:* nitrogen isotopes, soil nitrogen, plant nitrogen

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1. Introduction

[2] The growing rate of anthropogenically-derived N deposition worldwide [Galloway, 1998] has focused attention on the ability of terrestrial ecosystems to withstand or adapt to this nutrient influx. Ecosystem responses are variable, ranging from enhanced net primary productivity [Vitousek and Howarth, 1991] to, at the other extreme, N saturation with associated declines in productivity [Aber et al., 1989]. There is a growing body of knowledge of how specific ecosystems respond in the short term to these novel N inputs [Vitousek et al., 1997] and yet, in the absence of

many long-term N cycling studies, it is difficult to extend these studies spatially across broad gradients of climate and geography.

[3] Decades of research have shown that the global pattern of soil organic nitrogen (SON) storage in undisturbed ecosystems is a function of a suite of ecosystem variables [Jenny, 1941; Post et al., 1985], among the most important being mean annual precipitation (MAP) and mean annual temperature (MAT) [Jenny, 1928]. Climate affects SON storage by moderating N input and output rates [Olson, 1958]. Input rates are controlled by combined rates of atmospheric deposition [Holland et al., 1999] and N fixation [Cleveland et al., 1999]. Output rates are mediated by microbial N processing and are proportionally related to the total SON pool size and to MAT and MAP. However, patterns of total SON storage versus climate do not by themselves provide insights into the mechanisms that transfer N through the soil (Figure 1).

[4] Here we show, following on previous work [Austin and Vitousek, 1998; Handley et al., 1999; Martinelli et al., 1999; Schuur and Matson, 2001], that the natural abundance of N isotopes in soils and plants is also correlated with environmental variables, most importantly climate, at both local and global scales. In addition, we focus on the isotopic difference between plants and soils with climate. These patterns of N isotopes, when interpreted via mass balance models [Amundson and Baisden, 2000; Brenner et al., 2001], suggest systematic spatial variations in N cycling processes that

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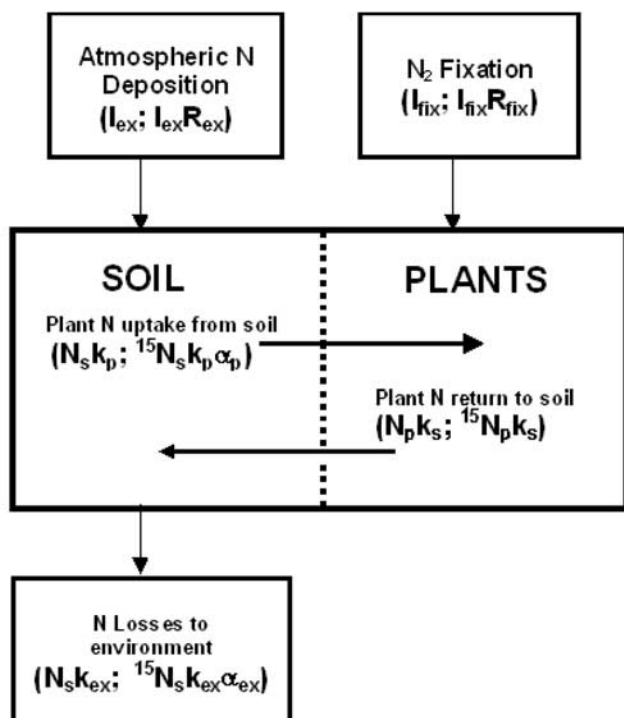


Figure 1. Schematic diagram of soil and plant N and ^{15}N “black box” mass balance model. Terms in parentheses are the flux terms for N and ^{15}N , respectively, and are defined in text.

may in turn be indicative of the response of ecosystems to increased N deposition or other forms of disturbance.

2. Background of N Isotope Research

[5] *Hoering* [1955] first reported the natural abundance of N isotopes in natural compounds using present-day mass spectroscopic technology and standards ($\delta^{15}\text{N}(\text{‰}) = [(R_{\text{sample}}/R_{\text{air}}) - 1] \times 1000$, where $R =$ the $^{15}\text{N}/^{14}\text{N}$ of a sample or standard, and where the standard is atmospheric N_2). Atmospheric $\text{N}_2 = 0.3663$ atom% ^{15}N [*Junk and Svec*, 1958] and is invariable over a wide geographical area [*Mariotti*, 1983]. The use of N isotopes in ecology and agriculture arose primarily through the use of ^{15}N to trace the fate of agricultural N in the environment [*Kohl et al.*, 1971], later subjected to a variety of criticisms [e.g., *Bremner and Tabatabai*, 1973], and the use of plant $\delta^{15}\text{N}$ values to quantify the amount of biologically fixed N utilized by that plant [e.g., *Shearer and Kohl*, 1986]. In the $\delta^{15}\text{N}$ method of measuring biological N fixation, the $\delta^{15}\text{N}$ value of biologically fixed N is well known (0 ± 2 ‰ [*Shearer and Kohl*, 1986]) while the $\delta^{15}\text{N}$ value of the other plant N source (soil N) is highly variable.

[6] In order to better constrain the soil N isotopic signature for N fixation studies, *Shearer et al.* [1978] examined the $\delta^{15}\text{N}$ values of soil surface samples (0–15 cm) from North America. They found that soil $\delta^{15}\text{N}$ values decreased with increasing precipitation, but were unable to offer a hypothesis to account for this trend. Studies of $\delta^{15}\text{N}$ values

of whole soils (below surface horizons) across geographical gradients were not initially as commonly measured. *Mariotti et al.* [1980] examined the plant and soil $\delta^{15}\text{N}$ value variation along an elevation gradient (climosequence) in France, and found that both plant and soil $\delta^{15}\text{N}$ values declined with increasing elevation (and declining temperatures and increasing precipitation), though they did not specifically address the mechanisms responsible for the isotopic variations.

[7] More recent studies of soils and plants have been made along controlled environmental gradients. *Vitousek et al.* [1989] examined soil and plant $\delta^{15}\text{N}$ values along a Holocene to Pliocene time gradient in Hawaii, while *Hobbie et al.* [1998] characterized plant and litter $\delta^{15}\text{N}$ values along a Holocene time gradient in Alaska. *Austin and Vitousek* [1998] measured soil and plant $\delta^{15}\text{N}$ values along a rainfall gradient on young (~3000 years) soils in Hawaii, and *Schuur and Matson* [2001] conducted detailed $\delta^{15}\text{N}$ studies on ecosystems along a rainfall gradient on much older landscapes. Two recent data sets have been compiled of soil and plant isotope patterns [*Handley et al.*, 1999; *Martinelli et al.*, 1999] that add to these climatic and geographical comparisons.

[8] The role of climate on soil and plant $\delta^{15}\text{N}$ values has gained increasing attention. *Austin and Vitousek* [1998] showed that ecosystem $\delta^{15}\text{N}$ values decreased with increasing precipitation, and discussed the likelihood that the forms (and isotopic composition) of N that is lost change systematically as precipitation increases. *Handley et al.* [1999], using a data set gleaned from the literature and unpublished data, generally expanded the importance of water availability on ecosystem $\delta^{15}\text{N}$ values, although their discussion of the strength of the relationship to precipitation was somewhat equivocal. *Handley et al.* [1999] also developed a conceptual and schematic model of soil N cycling and noted that the cause of the geographical patterns of soil $\delta^{15}\text{N}$ values likely resides in differences in the isotopic composition of N leaving the system. *Martinelli et al.* [1999] assembled a large data set in order to compare the $\delta^{15}\text{N}$ values of soils and plants in tropical versus temperate forests. They noted that tropical forest ecosystems are commonly enriched in ^{15}N relative to their temperate counterparts, and attributed these differences to the differential importance of N as a limiting plant element in the tropics versus temperate regions, and to the increased “openness” (rates of N input/output versus internal N cycling) of the N cycle in tropical forests.

[9] *Amundson and Baisden* [2000] and *Brenner et al.* [2001] presented a simplified ecosystem N and ^{15}N mass balance model that contains elements of previous models [e.g., *Handley et al.*, 1999; *Herman and Rundel*, 1989; *Shearer et al.*, 1974], but which differs due to its focus only on system inputs/outputs, the only processes which can ultimately alter the isotopic composition of an ecosystem (Figure 1). The mass balance expressions for total N in the soil/plant system are

$$\frac{dN_s}{dt} = \underbrace{I_{\text{ex}} - k_{\text{ex}}N_s}_{\text{environment}} + \underbrace{k_s N_p - k_p N_s}_{\text{plants}} \quad (1)$$

$$\frac{dN_p}{dt} = \underbrace{k_p N_s - k_s N_p}_{\text{soil}} + \underbrace{I_{\text{fix}}}_{\text{N-fixation}} \quad (2)$$

where N_s , N_p = soil and plant N pools (kg m^{-2}), respectively; I_{ex} , I_{fix} = atmospheric N inputs ($\text{kg m}^{-2} \text{yr}^{-1}$) and biological N fixation, respectively; k_{ex} = soil N loss decay constant (yr^{-1}), k_p = plant available N decay constant, and k_s = constant describing annual N return to the soil from plants.

[10] The expressions that define ^{15}N are

$$\frac{d^{15}N_s}{dt} = \underbrace{I_{\text{ex}}R_{\text{ex}} - k_{\text{ex}}\alpha_{\text{ex}}^{15}N_s}_{\text{environment}} + \underbrace{k_s^{15}N_p - k_p\alpha_p^{15}N_s}_{\text{plants}} \quad (3)$$

$$\frac{d^{15}N_p}{dt} = \underbrace{k_p\alpha_p^{15}N_s - k_s^{15}N_p}_{\text{soil}} + \underbrace{I_{\text{fix}}R_{\text{fix}}}_{\text{N-fixation}} \quad (4)$$

where $R = ^{15}\text{N}/^{14}\text{N}$ of subscripted flux or pool and $\alpha =$ isotopic fractionation factor (unitless) accounting for isotopic discrimination during subscripted process.

[11] The steady state solution of this model for soil is (see *Brenner et al.* [2001] for more details)

$$R_s = \frac{R_{\text{ex}}I_{\text{ex}} + R_{\text{fix}}I_{\text{fix}}}{\alpha_{\text{ex}}(I_{\text{ex}} + I_{\text{fix}})} \equiv \frac{\bar{R}_{\text{total}}}{\alpha_{\text{ex}}} \quad (5)$$

where \bar{R}_{total} is the weighted mean isotopic ratio of inputs, and for plants:

$$R_p = \frac{k_p\alpha_p N_s R_s + I_{\text{fix}}R_{\text{fix}}}{k_p N_s + I_{\text{fix}}} \quad (6)$$

which, if no N fixation occurs, equals

$$R_p = \alpha_p R_s. \quad (7)$$

[12] One of the key implications of this model is that the isotopic composition of the total soil N pool at steady state is determined only by the isotopic composition of the inputs and losses. This straightforward mathematical result has been recognized by some [*Handley et al.*, 1999], but the concept is obscured with the rates of N cycling and loss in other papers. Virtually all soil systems, with the exception of those in hyperarid climates that have no leaching [*Böhlke et al.*, 1997], are open and have N losses that eventually approach input rates. The key factor controlling the steady state isotopic composition of soils is the value of the fractionation factor α_{ex} . Along these lines, *Austin and Vitousek* [1998] defined ecosystem openness in terms of the form (and isotopic composition) of N lost, a definition that is consistent with isotopic mass balance.

[13] The mass balance model considers the integrated soil N pool and does not address the ^{15}N variations that may occur with depth. Observations in a variety of climates suggest that the $\delta^{15}\text{N}$ value of soil N can vary in a number of ways with depth: (1) Along a montane elevation gradient in Hawaii, there was little or no depth variation [*Uebersax*, 1996], (2) in gravelly desert soils with irregular root distributions, $\delta^{15}\text{N}$ varied randomly (in concert with roots)

with depth [*Brenner*, 1999], and (3) most commonly, in grassland soils, $\delta^{15}\text{N}$ values display a remarkably consistent exponential increase with depth [*Mariotti et al.*, 1980; *Brenner et al.*, 2001]. Modeling these patterns requires the inclusion in mass balance models of (1) transport processes, (2) depth-dependent plant N inputs, and (3) multiple N pools. To our knowledge, only models describing the exponential increase in ^{15}N with depth have been presented [e.g., *Amundson and Baisden*, 2000; *Baisden*, 2000; *Baisden et al.*, 2002]. While these models offer mechanistic insights into soil N processing, data to constrain the models (particularly soil N transport rates) is difficult to obtain. In summary, the black box model is particularly appropriate for comparative analyses of commonly available data collected across broad geographical gradients, the objective of this paper.

3. Methods

[14] We combined new data from Hawaii and Tanzania [*Uebersax*, 1996], French Polynesia [*Matzek*, 1999], California and Nevada [*Brenner*, 1999], and recent compilations of global soil and plant $\delta^{15}\text{N}$ values [*Handley et al.*, 1999; *Martinelli et al.*, 1999] and other data from the literature (see supplementary data¹). For the new data, soils were sampled by horizon. Samples (depending on remoteness of the site) were either air or freeze dried, and ground. Samples from Hawaii and Tanzania were reacted with 1 N HCl to remove carbonates, while those of French Polynesia were acidified with 0.5 N HCl. The C and N content was measured on a Carlo-Erba elemental analyzer. Samples from Hawaii and Tanzania were combusted in sealed tubes [*Kendall and Grim*, 1990], and the purified N_2 isotopically analyzed on a VG Prism isotope ratio mass spectrometer. Samples from California, Nevada, and French Polynesia were isotopically analyzed via elemental analyzer/continuous flow mass spectrometry (VG Optima and Europa 20/20). Plant tissue samples were analyzed by the same methods. Soil bulk density, where possible, was measured on soil cores of known volumes. The weighted mean (by depth, N content, bulk density) $\delta^{15}\text{N}$ value in all soils was calculated to depths of both 10 and 50 cm. Many reports from the literature lack bulk density (and commonly total N), and thus the weighted means in these data were based only on horizon thickness.

[15] Previous soil data analyses have reported the upper 10 cm of soils [*Handley et al.*, 1999]. We used studies reporting soil $\delta^{15}\text{N}$ values to 50 cm because that quantity gives a more integrated view of total soil N storage and cycling. Nonetheless, soil $\delta^{15}\text{N}$ values to 10 cm are well correlated to those of 50 cm ($r^2 = 0.85$, $n = 50$), but are about 1.4 ‰ more negative (y intercept) due to the commonly observed increase in $\delta^{15}\text{N}_{\text{soil}}$ with depth. If multiple soils were sampled within the same climatic zone, the values were averaged to eliminate overrepresentation artifacts. Statistical

¹ Supporting material is available via Web browser or via Anonymous FTP from <ftp://ftp.agu.org>, directory "append" (Username = "anonymous", Password = "guest"); subdirectories in the ftp site are arranged by paper number. Information on searching and submitting electronic supplements is found at http://www.agu.org/pubs/esupp_about.html.

Table 1. Summary of Regression Models, Where Parameters are Reported Only in Cases Where $p < 0.10^a$

Ecosystem Property	Intercept	MAT,		Model r^2	n
		C	MAP, mm		
Soil $\delta^{15}\text{N}$ (10)	3.1985	0.1340	-0.0005	0.11	85
Soil $\delta^{15}\text{N}$ (50)	3.8864	0.1680	-0.007	0.19	47
Soil $\delta^{15}\text{N}$ (50) climosequences	4.3266	0.2048	-0.0012	0.39	29
Plant $\delta^{15}\text{N}$	0.0697	0.1548	-0.0016	0.34	106
$\Delta_{\text{soil-plant}}$ (10)	-4.6926	0.0911	-0.0007	0.13	49
$\Delta_{\text{soil-plant}}$ (50)	-7.2813	0.1718	-	0.23	30
$\Delta_{\text{soil-plant}}$ (50) climosequences	-8.4012	0.1852	-	0.37	21

^aData for models are discussed in section 3.

analyses of the data were performed using JMP[®] statistical software. The resulting regression equations were illustrated spatially using global mean annual temperature and precipitation (0.5×0.5 degree grids) data compiled by *Willmott and Matsuura* [2000].

4. Results and Discussion

4.1. Soil and Plant $\delta^{15}\text{N}$ Values Versus Climate

[16] We began by further testing the hypothesis that climate, especially precipitation, exerts a first-order control on

ecosystem $\delta^{15}\text{N}$ values as suggested in previous papers [e.g., *Mariotti et al.*, 1980; *Austin and Vitousek*, 1998; *Handley et al.*, 1999; *Amundson and Baisden*, 2000; *Schuur and Matson*, 2001]. In the regression analyses, MAT and MAP were chosen as the independent variables representing climate because of their well-known controls on N cycling processes as discussed above. While the inclusion of latitude improved model explanatory capabilities in some cases (as noted by *Handley et al.* [1999]), the general relationship between climate and latitude caused us to drop latitude as an independent variable.

[17] Our analysis shows that $\delta^{15}\text{N}_{\text{soil}}$ decreases with decreasing MAT and (less significantly) with increasing MAP (Table 1). The r^2 of the climate to soil $\delta^{15}\text{N}$ relationships increased when soil to 50 cm was used (versus 10 cm depth) and when studies designed explicitly to examine climate effects on soil N (climosequences, Table 2) were used. The regression model that described the “climosequence” data was then used to portray spatial trends in soil $\delta^{15}\text{N}$ values (Figure 2a). The global trends resulted in strong latitudinal banding, with high northern latitude ecosystems having the most depleted soil $\delta^{15}\text{N}$ values and arid and tropical zones having the most positive soil $\delta^{15}\text{N}$ values. We note that while this global perspective is admittedly generated from a small data set, the general trends with climate

Table 2. N Isotope Composition of Soil and Plant N for Climosequences Analyzed in Table 1

Site	Country	Vegetation	Elevation, m	MAT, C	MAP, mm	Soil $\delta^{15}\text{N}$	Soil $\delta^{15}\text{N}$	$\delta^{15}\text{N}$ Plants	$\Delta_{\text{plant-soil}}$	$\Delta_{\text{plant-soil}}$	Reference ^a
						to 10 cm, ‰	to 50 cm, ‰		to 10 cm, ‰	to 50 cm, ‰	
Kyle Canyon, NV	USA	creosote	840	18	160						
		joshua tree	1400	14	326	5.9	6.8	2.9	-3	-3.9	1
		pinyon-juniper	1750	12	436	3.7	4.9	-2.2	-5.9	-7.1	
		ponderosa	2150	9	549	3.8	4	-2.8	-6.6	-6.8	
Sierra Nevada, CA	USA	oak grassland	470	18	330	1.5	2.8	-1.9	-3.4	-4.7	
		oak woodland	730	15	570	2.5	4.3				
		mixed conifer	1240	12	910	0.8	2.6	-4.5	-5.3	-7.1	
		mixed conifer	1950	8	1055	2.7	3.4				
		mixed conifer	2890	3	1270	2.5	4.7	-2.4	-4.9	-7.1	
		montane forest	1829	19	1970	2.2	3.6	-1.2	-3.4	-4.8	
Mt. Kilimanjaro	Tanzania	montane forest	2454	14	1670	2.3	4.5	-1.1	-3.4	-5.6	2
		grassland	2545	14	1570	2.1	4.9	-1.5	-3.6	-6.4	
		grassland	2990	12	1320	3.6	5.4	-2.1	-5.7	-7.5	
		heather	3505	9	1040	4.8	6	-3.1	-7.9	-9.1	
			3901	6	820	4.9	5.9				
Kohala Mountains	Hawaii	piligrass, keawe	122	23	180	12.08	12.5				2
		buffelgrass, lantana, keawe	674	20	570	13.25	13.1				
		pasture with kikuyu grass	992	18	1060	9.18	8.4				
		pasture with kikuyu grass	1200	17	2500	5.43	4.7				
Maui, Hawaii	USA	ohia, fern-trees	1254	17	3000	3.07	1.7				3
		metrosideros forest	1370	16	2209	5.79	5.17	2	-3.79	-3.17	
		metrosideros forest	1370	16	2435	6.12	4.47	1	-5.12	-3.47	
		metrosideros forest	1370	16	2759	4.87	5.61	-1	-5.87	-6.61	
		metrosideros forest	1320	16	3338	7.35	6.27	0.8	-6.55	-5.47	
		metrosideros forest	1300	16	4030	3.2	3.46	-2	-5.2	-5.46	
France	S Geneva	metrosideros forest	1270	16	5066	2.95	0.65	-5	-7.95	-5.65	4
		not reported	1100	7 ⁵	1410 ⁵	4.14	5.1	-1.9	-6.04	-7	
			1440	5	1683	4.27	4.8	-1.8	-6.07	-6.6	
			1600	4	1811	2.66	3.8	-5	-7.66	-8.8	
			1800	3	1972	1.55	3	-2.8	-4.35	-5.8	

^a1, *Brenner* [1999]; 2, *Uebersax* [1996]; 3, *Schuur and Matson* [2001]; 4, *Mariotti et al.* [1980]; 5, climate data for gradient estimated from regression of MAT and MAP versus elevation for nearby locations.

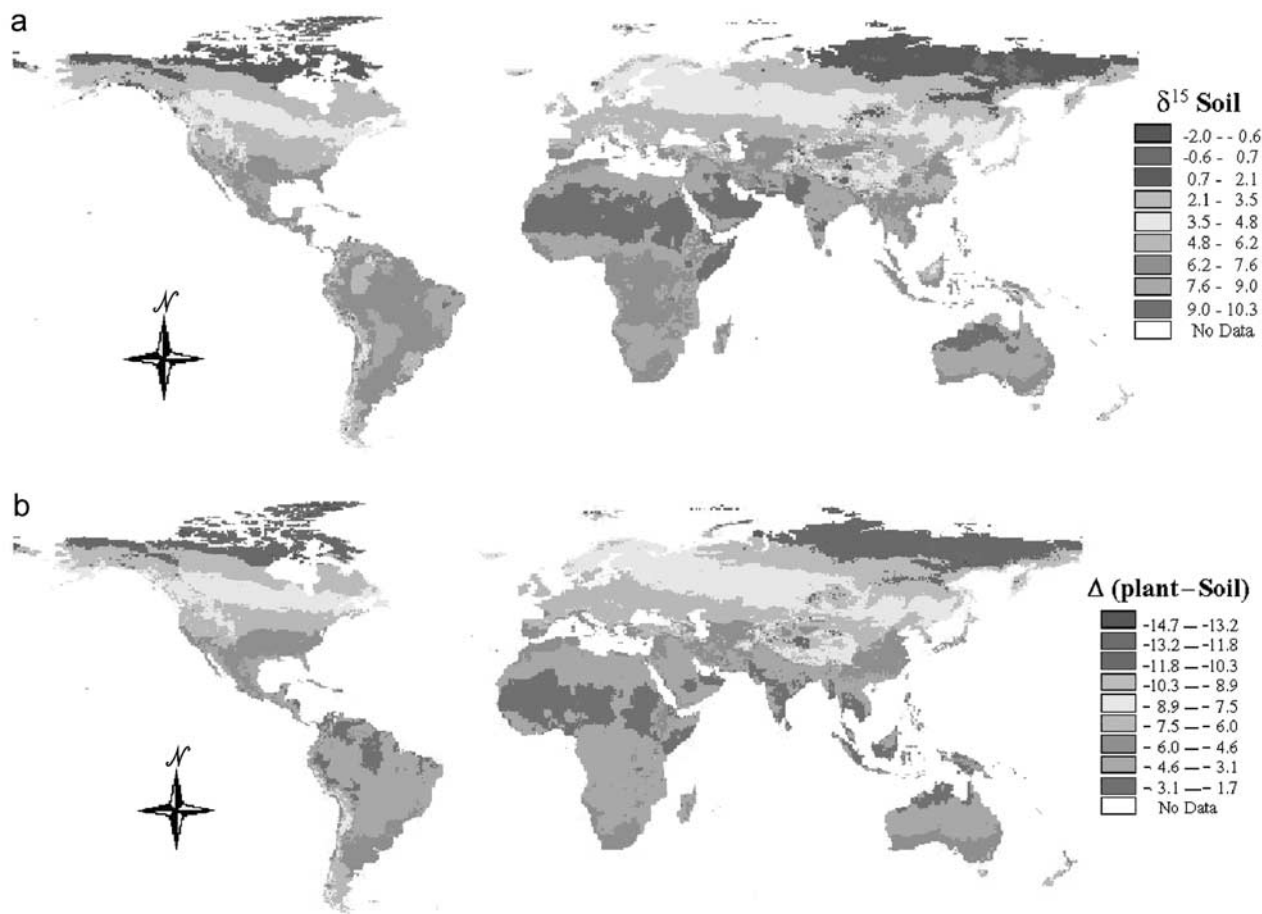


Figure 2. (a) Estimated geographical distribution of soil $\delta^{15}\text{N}$ values to 50 cm and (b) estimated geographical trends in $\Delta\delta^{15}\text{N}_{\text{plant-soil}}$. Global mean annual temperature and precipitation (0.5×0.5 degree grids) data are obtained from *Willmott and Matsuura* [2000]. See color version of this figure at back of this issue.

would also occur with the larger data set for soils collected to 10 cm (Table 1). Therefore, pending the availability of more soil ^{15}N analyses, the present Figure 2 represents our best estimate of trends (but possibly not absolute values) in global soil $\delta^{15}\text{N}$ values.

[18] In interpreting these apparent climatic trends, we begin with the assumption [*Handley et al.*, 1999] that the $\delta^{15}\text{N}$ value of N inputs to the soils varies within a restricted range geographically. Clearly this hypothesis requires long-term data collected at widely dispersed sites to fully support it. It is known that the $\delta^{15}\text{N}$ value of atmospherically derived N exhibits large temporal and spatial variations [*Kendall*, 1998; *Heaton*, 1987], and (especially downwind of human impacted areas) that nitrate is commonly enriched in ^{15}N relative to that of ammonium [*Kendall*, 1998]. Nonetheless, when means of annual inputs are calculated, it has been suggested that inputs range between -3 and $+3\text{‰}$ [*Handley et al.*, 1999]. Whether this mean applies to the entire globe remains uncertain, but the hypothesis of a restricted range of inputs for individual climosequences used in our regression analysis is supportable. All these sequences were established along elevation gradients, where sites are within 50 km or less of each other.

[19] If the range of $\delta^{15}\text{N}$ values of N inputs is restricted globally, then the variation in soil $\delta^{15}\text{N}$ values entirely reflects variations in α_{ex} (equation (5)). The data (Table 1) suggest that as MAP increases and MAT decreases (1) α_{ex} apparently approaches 1, (2) the steady state $\delta^{15}\text{N}$ value of soil approaches that of estimated atmospheric N inputs (as required by equation (5)), and (3) the isotopic composition of losses equal that of the soil N. Nonfractionated losses (relative to the soil N pool) may occur in the form of dissolved organic N (DON) and/or particulate N in eroded soil material, though there have been few published measurements to date of the isotopic composition of DON [*Feuerstein et al.*, 1997], and none have been directly applied to soil processes. In the Great Lakes, *Feuerstein et al.* [1997] noted that DON was a few per mil more negative than coexisting particulate organic matter in the water column. Recently, *Perakis and Hedin* [2002] have shown that in middle- to high-latitude South American temperate forests, the primary form of N loss from the soils is DON (up to about $3 \text{ kg N ha yr}^{-1}$). This follows the work of *Hedin et al.* [1995], who showed that along an elevation gradient on the southern Chilean coast, the ratio of NO_3^-/DON and $\text{NO}_3^-/\text{NH}_4^+$ decreased system-

atically with increasing elevation (and decreasing temperature). These findings are consistent with the soil isotopic trends derived here if DON losses are relatively non-fractionating. In contrast, the apparent propensity of ecosystems to lose ^{15}N -depleted forms of N (relative to the soil N pool) with decreasing MAP and increasing MAT is striking. These ^{15}N -depleted forms of N loss might be expected to include NO_3^- , N_2O [Pérez *et al.*, 2000], and other mineralized forms of N, all of which are thought to be ^{15}N -depleted relative to total soil N [Shearer and Kohl, 1986]. However, complications to this interpretive scenario occur when kinetic limitations or competing N pathways cause the observed fractionation to be different than optimal values (see Shearer and Kohl [1986] for expanded discussion). Regardless of the form of N lost from soils, there is a consistent trend in the apparent isotopic composition of the loss (relative to the soil N pool) with climate.

[20] Plant $\delta^{15}\text{N}$ values decreased with increasing MAP and with decreasing MAT (Table 1), like the soils, but the magnitude of the difference between plant and soil $\Delta\delta^{15}\text{N}$ values ($\Delta\delta^{15}\text{N}_{\text{plant-soil}}$) decreased with increasing MAT (and less strongly with decreasing MAP) (Table 1, Figure 2b). We note that plant $\delta^{15}\text{N}$ values can vary up to several per mil with season, plant part, and between different types of plants at the same site [Handley *et al.*, 1999]. Most analyses in the data set used here are foliar tissue, and minimize the plant tissue effect. While recognizing the potential variability in plant isotope values, the $\delta^{15}\text{N}$ value of non-N fixing plants should, as we hypothesize in equation (4), reflect the isotopic composition of mineral forms of N derived from the soil N pool (e.g., α_p). Therefore, the simple measure ($\Delta\delta^{15}\text{N}_{\text{plant-soil}}$, which is equivalent to $10^3 \ln \alpha_p$, might be interpreted as the isotopic composition of plant-available N provided that isotopic discrimination does not occur during plant uptake and assimilation. There is presently disagreement over the important issue of assimilation-based N isotope discrimination. Evans *et al.* [1996] reported little isotopic discrimination during the uptake of either NO_3^- or NH_4^+ by tomatoes at concentrations comparable to field conditions. In contrast, Yoneyama *et al.* [2001] and others [e.g., see Högberg, 1997] report small discrimination during the uptake of NO_3^- by rice at field concentrations, but relatively large discriminations during NH_4^+ uptake (with discrimination increasing with concentration). Clearly, this is an area deserving of additional work. Even if assimilation-based discrimination does not occur, the isotopic composition of plant available N deduced from ($\Delta\delta^{15}\text{N}_{\text{plant-soil}}$ is only suggestive of N forms. For example, an increase in ($\Delta\delta^{15}\text{N}_{\text{plant-soil}}$ may be interpreted as a shift in the N source for plants from organic N or NH_4^+ (which may be only a few ‰ more negative than soil N) to NO_3^- , which may be about 10‰ or more negative than the organic N from which it is derived (see Shearer and Kohl [1986] for summary of observed fractionation factors for these processes).

[21] The apparent $\Delta\delta^{15}\text{N}_{\text{plant-soil}}$ trend with changes in MAT can be reconciled with hypothesized shifts in soil N economies from organic/ NH_4^+ -dominated in cool temperate forests [e.g. Hedin *et al.*, 1995] to NO_3^- -dominated in

tropical forests [Aber, 1992; Matson *et al.*, 1999]. In cold ecosystems with large differences in $\Delta\delta^{15}\text{N}_{\text{plant-soil}}$, two mechanisms may be responsible: (1) The organic N/ NH_4^+ plant-available sources in northern latitudes are ^{15}N -depleted and/or (2) isotopic discrimination during NH_4^+ uptake is occurring. A mechanism consistent with (1) that has been recently proposed [Hobbie *et al.*, 1999, 2000] is that plant N sources in northern latitudes may be depleted in ^{15}N through mycorrhizal fungi/plant interactions (reviewed by Högberg [1997]). The possibility that the second mechanism occurs was discussed above. In contrast, the small $\Delta\delta^{15}\text{N}_{\text{plant-soil}}$ at high temperatures may be explained by increased microbial competition with plants for N with increasing temperature, resulting in a relatively low concentration of mineral N available as NH_4^+ and with subsequent isotopic enrichment of any NO_3^- that is plant available. Alternatively, denitrification or other competing processes may enrich remaining soil NH_4^+ or NO_3^- with increasing temperature, resulting in low plant-soil values.

[22] What is particularly striking is the apparent independent behavior of both α_p (as estimated by $\Delta\delta^{15}\text{N}_{\text{plant-soil}}$ and α_{ex} with climate [see also Schuur and Matson, 2001]. The available data suggest that as MAP increases and MAT decreases, the isotopic composition of N leaving the soil approaches that of the soil N pool (e.g., reflecting little isotopic fractionation) while the form of N taken up by plants becomes increasingly depleted relative to the soil N pool. Assuming that the trends reflect true values of plant available N, the most likely explanation of this apparently incompatible relationship is that plants, and all ecosystem N consumers, become increasingly efficient at mineral N cycling with increasing moisture [Austin and Vitousek, 1998] such that only non plant-available forms of N are subject to leaching or erosional losses.

4.2. Other Controls on Ecosystem $\delta^{15}\text{N}$ Values

[23] The modest r^2 of the statistical relations between plant/soil $\delta^{15}\text{N}$ values and climate (Table 1) indicates a possible suite of other controls on ecosystem $\delta^{15}\text{N}$ values. One obvious source of variability, already discussed, are spatial variations in the isotopic composition of atmospheric N inputs. Yet, beyond this explanation are other controls (ecosystem state factors [Jenny, 1941]) on ecosystem N cycling that have been shown or are suspected of exerting secondary (or even primary) controls on total soil N and $\delta^{15}\text{N}$ values. The known ranges of the effects of each of these factors on soil $\delta^{15}\text{N}$ values (discussed below) are illustrated in Figure 3.

[24] Soil age is an important control on soil and plant $\delta^{15}\text{N}$ values for two reasons. First, for sites not yet at steady state, the $\delta^{15}\text{N}$ value of the soil is dependent on soil age and the kinetics of N cycling (equations (1)–(4)). There are, to our knowledge, no detailed studies of soil and plant N isotope variation over timespans pertinent to the approach to steady state (10^2 to 10^3 years based on soil N chronosequence data [Syers *et al.*, 1970]). Hobbie *et al.* [1998, 1999] examined plant and soil organic horizons (as opposed to mineral soil horizons emphasized here) in Alaska and found pronounced trends in plants over a 250-year timespan, with the plant trend dependent on whether the plant derived N

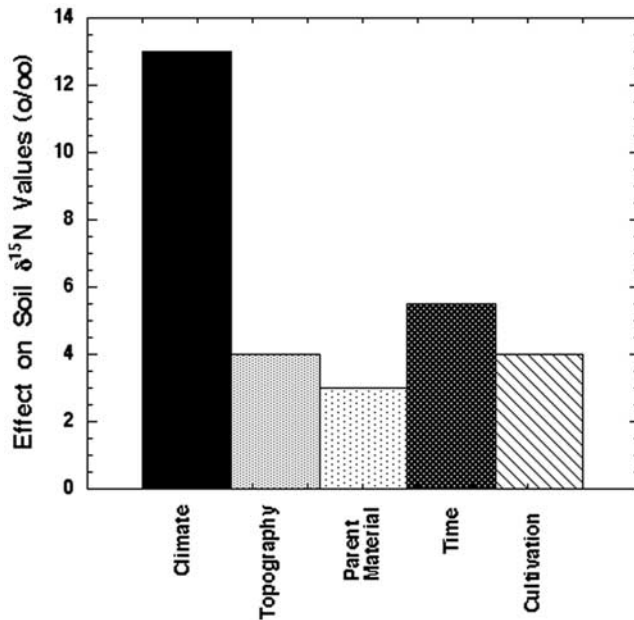


Figure 3. Estimated range in the effect of individual state factors [Jenny, 1941] on the $\delta^{15}\text{N}$ value of soil N. Sources of values illustrated are discussed in the text.

from soil N, N fixation, or symbiotic relations with mycorrhizal fungi.

[25] Soil age also exerts an influence on ecosystem $\delta^{15}\text{N}$ values over longer timescales. It has been demonstrated convincingly in Hawaii [Vitousek *et al.*, 1989; Martinelli *et al.*, 1999], and also California [Brenner *et al.*, 2001], that the $\delta^{15}\text{N}$ values of soils and plants vary as sites age from 10^3 to 10^6 years. All these sites may be viewed as having obtained their own steady state, but the N cycling processes differ between sites due to changes in the relative importance of N versus P (or other elements) as limiting nutrients versus time. It has been hypothesized for the chronosequence in California [Brenner *et al.*, 2001] that as P becomes plant limiting (due to weathering losses of this element), N becomes an “excess” element (which is reflected in elevated NO_3^- concentrations in soil lysimeters) [White and Brantley, 1995], and sites experience larger amounts of mineral N (and ^{15}N depleted) forms of loss. In summary, because the Earth’s surface is a complex suite of deposits and outcrops of greatly varying ages, it is likely that age plays a critical role in ecosystem N isotope variability. The largest reported range in soil $\delta^{15}\text{N}$ values caused by soil age (Hawaii) is about 5.5‰ [Martinelli *et al.*, 1999].

[26] Topographic position plays a key role in N cycling [Schimel *et al.*, 1985], and preliminary work shows it affects soil $\delta^{15}\text{N}$ values [Karamanos and Rennie, 1980a; Sutherland *et al.*, 1993]. First, topographic positions subject to water collection and anaerobic conditions may exhibit denitrification and the residual accumulation of ^{15}N [Karamanos and Rennie, 1980b]. However, more generally, convex portions of the landscape are subject to pervasive erosive removal of soil material and undergo constant rejuvenation [McKean *et al.*, 1993; Heimsath *et al.*,

1997]. The net rates of soil movement on slopes are proportional to slope [Heimsath *et al.*, 1997]:

$$Q_s = D(-dz/dx) \quad (8)$$

where Q_s = sediment flux ($\text{cm}^2 \text{ yr}^{-1}$) and D = soil diffusivity ($\text{cm}^2 \text{ yr}^{-1}$). Briefly, the slope of an upland soil is proportional to the soil’s residence time (τ) as follows:

$$\tau \propto \frac{\text{SoilThickness}}{\text{SedimentFlux}} \propto \frac{1}{\text{slope}}. \quad (9)$$

[27] These relationships suggest that steeply sloping soils, which have low residence times, should be far from the steady state N (equation (1)) and $\delta^{15}\text{N}$ values (equation (3)) for level soils at the same location, and should have $\delta^{15}\text{N}$ values that approach atmospheric inputs. There are presently no published data to test this hypothesis. Here, we present part of a data set for a small zero order watershed in the central California coast range (Figure 4). At this site, previous research has shown that soil transport is proportional to slope [Heimsath *et al.*, 1997], indicating that equation (9) is appropriate to interpret the data. The soils sampled follow a trend of decreasing $\delta^{15}\text{N}$ values with increasing slope (decreasing residence time) (Figure 4). The $\delta^{15}\text{N}$ value of the surface horizon, as residence time approaches 0, is 2.3‰ and similar to the presumed range in atmospheric N inputs. The y-intercept for the second soil horizon is enriched in ^{15}N ($\delta^{15}\text{N} = 3.9\%$), suggesting (as expected) that a portion of the N inputs to this horizon are derived from microbially altered N transported downward from the overlying horizon. In summary, these preliminary data suggest that hillslope position can impart up to a 2‰ variation in soil $\delta^{15}\text{N}$ values at a given location. In a

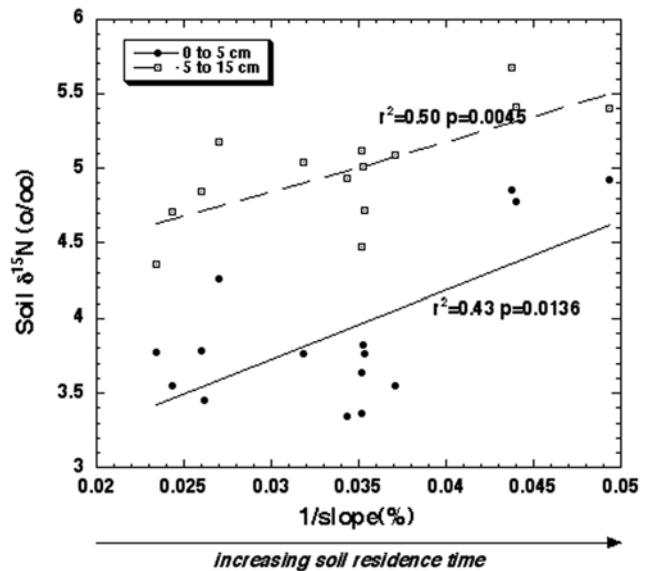


Figure 4. Observed relationship between the $\delta^{15}\text{N}$ value of soil N and $1/\text{slope}$ on the convex portions of a zero-order watershed in Marin County, California. Slopes were calculated based on elevation data and a kriging algorithm.

topographic study in Saskatchewan that included both erosional landscape segments and the wetter depositional areas, the total range in soil $\delta^{15}\text{N}$ values was reported to be about 4‰ [Sutherland *et al.*, 1993].

[28] The nature of the soil parent material has been shown to exert a control on soil and plant $\delta^{15}\text{N}$ values. So-called “white sand” soils of the tropics, which are N limited, support plants lower in N, and depleted in ^{15}N , relative to other soils in the region [Martinelli *et al.*, 1999]. Matzek [1999] showed that in the island ecosystems of French Polynesia, soils and plants on coral substrate had more negative $\delta^{15}\text{N}$ values than nearby ecosystems on comparably aged volcanic alluvium due to what was suspected to be greater DON losses. While there are not, to our knowledge, other explicit parent material comparisons on soil N isotopes, the wide variety of rock and sediment types globally suggest that this variable will exert considerable influence on N isotopes in soils and plants. Based on the work of Matzek [1999], the parent material effect on soil $\delta^{15}\text{N}$ values at a given location is at least 3‰.

[29] Finally, human activity has caused a wholesale disruption of the global N cycle [Vitousek *et al.*, 1997] and aspects of its N isotope composition. Because cultivation greatly accelerates loss of soil N through enhanced decomposition rates, there can be a pronounced increase in the $\delta^{15}\text{N}$ value of the remaining soil N in certain soil N pools, although isotopic changes in the total N pools are not necessarily noted [Tiessen *et al.*, 1984; Shearer and Kohl, 1986]. Riga *et al.* [1970] report up to a 3‰ increase in soil $\delta^{15}\text{N}$ values to 60 cm due to cultivation. The addition of N fertilizers derived from atmospheric N_2 , or manures (which are commonly greatly enriched in ^{15}N because of ammonia volatilization) also have an impact on soil and crop isotopic values. Riga *et al.* [1970] showed that fertilization with manure can increase soil $\delta^{15}\text{N}$ values by about 1‰ relative to treatments without manures.

[30] While our analysis here focused deliberately on “undisturbed” ecosystems, the impact of humans on the N isotope biogeochemistry of these remaining parts of the planet is deserving of greater scrutiny. Most “undisturbed” ecosystems have experienced increased rates of atmospheric N deposition [Holland *et al.*, 1999], likely driving some systems out of steady state [Vitousek *et al.*, 1997; Perakis and Hedin, 2002]. It has been proposed that in temperate forests, the increasing N inputs result in an increased NO_3^-/DON ratio of N losses from the soils [Perakis and Hedin, 2002; van Breeman, 2002], a process that likely affects the isotopic composition of the total soil and plant N pool. Additionally, the changes that atmospheric pollution have imparted on the long-term $\delta^{15}\text{N}$ value of N deposition is not well known [Kendall, 1998].

4.3. Significance of Observations

[31] The climatic and spatial trends of soil and plant $\delta^{15}\text{N}$ values we developed here are consistent with interpretations from previous work and data analyses, although it is clear that additional ecosystem measurements along well-constrained environmental gradients will greatly enhance the details of the climatic trends. However, even at this stage of our knowledge, it is important to address how these appa-

rent ecosystem $\delta^{15}\text{N}$ patterns might prove useful in environmental and ecological research.

[32] We hypothesize that as an integrator of long term N cycling [Robinson, 2001], N isotopes are indicators of systematic variations in ecosystem N cycling processes and efficiencies, and to the resilience of an ecosystem to enhanced N deposition through anthropogenic activities. Aber [1992] reviewed attributes of N-limited versus N-saturated ecosystems in the context of their response to atmospheric N deposition. In terms of characteristics relevant to N isotopes [Aber, 1992, Table 1], N-limited ecosystems are characterized by (1) NH_4^+ (versus NO_3^-) uptake by plants, (2) high rates of NO_3^- and NH_4^+ immobilization, (3) high fraction of soil fungi that are mycorrhizal, and (4) very low rates of N_2O production. Characteristics 2 and 4, which are considered characteristic of many temperate forests [Martinelli *et al.*, 1999], are consistent with the spatial patterns of low soil $\delta^{15}\text{N}$ values in cool, moist environments (and the opposite trends in tropical latitudes) (Figure 2a). Characteristics 1 and 3, considered characteristic of temperate to boreal ecosystems [Martinelli *et al.*, 1999; Höberg, 1997], are consistent with the trends in ($\Delta\delta^{15}\text{N}_{\text{plant-soil}}$ with climate (Figure 2b). Additionally, Aber [1992] proposed that high soil C/N ratios are indicative of N-limited ecosystems. There is a strong relationship between soil C/N ratios derived from work by Post *et al.* [1985] and climate ($r^2 = 0.47$, $p < 0.01$, $n = 26$), and there is an inverse relationship ($r^2 = 0.38$, $p < 0.01$, $n = 30$) between total soil C/N ratios and mean soil $\delta^{15}\text{N}$ values to 50 cm (using our climosequence data).

[33] Therefore, we argue that the $\delta^{15}\text{N}_{\text{soil}}$ and $\Delta\delta^{15}\text{N}_{\text{plant-soil}}$ patterns (Figures 2a and 2b) accurately portray the sensitivity of ecosystems to increased rates of anthropogenically derived N, with those ecosystems with the most negative $\delta^{15}\text{N}$ soil values and the largest $\Delta\delta^{15}\text{N}_{\text{plant-soil}}$ being the least susceptible to immediate negative impacts of increased N deposition. While the locations and spatial patterns of sensitive ecosystems illustrated by N isotopes are not novel, they do illustrate that N isotopes, which integrate an array of properties and processes of N-sensitive ecosystems [Aber, 1992], are a useful tool in broad scale, or possibly site-specific, assessments of ecosystem N status.

[34] Beyond the possibly direct link to N sensitivity, the N isotope patterns and relationships outlined here suggest an array of fruitful experiments and observations to test or determine the processes behind the patterns. Some of the obvious avenues of research include (1) spatially and temporally broad measures of the $\delta^{15}\text{N}$ value of total N deposition, as well as the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of NO_3^- ; (2) well-designed temporal observations of the isotopic composition of NH_4^+ , NO_3^- , N_2O and other species in soil waters of undisturbed terrestrial ecosystems to better constrain the relation of N fluxes to integrated soil $\delta^{15}\text{N}$ values; (3) experiments on a broader range of naturally occurring plants (as opposed to select agricultural cultivars) to determine the degree of isotopic discrimination during plant N assimilation; and (4) further studies on the role and extent of mycorrhizal fungi on N uptake and isotope discrimination. Study of these topics will not only illuminate N isotope

patterns, but will provide a more mechanistic understanding of the terrestrial N cycle.

5. Conclusions

[35] Our data analysis indicates that climate plays a significant role in soil N and N isotope processing and retention. The presence, and explainable nature, of global $\delta^{15}\text{N}$ patterns in soils and plants provides insights into the cycling of terrestrial N and ecosystem response to climatic change and to increasing fluxes of anthropogenically derived N. While the data indicate that there is a global pattern of ecosystem $\delta^{15}\text{N}$ values that appears to be driven primarily by climate, our understanding of the mechanisms behind the processes is in its infancy. Multiple opportunities for research exist to test hypotheses about terrestrial N cycling that will greatly refine our understanding of these N isotope patterns.

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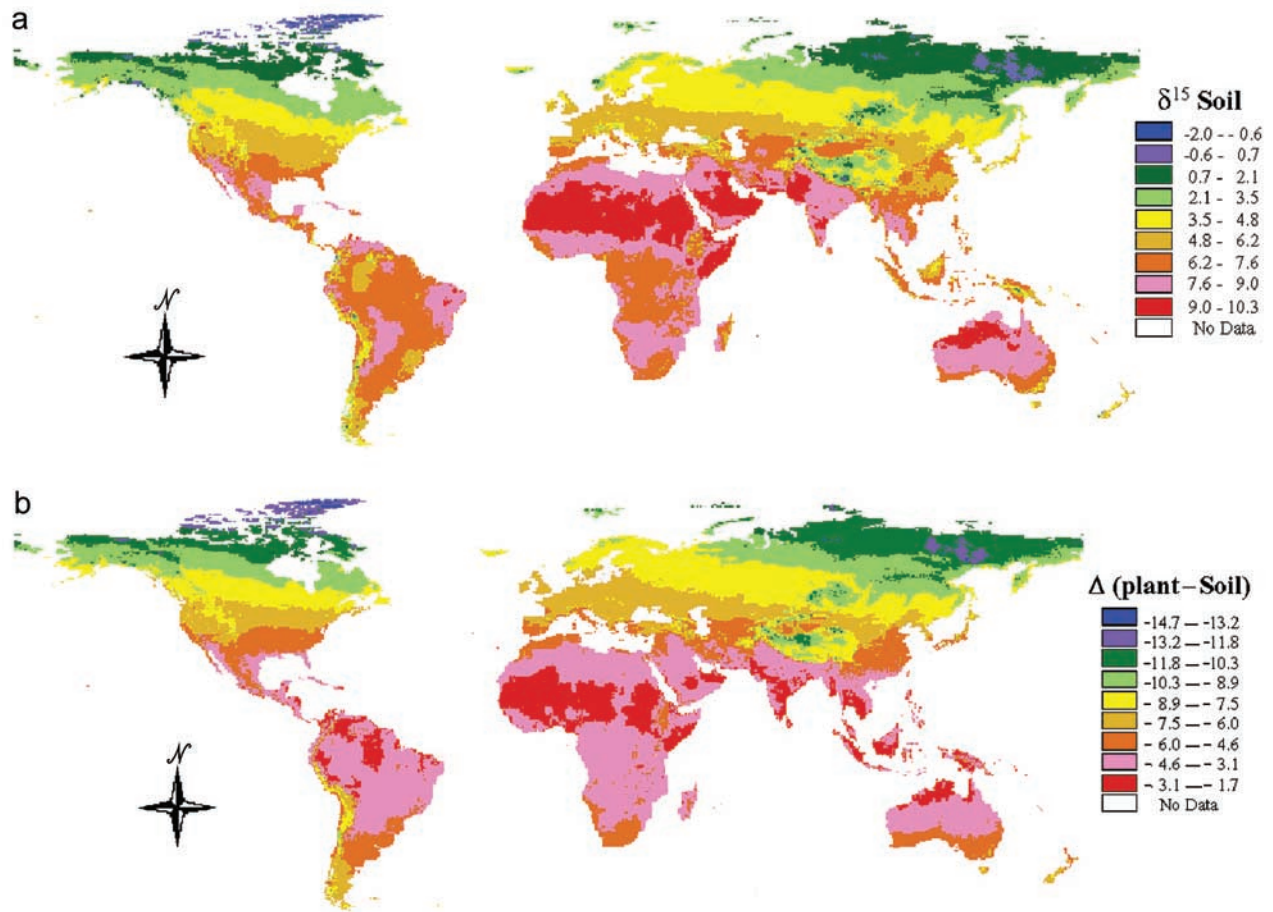


Figure 2. (a) Estimated geographical distribution of soil $\delta^{15}\text{N}$ values to 50 cm and (b) estimated geographical trends in $\Delta\delta^{15}\text{N}_{\text{plant-soil}}$. Global mean annual temperature and precipitation (0.5×0.5 degree grids) data are obtained from *Willmott and Matsuura* [2000].