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Human-Induced Changes in Holocene Nitrogen Cycling in North China: An Isotopic Perspective From Sedimentary Pyrogenic Material

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Key Points:
- N isotope of pyrogenic material can be a novelty proxy of N cycle on land
- Humans have drastically changed N cycle in North China since 7,400 cal. years BP
- A several hundred year recovery period is projected for N cycling in a temperate forest-steppe ecosystem

Supporting Information:
- Supporting Information S1

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Abstract Reactive nitrogen (N) deposition from human activity significantly impacts temperate vegetation in areas where low natural N availability limits vegetative productivity. However, the ecosystem response to anthropogenic N deposition remains elusive owing to the scarcity of long-term empirical observations. Here a N isotope of a pyrogenic material was used to investigate long-term N availability evolution in a forest-steppe ecosystem in North China. The N availability was found to have significantly increased since circa 7,400 years BP when primitive agriculture began. Different N availability changes were observed under primitive agriculture (6,600–3,500 cal. years BP) and Sui-Tang traditional agriculture (AD 581–907), implying dependency on the agricultural mode. A 220-year N availability recovery period after Sui-Tang agriculture was observed. On this basis, a minimum of several hundred years is projected for the restoration of the temperate ecosystem if the modern N cascade were to be stopped.

Plain Language Summary The manner in which a temperate ecosystem responds to continuous anthropogenic nitrogen (N) deposition remains an open question. The lack of long-term empirical observation has limited the understanding of this ecological issue. Agricultural practices over the past several thousand years in North China may be an ancient reference for the modern use of N fertilizer. In the present study, we used a geochemical method to reconstruct a 10,000-year history of N changes in the plant-soil system of the Daihai Lake region in North China. The reconstructed N history was then compared with archeological evidences of early agriculture in the region. We found that early agriculture significantly influenced N changes in the plant-soil system about 7,400 years ago and that 220 years were required for the plant-soil system to recover from the N disturbance caused by agricultural activity during the Sui-Tang dynasty (AD 581–907). On this basis, it is predicted that several hundred years would be required to reverse the effects of modern N disturbance on a temperate ecosystem.

1. Introduction

Over the past century, humans have drastically disrupted the nitrogen cycle through the generation of excess reactive nitrogen (Nr) via the agricultural overuse of N fertilizers (Socolow, 1999) and the burning of fossil fuels (Vitousek et al., 1997). This has led to a host of environmental problems such as extensive eutrophication of surface waters (Hundey et al., 2016; Owens et al., 1992), ecosystem stress (Emmett et al., 1998), and augmentation of the greenhouse effect (Liu & Greaver, 2009). To date, numerous studies have been conducted to investigate N cycling and its environmental and ecological effects (Hyvönen et al., 2008; Matson et al., 2002; Xia et al., 2009). However, most of these studies were based on time-limited observations, covering only recent years or recent decades at the most, which is insufficient for a thorough understanding of the relationship between disturbed N cycling and environmental/ecological changes. There is thus a great need for broader contexts of modern changes in N cycling, and sedimentary records can potentially be uniquely used for this purpose. The examination of long-term empirical records is of merit in this regard, but such records are usually scarce.

The practice of agriculture began at least 8,000 years ago in Eurasia and is thought to account for the anomalous CO_2 rise during the Holocene (Ruddiman, 2003, 2007). More recently, a comprehensive synthesis study showed that the major farming settlements in North-Central China were initiated around 7,000 years ago (Hosner et al., 2016). However, it remains unclear when early human activity began to change the N cycle and how the N cycle evolved in association with land use changes. Clarification of these issues is essential to understanding the consequences of human-altered N cycles and the response of ecosystems to anthropogenic N perturbation. Critical to this purpose is the reconstruction of a long-term record of the N cycle in regions associated with ancient land use changes.

Nitrogen isotope studies provide insight into the nature of the N cycle in ecosystems, with higher $\delta^{15}N$ values reflecting greater N availability and a more open N cycle (Högberg, 1997; Pardo et al., 2006). The link between $\delta^{15}N$ and N availability lies in some key processes of the N cycle, namely, nitrification and denitrification, which discriminate against ^{15}N (Houlton & Bai, 2009). For instance, when the N supply is higher than the biotic demand, N is lost as gaseous compounds through fractionating pathways, and the remaining ecosystem N is enriched in ^{15}N and thus has a higher $\delta^{15}N$. Accordingly, with increasing N availability, the internal N cycle begins to shift from a closed N cycle with little N loss to an open N cycle with substantial N loss (Aber et al., 1998). Lake sediments serve as a good archive, tending to remain intact deposited, and also afford more accurate time control based on Accelerator Mass Spectrometry (AMS) ^{14}C dating. However, a sedimentary organic N isotope record of a lake cannot be directly linked to changes in the N cycle of surrounding vegetation or soil. This is because of the complexity of organic N sources and the variety of factors that impact the relevant kind of $\delta^{15}N$. Black carbon (BC) is a pyrogenic material produced by the incomplete combustion of vegetation and represents a continuum of carbonaceous materials ranging from elemental or graphite carbon (or soot) to charcoal, char, and partially carbonized plant tissue (Masiello, 2004; Schmidt & Noack, 2000). A recent study in which burning experiments were performed on various plants revealed that the nitrogen isotopes contained in combustion residues were highly correlated with those in the precursor plants (Wang et al., 2008). In this case, the $\delta^{15}N$ of the pyrogenic material (especially partly charred plant fragments) has the potential of being used to trace the N isotopic composition of the burnt vegetation (see supporting information for detailed discussion).

In the present study, we reconstructed past terrestrial N availability by unprecedentedly measuring the stable N isotope of BC ($\delta^{15}N_{BC}$) in a Holocene sediment core (DH99a) obtained from the Daihai Lake in North China. The $\delta^{15}N_{BC}$ was used as an indicator of the N availability in the vegetation surrounding the lake. The Daihai Lake region has a long history of human activity, with many Neolithic archaeological sites distributed within it (Figure S1). Agriculture was initiated in the region around 7,000 cal. years BP according to archaeological records, and there was a later shift to a farming-grazing transitional culture 3,500 cal. years BP, when the climate became cold and dry (Lian & Fang, 2001). This observation enabled an investigation of the initial impact of early agricultural activity on terrestrial N cycles and the evolution of the cycles in association with land use changes.

2. Study Area

The Daihai Lake (40°29′ to 40°37′N and 112°33′ to 112°46′E) is a semibrackish closed lake in Inner Mongolia, North-Central China (Figure S1). It has an area of 133 km^2, a maximum water depth of 14 m, and an elevation of 1,221 m. The lake basin is bordered by the Manhan Mountains (main peak at 2,305 m) on the north, the Matou Mountains (main peak at 2,035 m) on the south, distributed hills on the east, and plains along its western shore. The lake has a catchment area of 2,289 km^2, is fed by five major rivers, and has no river drainage (Xiao et al., 2004).

The Holocene climate of the Daihai Lake region can be divided into three distinct periods: mild/dry early Holocene (ca. 10,250–7,900 cal. years BP), warm/humid middle Holocene (ca. 7,900–3,100 cal. years BP), and cool/dry late Holocene (ca. 3,100 cal. years BP; Xiao et al., 2004; Peng et al., 2005). In a previous study, the present authors reconstructed past rainfall in Daihai using $\delta^{13}C_{BC}$ based on the negative correlation between C_3 plant $\delta^{13}C$ and precipitation in North China (Wang, Cui, et al., 2013). The results inferred highly variable rainfall ranging between 170 mm lower and 310 mm higher than the present level during the middle Holocene and generally ~70 mm lower than the present level during the early and late Holocene.

Prehistoric human activity in the Daihai Lake region can be traced back to at least 7,000 years ago (Tian, 2000), coinciding with the onset of the warm/humid middle Holocene. To date, a total of 12 Neolithic archaeological sites have been discovered on the mountain slopes around the Daihai Lake (Figure S1).

Most of these archaeological sites belong to the Yangshao culture (ca. 6,500–5,000 cal. years BP) and Longshan culture (ca. 5,000–4,000 cal. years BP; Tian, 1991a, 1991b). The cultural remains in the region indicate that the prehistoric settlers were primarily engaged in primitive agriculture (Lian & Fang, 2001). The primitive agricultural cultures developed and flourished during the middle Holocene. Unfavorable climate after circa 3,500 cal. year BP led to the cessation of agricultural activity in the region.

The previous study of the authors also revealed two phases of obvious increases in the inferred fire episode frequency in the Daihai region, beginning circa 8,000 and 2,800 cal. years BP, respectively (Wang, Xiao, et al., 2013). These changes were attributed to the appearance of early agriculture and the expansion of human land use in the region, because they contradicted the common climate-fire relation, which indicates the frequent occurrence of wild fires under the cold/dry climate of North China. The reconstructed Holocene fire history was based on the BC mass sedimentation rate (BCMSR) record in the DH99a sediment core. The local fire episode frequency was determined by counting the BCMSR peaks, which were identified as positive deviations from the BCMSR background (i.e., a locally weighted mean of the BCMSR data) using a certain threshold value within a 2,000-year time window. Each BCMSR peak represented a local fire event or episode. The fire episode means more than one fire occurred during a given time period. This interpretation was based on the assumption that a local fire event produced a large number of charcoal particles exceeding the amount originating from other processes (Whitlock & Millspaugh, 1996). The magnitude of a BCMSR peak is related to the local fire size and fire intensity. From a BCMSR peak time series, it could be determined that large/intensive local fires occurred during the primitive agriculture period and the Sui-Tang dynasty (Figure 1e). The BC deposited in the lake thus likely mainly originated from local fires during these periods. During other periods, local fires were relatively small and regional fires probably also contributed to the BC production.

3. Material and Method

3.1. Lithology, Sampling, and Chronology of DH99a Sediment Core

In the summer of 1999, a piston corer driven by a Japanese-made TOHO drilling rig (Model D1-B) was used to obtain sediment cores at a water depth of 13.1 m in the central part of the Daihai Lake. The sediment cores were extracted to a depth of 12.02 m beneath the lake floor. They were collected in half-cut polyethylene tubes and designated DH99a. The core sections were later split, photographed, and described on location. The cores were subsequently continuously cut into 2-cm segments to obtain samples for laboratory analyses. The core sediments were composed of grayish-green to grayish-black homogeneous mud. The present study specifically utilized the upper 10.63 m of a DH99a sediment core, which was sampled at 4-cm intervals, resulting in a total of 260 samples. The samples were used for $\delta^{15}N_{BC}$ analyses.

The time scale of the DH99a sediment cores was provided by Xiao et al. (2004). It was obtained by AMS ^{14}C dating of eight bulk samples collected from the organic-rich sediments. The dating of the radiocarbon samples was performed using a High Voltage Engineering Europa B.V. (HVEE) Tandetron AMS-II system at the Center for Chronological Research, Nagoya University. The AMS ^{14}C data indicated that the Daihai Lake sediments attained a thickness of about 11 m in the Holocene Epoch. An average sedimentation rate of about 100 cm/kyr based on a sampling interval of 4 cm of the DH99a cores indicated a potential temporal resolution of about 40 years.

3.2. Black Carbon (BC), $\delta^{15}N$, and C/N Ratio Measurements

To determine the BC component of the Daihai Lake sediments, the carbonates and part of the silicates in the samples were removed by sequential three N HCl and HF/HCl (10 N:1 N) treatments. The treated samples were then oxidized using a solution of $K_2Cr_2O_7/H_2SO_4$ (0.1 mol/L:2 mol/L) at 55 °C for 60 hr to remove the soluble organic matter and kerogen. The remaining refractory carbon was considered as BC (Lim & Cachier, 1996). Further $\delta^{15}N$ analysis of the BC was performed using a Flash EA 1112 elemental analyzer coupled with a mean annual temperature (MAT) 253 isotope ratio mass spectrometer (Thermo Finnigan). To effectively eliminate the isobaric effect of the CO_2 generated from BC, the gas was extracted by a CO_2 absorbent packed above granular Mg $(ClO_4)_2$ in a water trap (Cui et al., 2019). Repeated measurement of the international reference material IAEA-NO-3, which has a certificated $\delta^{15}N_{air\text{-}N2}$ value of +4.7‰, was used to

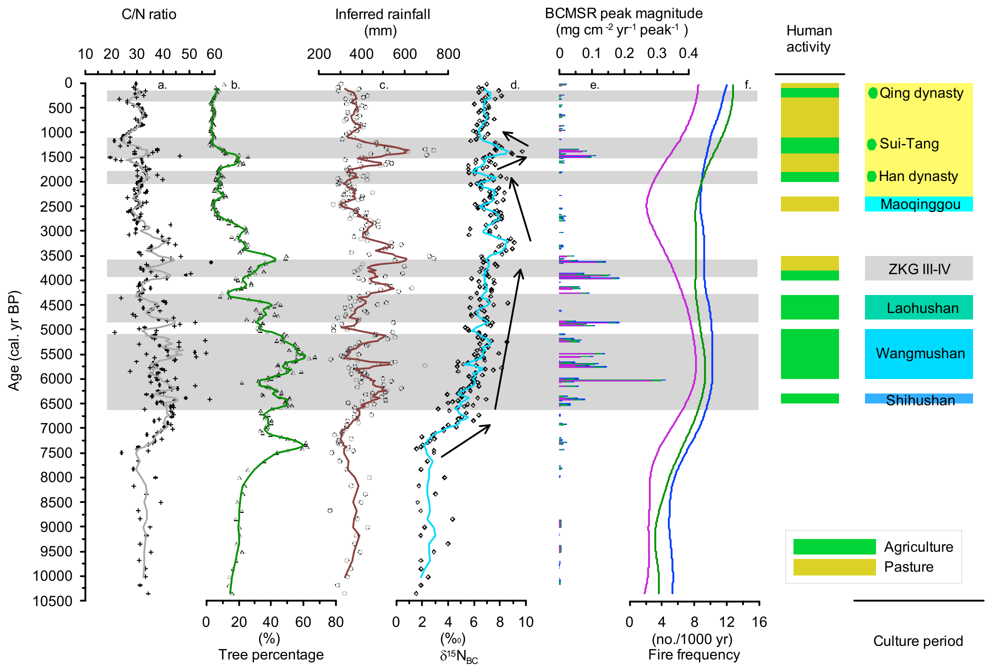

Figure 1. Sedimentary records obtained from Core DH99a as a function of calendar age before the present. (a) C/N ratio of black carbon, (b) tree percentage of pollen sum (Xiao et al., 2004), (c) inferred rainfall (Wang, Xiao, et al., 2013), (d) $\delta^{15}N_{BC}$, (e) BCMSR peak magnitude (Wang, Xiao, et al., 2013), and (f) inferred human fire frequency (Wang, Xiao, et al., 2013). The blue, green, and purple lines correspond to threshold ratio values of 1.06, 1.10, and 1.20, respectively. Three threshold values were used to obtain a full picture of the local fire occurrences because no historical fire observation provided and appropriate threshold value. The solid curves in panels (a), (b), (c), and (d) represent the five-point average values. The presented data were compared with archaeological records and human activity over the Daihai Lake region. Shihushan and Wangmushan belong to the Yangshao period (ca. 6,500–5,000 cal. years BP); Laohushan belongs to the Longshan period (ca. 5,000–4,000 cal. years BP); ZKG III-IV denotes the Zhukaigou III and IV periods (ca. 4,000–3,600 cal. years BP); and the Maoqinggou culture belongs to the Ordos Bronze period (ca. 2,600–2,300 cal. years BP). The blank white spaces indicate areas with no archaeological indication of settlement in the region. The colored boxes indicate the approximate chronological occurrence and duration of these periods.

calibrate the $\delta^{15}N$ of the BC samples. Analytical precision was better than ±0.2‰. All the reported values are relative to the AIR scale.

The carbon and nitrogen percentages of the BC were also measured using the Flash EA 1112 elemental analyzer. Sextuplicate measurements of one sample using the chemical treatment procedure described above revealed that the relative errors of the determined C and N percentages were within 5.44% and 3.85%, respectively. The atomic C/N ratio was calculated as the ratio of the C wt% to that of the N wt% multiplied by 1.17.

4. Results

4.1. Variation of C/N Ratio of BC

The C/N ratio of BC varied between 20 and 59 for the entire obtained records (Figure 1a). Previous studies found that the C/N ratio of bulk organic matter obtained from aquatic biomass was within 3–9, whereas that of organic matter obtained from terrestrial biomass was higher than 20 (Meyers, 1997; Meyers & Ishiwatari, 1993; Perdue & Koprivnjak, 2007). The C/N ratios of the present BC samples were within 20–59, clearly corresponding with those of terrestrial plants. This ruled out any contamination with aquatic organic matter.

4.2. Variations of $\delta^{15}N_{BC}$

The measured $\delta^{15}N_{BC}$ values were relatively low, varying between 1.5‰ and 4.3‰, before circa 7,400 cal. years BP (Figure 1d). There was a subsequent sharp increase in $\delta^{15}N_{BC}$ that lasted until circa 6,700 cal. years BP, followed by further gradual increase from 6.3‰ to 8.2‰ during the period of primitive agriculture (ca. 6,700–3,500 cal. years BP). The $\delta^{15}N_{BC}$ value continued to increase until a maximum of 9.1‰ was attained and maintained until circa 3,160 cal. years BP. This was followed by a general decrease before

10.1029/2019GL082306

circa 2,000 cal. years BP. Within the last 2,000 years, there have been three clear increases in $\delta^{15}N_{BC}$ during the Han, Sui-Tang, and Qing dynasties, respectively, over which time traditional agriculture expanded in the region (Figure 1d). The most striking relative increase in $\delta^{15}N_{BC}$ occurred during the Sui-Tang dynasty (AD 581–907).

5. Discussion

5.1. Explaining $\delta^{15}N_{BC}$ Record of Daihai Lake Region

Before presenting a definitive explanation of the changes in the present $\delta^{15}N_{BC}$ values, it is useful to briefly review the factors that influence the N isotopes of plants and soil. First, climate changes may influence the $\delta^{15}N$ of terrestrial vegetation. Globally, plant and soil $\delta^{15}N$ values systematically decrease with increasing mean annual precipitation (MAP) and decreasing MAT (Amundson et al., 2003). The variation with the MAP is the same in the semiarid region of North China, where $\delta^{15}N = -0.0139MAP + 5.12$ ($R^2 = 0.405$) for plant litter and $\delta^{15}N = -0.0131MAP + 8.42$ ($R^2 = 0.522$) for soil (Liu & Wang, 2009). Contrary to the above global pattern, a negative correlation has been observed between the $\delta^{15}N$ values of plants ($R^2 = 0.396$) and soils ($R^2 = 0.148$) and the MAT in North China (Liu & Wang, 2009). However, this likely represents an artificial relationship, as temperature is positively correlated with precipitation in a monsoon climate. Overall, precipitation is therefore considered to be the dominant factor in determining the isotopic composition of plant-soil N in North China (Liu & Wang, 2009).

If climate controls the N isotope composition of plants and soils in the region, then the N isotopes of BC should be characterized by high $\delta^{15}N$ values during the early and late Holocene when the climate is dry and by low $\delta^{15}N$ values during the middle Holocene when the climate is humid. However, the opposite was observed in the $\delta^{15}N_{BC}$ values (Figure 1d). In addition, the ratio of nitrogen-fixing plants to non-N-fixing plants may also influence the $\delta^{15}N_{BC}$ values because legumes have 0.5‰–1‰ lower $\delta^{15}N$ values compared with nonlegumes (Hietz et al., 2011). Nevertheless, the percentage of nitrogen-fixing plants as observed in pollen assemblages is rather low (<1%; Xiao et al., 2004), excluding it as the cause of the changes in $\delta^{15}N_{BC}$. In this context, the increases in $\delta^{15}N_{BC}$ since circa 7,400 cal. years BP are probably governed by human activities in the Daihai Lake region.

Interestingly, a statistical analysis showed a slightly positive correlation between $\delta^{15}N_{BC}$ and MAP ($R^2 = 0.091$, Figure S4a). The positive correlation was more robust during circa 7,400–6,500 and 3,500–2,300 cal. years BP (Figures S4b and S4c). Based on the aforementioned relationship between plant $\delta^{15}N$ and precipitation, we consider that this positive correlation is not directly related to rainfall but reflects the shifting agricultural practice with changing climate. For example, primitive agriculture was practiced circa 7,400–6,500 cal. years BP when the climate was relatively warm and humid, whereas agricultural activity ceased circa 3,500–2,300 cal. years BP when the climate deteriorated to a cold and dry condition.

5.2. Human Land Use and N Cycles in Daihai Lake Region

An in-phase comparison showed that our $\delta^{15}N_{BC}$ record generally mimicked the changes in the human-induced fire episode frequency in the Daihai region (Figures 1d and 1f). There was a moderately positive correlation ($R^2 = 0.321–0.355$) between $\delta^{15}N_{BC}$ and the fire episode frequency for the latter's threshold values of 1.06 and 1.10 (Figures S5a and S5b). The relatively weak correlation is attributed to the century-scale fire changes not being represented by our fire episode frequency curves. No correlation was observed between $\delta^{15}N_{BC}$ and the fire episode frequency for a 1.20 threshold. This was because the fewer fire episodes detected under the condition might not reflect the actual human activities. Nevertheless, the time of elevated $\delta^{15}N_{BC}$ values corresponded to the period of high BCMSR peaks (Figures 1d and 1e), indicating a link between N availability and the human-induced fire size or intensity during the practice of agriculture. Overall, the foregoing indicates that $\delta^{15}N_{BC}$ is governed by human activities in the region. The obtained results provide initial evidence of long-term N cycle changes in association with the agricultural history of North China.

The first increase in $\delta^{15}N_{BC}$ began circa 7,400 cal. years BP in connection with the initial increase in human fire frequency when primitive agriculture was commenced in the Daihai region [Wang, Cui, et al., 2013]. The time of this first $\delta^{15}N_{BC}$ increase also coincides with the establishment of major farming settlements in North-Central China circa 7,000 years ago (*Hosner* et al., 2016). The first increase in $\delta^{15}N_{BC}$ was characterized by a steep rise at a rate of 0.6‰ or 0.7‰ per century and continued until circa 6,700 cal. years BP. There was a simultaneous sharp decrease in the tree percentage from 62% to 33% circa 7,400–7,000 cal. years BP, with a subsequent stabilization at about 35% until circa 6,700 cal. years BP (Figure 1b). In contrast, there was an obvious increase in the inferred rainfall during the same time (Figure 1c), which cannot explain the vegetation change. The use of fire for land clearance by prehistorical settlers in preparation for agriculture seems to offer a much more plausible explanation. In this case, forest fires consumed the upper ^{15}N-depleted surface layer, forcing plants to obtain N from lower horizons, resulting in an increase in the plant $\delta^{15}N$ (Högberg, 1997). Moreover, an increase in nitrification after a fire may further increased the plant $\delta^{15}N$ through the provision of ^{15}N-enriched NH_4^+ (Raison, 1979). This marked the onset of a shift in the regional plant-soil system to a more open, leaky N cycle. Subsequently, there was a reduction in the rate of increase of $\delta^{15}N_{BC}$ to approximately 0.08‰ or 0.10‰ per century circa 6,700–3,500 cal. years BP, the time the region witnessed the stabilization and spread of primitive agriculture, which was characterized by slash-and-burn and shifting cultivation (Li et al., 2009). This low rate is comparable to that observed in forested ecosystems under ecosystem development without chronic disturbance (Mclauchlan et al., 2007). It implies that the long-term, less-intensive primitive farming activities (i.e., planting and thinning) practiced in the Daihai region limitedly impacted the already open terrestrial N cycle but contributed to the maintenance of the N cycling in a nearly steady state. Interestingly, the increase of $\delta^{15}N_{BC}$ during this period was stepwise, covering three distinct cultural phases, namely, the Yangshao (ca. 6,500–5,000 cal. years BP), Longshan (ca. 4,800–4,300 cal. years BP), and Zhukaigou (ca. 4,000–3,500 cal. years BP) phases (Figure S6). This reflected a clear trend of episodic enhancement of the N availability with the gradual intensification of land use (Tian, 1991a, 1991b).

A transition from agriculture to pasturing occurred circa 3,800 cal. years BP, resulting from environmental deterioration involving obvious decreases in precipitation and temperature. Agricultural activity in the region eventually ceased circa 3,500 cal. years BP (Lian & Fang, 2001). However, $\delta^{15}N_{BC}$ continued to increase until circa 3,160 cal. years BP before sharply declining with an amplitude of 3.2‰ over the next 80 years. The prolonged increase in N isotopes during this period may be attributed to the "slow release" of essential macronutrients from manure-containing soils (Bogaard, 2012). Manure from farming animals during the subsequent pasturing period also could have contributed to increasing $\delta^{15}N_{BC}$. However, after circa 3,160 cal. years BP, $\delta^{15}N_{BC}$ generally decreased over the next 1,000 years when no land use was recorded, corresponding to a gradual reduction in fire frequency (Figures 1d and 1f). The overall rate of decrease was approximately 0.5‰ per century, reflecting a relatively slow recovery from the previous disturbances. In this case, the N availability did not return to the presettlement level even 1,000 years after the cessation of the chronic disturbance by agriculture and logging, suggesting a long-lasting effect of early human activity.

Over the last 2,000 years, there have been three spikes in the $\delta^{15}N_{BC}$ record, contemporaneous with the Han, Sui-Tang, and Qing dynasties, respectively (Figure 2). The most prominent peak centered circa 1,385 cal. years BP and corresponded to the Sui-Tang dynasty (AD 581–907). It was preceded by a high $\delta^{15}N_{BC}$ increase rate of 2.1‰ per century and followed by a high decrease rate of 1.8‰ per century. This $\delta^{15}N_{BC}$ peak also corresponded to the development of traditional agriculture over the Daihai Lake region under the warm and wet climate of the Sui-Tang dynasty (Wang, Xiao, et al., 2013). Traditional agriculture is an intensive and meticulous farming activity, involving iron-plow tilling using cattle power, the spreading of manure, and irrigation (Tan, 2009; Wang, 2011). This agricultural practice was significantly developed during the Sui-Tang dynasty, particularly the systematic distribution of manure over the field at different stages of the farming period to achieve high crop productivity. The process involved burying manure in the soil layers before sowing seeds, mixing manure and seeds during sowing, and applying manure during the growth of the crops (Hao, 2016). This intensive manure application definitely contributed to the observed $\delta^{15}N_{BC}$ spike during the Sui-Tang dynasty. The optimal conditions of this era also facilitated the geographical expansion of agriculture in North China with the northern boundary of farming moving 1° northward and increasing the crop yield (Wu & Dang, 1998). The accompanying field burning of crop stems further increased the $\delta^{15}N_{BC}$ peak.

The $\delta^{15}N_{BC}$ peak during the Han dynasty was the second highest at ~1.4‰. The lowness of the $\delta^{15}N_{BC}$ peak compared with that of the Sui-Tang dynasty is consistent with the less intensive agricultural activity, because

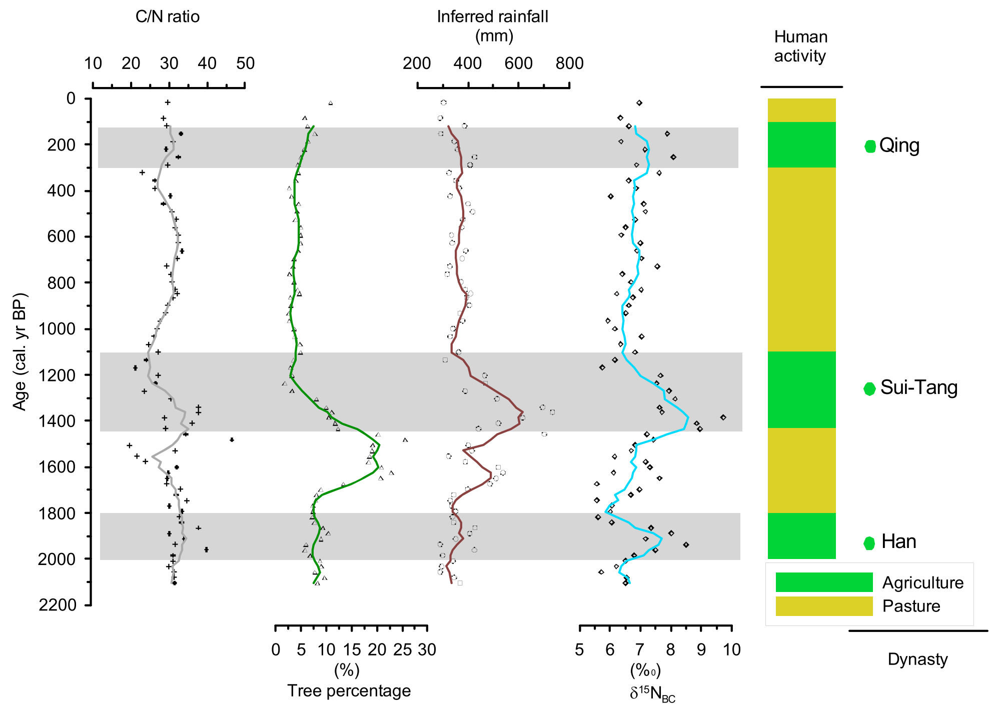

Figure 2. Expanded plot comparing the detailed $\delta^{15}N_{BC}$ changes with the C/N ratio of BC, the tree percentage, and the inferred rainfall during the Han, Sui-Tang, and Qing dynasties.

traditional agriculture had just been introduced at the time of the Han dynasty. The inferred rainfall during the Han dynasty was also not as high as that during the Sui-Tang dynasty (Figure 2). During the Qing dynasty, limited land was reclaimed for agriculture in the Daihai region because large patches of land were occupied by the Mongolians and used as meadows (Zhang & Wu, 2001) and the climate was relatively cold (Zhu, 1973). This resulted in an unstable increase of $\delta^{15}N_{BC}$ by a maximum of 1‰.

In summary, our $\delta^{15}N_{BC}$ record reinforced the idea that agricultural activity was very intensive during the Sui-Tang dynasty and that this was accompanied by a large cascade of reactive N into soils and plants. The $\delta^{15}N_{BC}$ increase rate during the Sui-Tang dynasty was comparable to that observed in modern tropical forests, which are characterized by leaf $\delta^{15}N$ increases of 1.4‰–2.6‰ over four decades due to elevated anthropogenic N deposition (Hietz et al., 2011). However, the mechanism of N deposition differs: N was directly added to the soil during past eras of traditional agriculture, whereas in modern systems, N is mostly through atmospheric deposition and/or runoff. The latter tends to dilute the anthropogenic N signal. Hence, the variation of N availability in the plant-soil system during the agricultural practice of the Sui-Tang dynasty may be used as an empirical lower-limit reference for assessing the ecological effect of modern N fertilizing.

5.3. Changing Regimes of N Availability in Plant-Soil Systems Under Different Agricultural Practices and Their Potential Implications

From the obtained $\delta^{15}N_{BC}$ record, we observed two different variation trajectories of the N availability in plant-soil systems in the Daihai Lake region. During the period of primitive agriculture, $\delta^{15}N_{BC}$ exhibited relatively slow increase and decrease rates of about 0.5‰–0.6‰ per century. In contrast, the rates during the traditional agriculture of the Sui-Tang dynasty were higher at about 2‰ per century. The differing N availability changes may be attributed to the differing N cycling regimes in the plant-soil ecosystems under the two different agricultural practices. Under primitive agriculture, the relative N availability in the ecosystem was increased through the clearing of forest vegetation and tilling of the soil, which reduced plant uptake of N and fixation of C (Compton & Boone, 2000). In this case, the accumulation of N in the plant-soil system was a slow process. Meanwhile, the reduction of the N availability in the ecosystem depended on vegetation restoration, which tended to be a long-term process and was impacted by climatic changes. For example, during the recovery process of the disturbed ecosystem after the cessation of primitive agriculture circa 3,500 cal. years BP, the cold and dry climate promoted the development of a shrub steppe over the Daihai Lake area (Xiao et al., 2004), delaying restoration of the disrupted N cycle. In contrast, traditional agriculture increases N availability through the application of N-containing manure and fertilizer to the soil, resulting in enhanced N accumulation in the plant-soil system. Manure is rich in ^{15}N, and its high δ^{15}N signal is imparted on the soil and plants (Bogaard et al., 2007). Furthermore, the high N input to a previously N-limited system increases nitrification, which produces ^{15}N-enriched NH_4^+ in the soil (Högberg, 1997). Uptake of the ammonium by plants accounts for the observed rapid increase in $\delta^{15}N_{BC}$. Interestingly, the disturbed N cycle also recovers soon after cessation of the human-induced N cascade. Only about 220 years was required to restore the preperturbation N availability level after the peak of the agricultural activity of the Sui-Tang dynasty. If this is used as a lower-limit reference, a minimum of several hundred years would be required to restore a temperate ecosystem to its predisturbance condition after cessation of anthropogenic N deposition.

6. Conclusions

In this study, we analyzed the $\delta^{15}N_{BC}$ of a lake sediment to investigate the long-term evolution of N availability in association with past land use changes. The observations indicated that human forces have been a major driver of the terrestrial N cycle in arid forest-steppe ecosystems in North China since circa 7,400 cal. years BP. The first significant increase in N availability began with the prehistoric colonization of the region by humans and the initiation of primitive agriculture circa 7,400 cal. years BP. This marked the beginning of an open terrestrial N cycle. The N availability then exhibited two different changing patterns, namely, slow increase/decrease during the practice of primitive agriculture and rapid increase/decrease during a later era of the traditional agriculture. This difference was due to the differing regimes of N accumulation under the two agricultural modes. The slow increase in N availability during the practice of primitive agriculture (before ca. 3,500 cal. years BP) indicates a steady state nitrogen cycle of the ecosystem under the long-term influence of the low-intensity agricultural activities. In contrast, traditional agriculture during the Sui-Tang dynasty (AD 581–907) significantly enhanced the N availability of the ecosystem through the use of N-containing manure. Interestingly, about 220 years was required to restore the preperturbation N availability level after the peak of agricultural activity during the Sui-Tang dynasty. To the best of our knowledge, this study provides the first estimates of recovery time for an anthropogenically altered ecosystem in terms of N cycling.

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