Separating the influences of diagenesis, productivity, and anthropogenic nitrogen deposition on sedimentary $\delta^{15}N$ variations

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Abstract

The stable isotopic composition of nitrogen ($\delta^{15}N$) in organic lake sediments is frequently used to infer changes in the source or cycling of N prior to sedimentation. However, diagenetic processes that occur after sedimentation can systematically alter the primary isotopic signal recorded in sedimentary organic matter and must be accounted for in order to detect changes in the $\delta^{15}N$ of nitrogen inputs to the sediment surface. Here we present a null model that estimates the diagenetic effect on sedimentary lake $\delta^{15}N$ records. The model was tested using lake sediment cores from alpine lakes in the Wind River and Teton Ranges of Wyoming, USA. Model-inferred increases in productivity were tested against independent productivity proxies, and inferred changes in anthropogenic nitrogen contribution were validated with records of atmospheric nitrogen deposition from the nearby Fremont Glacier, Wyoming. Diagenetic overprinting significantly altered sediment $\delta^{15}N$ profiles, and the degree of alteration was not constant through time. Of the cores analyzed, ~30 and 70% of the variability can be explained by diagenesis alone, with the remainder explained by either a change in productivity or a change in the isotopic composition of the source material. Our null model of isotopic fractionation proved to be successful at separating the diagenetic overprinting from other causes of isotopic shifts, thereby providing environmental scientists with an analytical tool to partition the effects of diagenesis and environmental change on sedimentary $\delta^{15}N$ values.

Key words: Nitrogen Isotopes, Lake Sediments, Diagenesis, Atmospheric Nitrogen Deposition, C:N ratio, Diatoms

1.0 Introduction

Stable nitrogen isotope ratios ($\delta^{15}N$) in lacustrine sediments provide an integrated record of long-term changes in ecosystem nitrogen dynamics. Interpretations of isotopic shifts have varied in scale from within-lake productivity changes (Talbot 2001), to regional or hemispheric N deposition (Holtgrieve et al. 2012; Wolfe et al. 2001), to global-scale variations in the nitrogen cycle (McLauchlan et al. 2013). An inherent assumption in many of these studies is that the primary $\delta^{15}N$ signal related to environmental change is recorded accurately, remains stable during and after sedimentation, or only undergoes constant fractionation. However, stable N isotopes undergo significant alteration during diagenesis, as shown in both field and laboratory studies (Möbius 2013; Bada et al. 1989; Lehmann et al. 2002; Macko et al. 1994; Macko and Estep 1984; Silfer et al. 1992). Through early diagenesis, organic material is subject to compositional and isotopic changes that occur during sedimentation through the water column and within the sediments. As a result, the remaining organic mass has a different collection of biochemical compounds than the original organic mass.

The preferential breakdown of the labile fractions changes both the relative abundance of carbon and nitrogen and their isotopic signatures. Studies of diagenetic alteration in sediments generally note downcore increases in the C:N ratio (Galman et al. 2008), and progressive enrichment of the remaining substrate in $\delta^{15}N$ (Fry et al. 1991; Altabet 1998; Altabet and Francois 1994; Altabet et al. 1999; Ostrom et al. 1998; Sachs and Repeta 1999; Saino and Hattori 1987; Libes and Deuser 1988; Lehmann et al. 2002; Macko et al. 1994; Wada 1980; Robinson et al. 2012). The reason for the observed shift in the C:N ratio is due to the relatively rapid breakdown of the labile N-bearing fractions (proteins and peptides) as compared to the structural carbon fractions (cellulose, lignan) (Galman et al. 2008; Lehmann et al. 2002; Colombo et al.

1996; Talbot 2001). The increase in substrate $\delta^{15}N$ is due to the preferential utilization of the lighter isotope (^{14}N) by bacteria that catalyze the mineralization reactions. ^{14}N is favored over ^{15}N because less energy is required to break the bonds with the lighter isotope. The bacterially-mediated breakdown of N-bearing compounds in sediments is achieved primarily through deamination (ammonification) (Silfer et al. 1992; Bada et al. 1989; Macko et al. 2003), whereby N is incorporated into bacterial biomass or released through bacterial metabolism to the dissolved pool (Macko and Estep 1984). This causes a progressive loss of the lighter isotope from the organic matter substrate in the sediments.

A recent review of over 100 studies on nitrogen isotope alteration during diagenesis in both natural and laboratory systems found overwhelmingly a progressive enrichment of the remaining substrate (Robinson et al. 2012); however, we found two studies, both in anoxic environments, that showed a progressive depletion of $\delta^{15}N$ through time (Lehmann et al. 2002; Gälman et al. 2009). The latter discrepancy may be due to the presence of exchangeable ammonium (NH_4^+). Dissolved ammonium (NH_4^+) can attach to negatively charged clay particles in the sediments. The presence of exchangeable NH_4^+ cannot be distinguished from organic bound N with conventional elemental analysis and can therefore compromise the isotopic measurement of the solid organic fraction. Exchangeable NH_4^+ often accounts for a relatively small fraction of total nitrogen in most sediments (<1%) (Freudenthal et al. 2001; Talbot 2001), but can be present in relatively high concentrations in anoxic organic-rich environments (Rosenfeld 1979). In the subsequent analysis we focus on lakes that are oxygenated to the hypolimnion, and note that the following approaches may not be applicable to eutrophic or hypertrophic lakes.

Lakes that are oxygenated to the sediment surface interface and below can have high organic matter loss rates of up to 85% in the water column, and up to 95% upon sedimentation, with the remaining fraction being relatively recalcitrant (Meyers and Ishiwatari 1993; Meyers and Eadie 1993). It would be remarkable if such a large loss in mass did not lead to changes in $\delta^{15}N$ given the discrimination that occurs against ^{15}N in almost all non-equilibrium reactions in the nitrogen cycle. Based on this rationale, diagenesis has a clear potential to alter the primary signal of algal $\delta^{15}N$ deposited in oxygenated lake sediments and in doing so complicates the interpretation of the other environmental determinants of sediment $\delta^{15}N$ signals. Accordingly, it is important to have a systematic approach for differentiating between diagenesis and environmental causes of change in the $\delta^{15}N$ profile of lake and oceanic sediments. One way to examine diagenetic pathways is through the use of compound specific isotopes, such as chlorins (Enders 2008), although this process is time consuming and the analysis of sedimentary pigments requires special handling of the core as pigments are rapidly degraded in the presence of light. In addition, a significant amount of dry sediment is required to acquire enough pigment for analysis. Alternatively, a quantitative mechanistic model could be used to determine the impact of diagenesis on sediment $\delta^{15}N$ records.

Here, we present a model for $\delta^{15}N$ changes associated with diagenesis and evaluate the model using sediment cores from the Wind River and Wyoming Ranges of Wyoming. The location is an ideal site for testing the effects of diagenesis, as we have detailed information on alternative influences on the $\delta^{15}N$ record including records of atmospheric $\delta^{15}N$ deposition from a nearby glacier and detailed independent records for productivity change in each lake. We use a Rayleigh equation that simulates microbial recycling and re-synthesis of organic matter, including inorganic NH_4^+ (Freudenthal et al. 2001; Macko et al. 2003; Möbius 2013). The model uses data typically collected in sediment core analyses (C:N, μgN g sediment^{-1}, $\delta^{15}N$) and requires no further analysis or use of sediment material.

2.0 Materials and methods

2.1 Model development

During diagenesis, the mineralization of organic N-bearing compounds into dissolved ammonium is primarily achieved through deamination (Silfer et al. 1992; Macko et al. 2003; Bada et al. 1989). Isotope enrichment factors (ε) for deamination have been experimentally derived and range from 2.5 to 5.8‰ (α =1.0025 to 1.0058) (Silfer et al. 1992; Bada et al. 1989), with the preferential loss of ^{14}N from the substrate. In an open system, where the product is continuously removed, the relationship produces a rapid decline in the ^{14}N concentration in the substrate. However, bacterial uptake of enriched component amino acids and the subsequent reincorporation of microbial biomass into the substrate will moderate the isotopic offset due to peptide bond breakage alone. Compared to a 'constant release model' in which NH_4^+ is permanently lost from the system, diagenesis can be better described using a Rayleigh-type equation that simulates the dampened effect due to microbial recycling and re-synthesis (Freudenthal et al. 2001; Macko et al. 2003; Möbius 2013). In the Rayleigh equation, (1) $R_f \approx R_i f^{(\alpha-1)}$, f is the fraction of the original substrate remaining, and R is the isotopic ratio of the initial substrate (R_i) and the remaining fraction (R_f) . Based on this rationale, for each sediment interval we apply a Rayleigh equation to calculate the diagenetic effect on the remaining organic nitrogen fraction, (2) $\delta^{15}N_{ON(f)} \approx \delta^{15}N_{ON(i)} - \varepsilon^{*}\ln(f)$. This equation produces a sediment $\delta^{15}N$ isotope profile for each lake core that varies simply as a function of diagenesis, which we term the "Null Model".

2.1.1 Determination of f, the fraction or organic N remaining

In the Rayleigh equation, *f* represents the fraction of the original substrate remaining. In sediments cores, this represents that amount of N remaining after diagenetic loss. There are two options for approximating this fraction:

(1) the concentration of nitrogen (μg N g^{-1}) within the sediments, hereafter referred to as Null Model-1;

(2) the less conventional approach of using the C:N ratio, hereafter referred to as Null Model-2.

In Null Model-1, the fraction remaining is determined by dividing the total N concentration in each sediment interval by the total N concentration in the surface sediment. We assume that the downcore variation in total N is entirely related to diagenetic loss. It does not include changes that might have occurred due to changes in productivity in the water column.

Null Model-2 uses the C:N ratio as a measurement of the relative loss of N through diagenesis. Although the C:N ratio is not a representation of mass remaining, it is a representation of the relative abundance of C and N over time. The C:N ratio of the original organic material can change either through selective loss or preservation of C or N through time. Evidence from the literature indicates that labile N-bearing compounds in sediments degrade relatively faster than carbon rich compounds, and a common diagenetic effect is the downcore increase in the C:N ratio (Galman et al. 2008; Lehmann et al. 2002; Colombo et al. 1996; Talbot 2001). This occurs because algae have relatively high concentration of N-rich proteins, which are among the most labile fractions within the organic substrate. Therefore, changes in the C:N ratio provide a relative measure of the loss of N bearing compounds, and can be used as an alternate approximation of *f* in the Rayleigh equation that is unaffected by changes in productivity. In this method, we use the C:N ratio in the surface sediments (C:N = 7–9) as proxy for initial algal biomass ratio and relate the downcore increase to selective loss of N. Null Model-2 does not account for changes in the C:N ratio that may result from changes in organic matter source, i.e., vascular plant material that is higher in structural carbon-rich compounds.

2.1.2 Determination of epsilon (ε) and the initial isotopic composition, $\delta^{15}N_{ON(i)}$

Epsilon values represent the integrated fractionation factor that incorporates lake specific processes in each lake, including different substrates, degradation rates, and sedimentary conditions. Accordingly, this factor incorporates the potential effects of different microbial communities and reaction kinetics involved with the breakdown of different N pools. Freudenthal (2001) and Möbius (2013) derived an epsilon value of 1.48 ± 0.13 (α = 1.0015) and 1.43 to 2.3 (α = 1.0014 to 1.0023), respectively, by plotting the increase in substrate $\delta^{15}N$ against the relative loss of organic N. We use a similar approach here but remove post-1950 sediments as they may be compromised by anthropogenic nitrogen deposition (see below). Long cores were modeled using epsilon values derived from the same lake short cores. Epsilon values can also be derived using a least-squares regression analysis, and we apply this method to the Teton Range lake cores for the pre-1950 record. We expected epsilon values to be similar to that measured by Freudenthal (2001) and Möbius (2013) and smaller than the range experimentally measured for peptide bond breakage alone (2.5 to 5.8‰; α =1.0025 to 1.0058) (Silfer et al. 1992; Bada et al. 1989).

2.1.3 Model interpretation

Null Models1 and 2 capture the isotopic variation due solely to diagenesis and with a constant initial isotopic composition. Therefore, departures of the bulk sediment $\delta^{15}N$ values from the null model predictions should represent the environmental changes of interest. When the measured values deviate from the model output, a model condition has been violated; either the source dissolved inorganic N (DIN) concentration has varied (e.g., due to anthropogenic N deposition), or *in situ* fractionation has altered the isotopic signature of the primary algal material (e.g., due to Rayleigh distillation in the epilimnion from intense N uptake). These changes should be reflected by positive or negative deviations from our null diagenesis model and thus one would conclude that other processes in addition to diagenesis are causing the observed shift in $\delta^{15}N$ over time. A conceptual model is presented in Figure 1 that shows the directional offset from the null model due to common environmental factors, e.g. increases in productivity, anthropogenic N deposition, or contributions of vascular plant material to the sediment organic pool.

Both models can be used to infer instances where productivity in addition to diagenesis influenced the bulk sediment $\delta^{15}N$ profiles. Positive or negative deviations from Null Model-1 should occur when changes in productivity increase or decrease the gross flux of N to sediments. If productivity and N deposition to sediment increase, a positive deviation in Null Model-1 would occur because higher N concentrations are attributed to a reduction in decomposition rate. For this reason, Null Model-1 would be most sensitive to changes in productivity; however, Null Model-2 would also be influenced by changes in productivity if they were large enough to induce Rayleigh fractionation in the epilimnion. In this case, positive deviations from Null-Model-2 would occur due to the progressive enrichment of ^{15}N in the sedimenting algal biomass.

There are several factors that could lead to negative deviations from the null models. As discussed above, a decrease in productivity could lead to a negative deviation from Null Model-1. A negative deviation from Null Model-2 can also indicate the presence of vascular plant material. If terrestrial or benthic vascular plant additions to the organic pool were increased, the model would overestimate $\delta^{15}N$ due to the implicit assumption that the higher C:N ratio is due to greater organic matter loss. In addition, because both models assume a constant initial source, negative deviations from both null models will occur if isotopically-light anthropogenic nitrogen deposition depletes the $\delta^{15}N$ of the source DIN pool in the lake epilimnion. A negative offset in from both null models would also occur with an increase in nitrogen fixation because the algal biomass itself may become depleted due to the uptake of N_2 from the atmosphere, which has a $\delta^{15}N$ value of 0.

2.2 Model evaluation

To test the models, we used sedimentary records from five remote high elevation lakes (Table 1). Two lakes are in the Wind River Range, and three lakes are in the Teton Range. Terrestrial inputs of vascular plant material should be small because many of the lakes are above tree-line and in catchments dominantly composed of bare rock. This setting provides an opportunity to test our diagenesis model with limited confounding factors. We validate model excursions using independent records. To evaluate model-inferred productivity increases we use diatom records; we use sediment diatom concentrations as a measurement of total productivity and the planktonic to benthic ratio as a measure of relative N utilization in the epilimnion, where Rayleigh distillation effects from N uptake can occur. We use a contemporary ice core record of $\delta^{15}N$ isotopes in atmospheric deposition from the Fremont Glacier, Wind River Range to help constrain changes in source $\delta^{15}N$. There is also a relatively good record of NO_x emissions from industrial activity in the Green River Valley to the west of the Wind River Range, and to the south and east of the Teton Range. Having independent proxies for all the factors that can create deviations from the null models allowed us to both test for the effects of diagenesis alone and to attribute deviations from our null models to changes in sources or processes altering $\delta^{15}N$.

Our five sites have only recently been exposed to slight increases in atmospheric nitrogen deposition. Although no major urban centers exist in this region, recent oil and gas development is an important source of atmospheric of atmospheric reactive N deposition. The Pinedale Anticline, located in west central Wyoming, is the third largest gas field in the USA. The first well was drilled in the 1920's and but the field did not begin to expand appreciably until the late 1950's. The industry expanded considerably again in 1980, and again in 2000 (WO&GCC 2011). From 2000-2008, 2683 wells were drilled and NO_x emissions increased from 3000 to 7800 cubic tons, peaking in 2006 (WO&GCC 2011). The Pinedale Anticline is located just west of the Wind River Mountains, and southeast of the Teton Range. The National Atmospheric Deposition Program (NADP) has been monitoring deposition in the region since the early 1980's. Wet deposition of inorganic nitrogen to the Wind River region has increased from < 0.5 kg ha^{-1} yr^{-1} in the 1980s to current rates of around 1.0–1.5 kg N $ha^{-1}yr^{-1}$, (NADP 2009). Unfortunately, no glacier data is available pre-1950 or post 1990, but isotopic values measured in the Fremont glacier are negative and range from (−3.15 to −5.88‰) with a 1-2 ‰ depletion in $\delta^{15}N$ recorded through the time period. An additional $\delta^{15}N$ value for the year 2000 (−4.0‰, n=6) was obtained from precipitation samples taken by the National Atmospheric Deposition Program at a nearby station (Naftz et al. 2011).

2.2.1 Model performance

As discussed above, the null models display the isotopic variation that would occur due to diagenesis and with a constant initial isotopic source. In the absence of any change in the primary environmental signal, the only influence on sediment $\delta^{15}N$ composition is diagenesis. Accordingly, our diagenesis null models were fit to the pre-1950 bulk $\delta^{15}N$ record in each lake using the correlation coefficient (*r*) and the root mean squared error (RMSE). A high correlation and low RMSE indicates a strong relationship between inferred model diagenesis and recorded $\delta^{15}N$, and hence a strong diagenetic control on lake sediment $\delta^{15}N$ variation.

We evaluated positive and negative isotopic deviations from the null models by examining independent records of productivity changes that can influence the $\delta^{15}N$ record. We did this by using absolute concentrations of diatoms, as well as the planktonic to benthic diatom species ratio in sediment intervals as measures of the relative uptake pressure on the dissolved inorganic nitrogen pool.

To evaluate the recent negative isotopic deviations from the null model profiles, we compared recent sediment upcore depletions in $\delta^{15}N$ to both known records of regional N emissions, and to the atmospheric $\delta^{15}N$ deposition record from the Fremont Glacier in the Wind River Range. We evaluate the relative effect of increased anthropogenic nitrogen deposition and diagenesis on upcore declines in $\delta^{15}N$ in two ways. First, we back-calculate the initial isotopic composition of the sedimented organic N using a rearranged form of equation (2), giving (3) $\delta^{15}N_{org\,(i)} = \delta^{15}N_{sed} + \varepsilon \ln(f)$, where $\delta^{15}N_{sed}$ represents the bulk sediment $\delta^{15}N$, and $\varepsilon \ln(f)$ represents the diagenetic change. This equation effectively removes the diagenetic component from the sediment signal, leaving the variation in source dissolved inorganic N (the anthropogenic N deposition signal) and algal uptake kinetics as the remaining error; we will refer to this profile as the 'diagenesis corrected record'. Using both the bulk and diagenesis corrected records, we determine the year when the $\delta^{15}N$ profiles register a significant depletion; the determined year is the best approximate for the onset of anthropogenic N deposition. We find the year using the Regime Shift Indicator (RSI) test developed by Rodionov (2004). The test determines the statistical breakpoints in the sediment profiles where a significant shift has occurred in the average value of the parameter in question, in this case $\delta^{15}N$. The RSI test is based on sequential analysis, where each new observation is used to test for the existence of a regime shift. The test statistic is a two-tailed Student's T-test. This RSI test allows for the detection of regime shifts without any *a priori* knowledge of the timing of a particular regime shift (Rodionov 2004). Once the onset year is determined, we calculate the average pre- and post- anthropogenic N deposition $\delta^{15}N$ value for both the diagenesis corrected and bulk records. The difference between the two time periods is our N deposition offset, referred to as the delta (Δ) value. We hypothesize that the diagenesis corrected record will better chronicle the onset of N deposition from the known emission history, as well as to better document the magnitude of the $\delta^{15}N$ decline as recorded in the glacier record.

Our second test compares the diagenesis corrected $\delta^{15}N$ record to the glacier $\delta^{15}N$ record itself. If the null model is effective at identifying diagenetic variability, then the diagenesis corrected record should reproduce the inflections observed in the glacier record better than the bulk sediment $\delta^{15}N$ profile alone. Though we expect this atmospheric signal to be somewhat attenuated by sediment mixing, the contribution of anthropogenic nitrogen deposition should still influence the inorganic nitrogen pool and be reflected in the sediment profile. We tested this assertion by evaluating the improvement in the correlation coefficient (r), and the reduction in error (RMSE) when comparing the glacier record to the diagenesis corrected record versus the glacier record to the unmodified bulk sediment $\delta^{15}N$ record. Because North Lake in the Wind River Range has recently (last 50 years) experienced large changes in species composition and productivity, while Lonesome Lake has not, we used sediments from Lonesome Lake in an attempt to control for the changes in *in situ* fractionation due to potential differences in N assimilation fractionation by different species.

2.3 Sediment Core Collection and Analysis

Lake sediment cores were collected in the summer of 2008 using a percussion coring system from North Lake (NOR08-2) in the southwest of the Wind River Range and Lonesome Lake (LSM08-2) in the southeast of the Wind River Range. Long cores were split, photographed, and sectioned at the National Lacustrine Core Facility at the University of Minnesota. Due to disturbance and potential loss of surface sediments through this coring method, short cores were obtained from the same lakes using a gravity coring system (NOR09-2, LSM09-2) in the summer of 2009. Cores were sectioned onsite at 0.25-cm intervals from 0 to 3 cm, and at 0.5-cm intervals for the remainder of the cores. Sediment cores from three lakes (Ramshead, Amphitheater, and Holly lakes) in the Teton Range were sampled using a gravity coring device and sectioned onsite at 0.25-cm intervals from 0-10 cm and at 0.5 cm for the remainder of the cores.

Diatom slides were prepared using standard techniques for the oxidation of organic matter (Battarbee et al. 2001). To compute sediment diatom concentrations, slides from the Wind River Range lake samples were prepared using Battarbee trays and the Teton Range lake samples were prepared using an aliquot of Polybead® 4.5 μm polystyrene microspheres at a concentration of 2.5 x 10^6 spheres mL^{-1}. Diatom species identifications were based on taxonomic literature that included several volumes (Krammer and Lange-Bertalot 1986, 1991, 1985; Krammer and Lange-Bertalot 1988, 2000; Patrick and Reimer 1975, 1966).

Wind River Range short cores (LSM09-2, NOR09-2) and Teton Range cores were dated using ^{210}Pb at MyCore Laboratories in Ontario Canada. Percussion cores (LSM08-2, NOR08-2) were dated using radiocarbon and $^{239+240}$Pu isotopes. Radiocarbon samples were processed at the ^{14}C laboratory at the U.S. Geological Survey in Reston, Virginia, and ^{14}C ages were determined at the Center for Accelerator Mass Spectrometry at the Lawrence Livermore National Laboratory, Livermore, California. Plutonium isotope analysis was performed at the University of Northern Arizona. We used the CLAM software for locally weighted spline age-depth modeling. CLAM uses IntCal09 and depth ages are weighted to their calibrated age probabilities (Blaauw 2010). Wind River Range cores were analyzed for carbon and nitrogen elemental concentrations and isotopic composition with a Finnigan MAT Delta Plus mass spectrometer at the University of Regina. Teton Range lake cores were analyzed for the same constituents at the University of California Davis Stable Isotope Facility. For both facilities, the replicate standard error was 0.7‰ and the sample replicate deviation was less than or equal to 0.5‰.

3.0 Results

Sediment profiles from all lakes showed upcore increases in nitrogen concentration and upcore decreases in the C:N ratio as we would predict from our null diagenesis model (Figure 1). Similarly, sediment profiles also showed a general trend of more depleted δ^{15}N values towards the sediment surface (Figure 1); however, notable deviations from this general trend are clearly evident (Figure 2-6, panels a, b).

3.1 Comparison of pre-1950 null models to measured $\delta^{15}N$ data

Derived epsilon (ε) values for the models ranged from 1.055 to 1.924 (Table 2). These values are within the expected range, similar to those derived by Freudenthal (2001) and Möbius (2013), and lower than epsilon values derived from peptide bond breakage alone. Pearson correlation coefficients and the RMSE for pre-1950 null models and the bulk record for all cores are shown in Table 2; however, we restrict figure panels to the null model (1 or 2) that best represented the respective lake records as discussed below. For each sediment record, one or both null models preformed reliably for select periods. Specifically, for pre-1950 sediments in Lonesome Lake, Pearson correlation coefficients were 0.89, $p<0.0005$ for Null Model-1, and for North Lake 0.96, $p<0.001$ for Null Model-2 (Table 2). In the Teton Range cores, Null Model-1 conforms well in magnitude, amplitude, and inflection for the pre-1950 eras for Ramshead ($r=0.75$, $p<0.0005$) and Amphitheater lakes ($r=0.43$, $p<0.05$). Null model-1 was significantly negatively correlated to bulk record ($r=–0.52$, $p<0.1$), and the Null-Model 2 was positively, but non-significantly, correlated to the bulk record ($r=0.39$) (Table 2).

3.2 Comparison of positive excursions from the model to lake productivity indicators

In all instances where measured $\delta^{15}N$ was more enriched than the null modeled $\delta^{15}N$ record (positive deviation) we found increases in one or both of the independent diatom measurements of productivity. A positive deviation near the surface of the North Lake short core (NOR09-2) sediment record is coincident with a rapid increase in planktonic diatom productivity, the bulk of which is accounted for by one species, *Asterionella formosa.* Cell counts indicate a total diatom increase from 400 to 1500 cells μg^{-1} sediment (Figure 3, panel c). Similarly in the Lonesome Lake long core (LSM08-2), a positive deviation occurred from 1200 to 1100 Cal Yr BP, coincident with a 6 fold increase in planktonic diatom productivity (Figure 2, panel e). The bulk $\delta^{15}N$ sediment record for Ramshead Lake, in the Teton Range showed a rapid enrichment in $\delta^{15}N$ values around 1940, followed by a substantial depletion by 5‰ from 1975 to 1990 (Figure 4, panel c, d). The diatom records indicated that these shifts can in part be explained by diatom productivity. Around 1940 a substantial increase in the planktonic to benthic diatom species ratio occurred that lasted approximately 30 years. In Holly Lake, the poor model fit pre-1950 can be explained by a positive deviation from the null model from the base of the core to ~1945. Again this appears to be related to changes in productivity as planktonic productivity in Holly Lake was relatively greater in the early part of the record, and showed a rapid and continued decline that began around 1950 (Figure 6, panel c, d).

3.3 Comparison of diagenesis corrected and bulk records to known N emission rates and isotopic composition of N deposition

All lake sediment core records showed upcore declines in the bulk $\delta^{15}N$ record, all of which were negatively offset from the null model results. The RSI test found significant upcore decreases in both the bulk and diagenesis corrected $\delta^{15}N$ records at $p<0.0001$ (Figures 2-6, Table 3). Bulk $\delta^{15}N$ data, however, indicated upcore delta offsets (Δ) as high as 3.4‰ that began before the turn of the century, which is inconsistent with the glacier record as well as the historical development of N emissions from the Pinedale Anticline (Table 3). The average bulk $\delta^{15}N$ estimated offset (Δ) is 2.49‰ (±0.93) for the Wind River Range and 2.96‰ (±0.48) for the Teton Range, approximately twice the estimated Δ using the diagenesis corrected records, which averaged 1.00‰ (±0.04) for the Wind River Range, and 1.85‰ (±0.41) for the Teton Range, and twice the decline in $\delta^{15}N$ deposition recorded in the Fremont Glacier (1–2‰)(Naftz et al. 2011).

The use of the diagenesis corrected records also provided a better estimate of the onset of anthropogenic nitrogen deposition than the bulk $\delta^{15}N$ records. Using bulk $\delta^{15}N$ records, estimated isotopic declines in source DIN begin between 1920 and 1960 in the Wind River Range, and as early as 1866 and as late as 1995 in the Teton Range. Using the diagenesis corrected records we estimated declines beginning at1960 in the Wind River region, and between 1967 and 1974 in the Teton region (Table 3). The diagenesis corrected estimated dates were consistent with the known development history in the Pinedale Anticline.

Using the difference between the bulk $\delta^{15}N$ and the diagenesis corrected $\delta^{15}N$ delta (Δ) values, we estimated the percent change in $\delta^{15}N$ that can be explained by diagenesis alone (Table 3). The results indicated that a substantial fraction of the upcore shift, from 28 to 69% of the variability is explained by diagenesis alone, with the remainder explained by a change in the isotopic composition of the source material.

Comparing the glacier $\delta^{15}N$ record to the diagenesis corrected $\delta^{15}N$ record, we can see that the corrected record reproduced inflections observed in the glacier record that were otherwise not observed in the bulk $\delta^{15}N$ sediment profile (Figure 7). Further, the diagenesis corrected record improves the correlation to the glacier record (r = 0.30 to 0.35) and decreases the RMSE from 6.18 to 3.59.

4.0 Discussion

The interpretation of sedimentary variations in $\delta^{15}N$ is often problematic because of the variety of processes that can influence the single $\delta^{15}N$ proxy. Our results indicate that several factors, including diagenesis, exert significant control on sediment $\delta^{15}N$ records. Strong correlations between the measured and modeled $\delta^{15}N$ variations in the early history of most

Wind River and Teton lake cores suggest that in many cases the preservation of organic material, or the degree to which diagenesis occurred, is a strong factor in controlling sedimentary changes in $\delta^{15}N$. Further, the null models indicate diagenetic shifts greater than 2‰ are preserved within the sediment record. This is an important observation because alternative explanations are often invoked based on isotope excursions of less than 2‰. To illustrate this, a decline in $\delta^{15}N$ that occurs from ~50 cm to 40 cm in the long North Lake core (NOR08-2; Figure 3, panel e) might be used as evidence for a slight decline in productivity through this period, yet absolute diatom counts demonstrate that productivity increased during this period. During this time period, the modeled data match the trend and inflections with a high degree of accuracy ($r = 0.92$), indicating that diagenesis rather than productivity likely controls the trend. Here, an increase in productivity may have increased sedimentation rates and thus reduced rates of decomposition, resulting in a relatively lower $\delta^{15}N$ value. This example illustrates that diagenetic overprinting of sediment $\delta^{15}N$ records is not limited to the surface sediments, but is preserved through the long-term record. Because organic matter degradation rates can vary with time, the assumption that the diagenetic overprinting on sediment records is uniform through time is not valid.

Comparisons between the bulk $\delta^{15}N$ and the diagenesis corrected $\delta^{15}N$ records to known emission and deposition records provided further evidence that 1) the null models are reasonably accurate at reproducing sediment profiles having undergone diagenesis alone, and 2) that diagenesis strongly influenced upcore declines in sediment $\delta^{15}N$, accounting for up to ~70% of the isotopic offset. These results indicate that diagenesis can have considerable and significant effects on sediment $\delta^{15}N$ profiles and thus researchers should be caution against the interpretation of $\delta^{15}N$ profiles without the consideration of diagenesis.

Beyond evaluating the effect of diagenesis on sediment $\delta^{15}N$ records, the use of one or both null models provides a useful framework for evaluating the controls on sedimentary $\delta^{15}N$ records. The deviations from null models can be used to provide additional information on sedimentary $\delta^{15}N$ shifts relating to both changes in the isotopic source composition or changes *in situ* fractionation.

4.1 Evaluating changes in productivity

With respect to shifts in productivity, the use of the null models can help to determine when productivity changed. As shown above, all positive deviations from the null models, including those found in North Lake (NOR09-2), Lonesome Lake (LSM08-2), Ramshead Lake, and Holly Lake, were temporally linked to increases in diatom productivity in the epilimnion. Though the latter two lakes did not show increases in overall diatom productivity, the ratio of planktonic to benthic diatom populations indicated shifts in productivity towards the epilimnion where nutrients can become more limiting throughout the growing period. These examples illustrate that when the null models underestimate the bulk $\delta^{15}N$ record, increased productivity is a probable cause. Accordingly, when the null models overestimate bulk sediment $\delta^{15}N$, a greater discrimination between the DIN and algae, resulting in lower $\delta^{15}N$ is possible. For example, in Amphitheater Lake, the null models overestimated $\delta^{15}N$ from 1900 to present (Figure 5, panel c). This offset is coincident with a drop in planktonic productivity, whereby cell counts dropped from an average of 1000 to less than 500 cells μg^{-1} sediment (Figure 5, panel d).

The use of this type of model can further aid in the determination of historical nutrient limitation. For example, in LSM08-2 the measured $\delta^{15}N$ from approximately 1200 to 1100 Cal Yr BP (35 to 45 cm) was considerably higher than the modeled values (Figure 2, panel e). At this time the lake experienced a large increase in planktonic diatom productivity. A similar increase in diatom productivity was recorded in the sediments from the nearby North Lake during this period, but without a positive isotope excursion. This may be because the productivity insufficient in North Lake to considerably draw down the nitrogen pool and induce Rayleigh fractionation. This suggests that nitrogen was not the limiting nutrient at this time. As this example illustrates, the use of models can provide substantively more information on the historical interpretation of sediment profiles than bulk $\delta^{15}N$ alone. Because a significant proportion of the organic nitrogen pool must be used for Rayleigh effects to occur, the use of models and diatom data in conjunction provides information on potential nutrient limitation by providing both a baseline $\delta^{15}N$ estimate and an independent measure of productivity.

4.2 Evaluating changes in organic matter source

Many of the lakes in the study region are alpine and have few, if any, sources of terrestrial vegetation providing organic matter inputs to the lake sediments. For example, the North Lake catchment is 92% bare rock, though some of the lakes (Lonesome, and Amphitheater) have small forested areas within the catchment. The C:N ratios in a few cases appeared to indicate the presence of vascular plant material. A peak in modeled $\delta^{15}N$ in Amphitheater Lake around the late 1800's correlated to a time of high sedimentation rates, or what appears to be a small landslide into the lake (Figure 5, panel c). The C:N ratios peaked at 18 during this time and the relative concentrations of organic matter were lower. A similar offset was present in the early history of North Lake (NOR08-2) (Figure 3, panel e). Null Model-1 reconstructed the measured values well throughout the North Lake core, while the bulk record showed a negative excursion from Null Model-2 from the base of the core to 30 cm (Figure 3, panel f). During this time C:N ratios were relatively high (12–14), suggesting a greater contribution of vascular plant organic material to the lake. Since there is little to no vegetation in the North Lake catchment, but some littoral vegetation in shallow regions, it is possible that there was a greater area of shallow habitat at this time, though currently we have no corroborating evidence for this hypothesis.

4.2 Evaluating anthropogenic nitrogen deposition

The regime shift indicator results (Table 3) revealed that the diagenesis corrected models do a substantially better job at reconstructing the known history of nitrogen deposition than the bulk $\delta^{15}N$ records. Though all bulk sediment records showed upcore declines in $\delta^{15}N$, the onset and degree of offset (Δ) varied significantly and were inconsistent with known N emission and $\delta^{15}N$ deposition records. In contrast, the diagenesis corrected records indicated declines in $\delta^{15}N$ that were both consistent with each other and with the known records of N emission and $\delta^{15}N$ deposition. Therefore the use of diagenesis corrected records can be valuable when reconstructing historical anthropogenic N deposition and its effects on lake ecosystems.

Our data also showed that the isotopic depletion of organic N due to N deposition could be completely offset by the isotopic enrichment due to increased productivity resulting in no apparent deviation from our null model. This is a totally plausible scenario in response to N deposition that could only be discerned by using ancillary data, such as changes in geochemistry or diatom assemblage.

5.0 Conclusions

Our results have important implications for efforts to use sedimentary $\delta^{15}N$ signatures to reconstruct historical aspects of the nitrogen cycle and can offer new insights into the $\delta^{15}N$ profiles of recently published high-profile papers (McLauchlan et al. 2013; Holtgrieve et al. 2012). We have demonstrated that diagenesis is an important process that can be evaluated in a systematic way and can enhance the source signal of interest. Our results indicate that diagenetic overprinting can account for up to 70% of the variation in sediment $\delta^{15}N$ and several parts per thousand, well within the range used to interpret environmental causes of $\delta^{15}N$ change. In particular, based on Rayleigh effects, a sediment column undergoing no change in environmental conditions will show an exponential upcore decline in $\delta^{15}N$. Therefore, although nitrogen deposition is occurring throughout many regions, the assumption that upcore declines in $\delta^{15}N$ are categorically related to environmental change is not justifiable.

There is no reason to assume that diagenesis would not affect sediment profiles over long time scales. Our results show that diagenetic overprinting varies through time and the associated shifts in $\delta^{15}N$ are preserved in the sediment. Further, given that sedimentary microbes remain active to considerable depths (Parkes et al. 1994), ammonification can be expected to continue even within deep sediments that have been buried for millennia. A net loss of only one atom of ^{14}N relative to ^{15}N for every billion nitrogen atoms would, for example, still produce a 2‰ shift over a time period such as the early Holocene. Although long term trends in organic sedimentary $\delta^{15}N$ may be used to interpret environmental changes in some settings, we know that diagenesis alters organic sedimentary $\delta^{15}N$ in many settings, which cautions against the use of $\delta^{15}N$ records without considering diagenesis.

The models presented here are a novel approach to deconvoluting the $\delta^{15}N$ signal in oxic lake sediment cores. This paper demonstrates a systematic framework for assessing the degree to which sediment records have been altered by diagenesis in oligotrophic and mesotrophic lakes in barren remote settings that are often used in reconstructing N cycle processes (Wolfe et al. 2001; Saros et al. 2003; Holtgrieve et al. 2012). We expect the models to be of use in other lake systems, although that will require further study. Certainly the results indicate that, in the absence of a mechanistic correction for diagenesis (such as the null models presented here), the effects of organic matter degradation on isotopic N signatures in sediments ought to be considered explicitly and effects ruled out when appropriate (e.g. Holtgreive et al. 2012 Supplementary Information) and not dismissed ad hoc. The models presented here appear useful for the interpretation of $\delta^{15}N$ sediment records relating to changes in anthropogenic nitrogen deposition, productivity, terrestrial plant contributions, and nitrogen fixation. The use of both null models can account for the effects of terrestrial contributions or the effect of productivity on N concentrations respectively, although the models may be less useful if sedimentary $\delta^{15}N$ are simultaneously affected by diagenesis, source concentration, productivity, and variation in terrestrial contributions.

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Table 1 Lakes analyzed in this study including regional nitrogen deposition from the National Atmospheric Deposition Program (NADP 2009) and total lake nitrogen concentrations (TN).

Lake	Range	Latitude	Longitude	Altitude	N deposition (kg ha^{-1})	TN (mg L^{-1})
Lonesome	Wind River	42.78	-109.22	3101	1.07 (±0.25)	0.162
North	Wind River	42.76	-109.06	3085	1.07 (±0.25)	0.234
Ramshead	Teton	43.78	-110.76	2898	1.01 (± 0.17)	0.111
Amphiteater	Teton	43.72	-110.78	2962	1.01 (± 0.17)	0.078
Holly	Teton	43.79	-110.79	2874	1.01 (± 0.17)	0.053

Table 2 Null Model parameters and results for Wind River and Teton Range lake sediment cores. Model epsilon and $\delta^{15}N_{ON(i)}$ values are shown for the null models used in the analysis and listed in the first column. Pre-1950 correlation and RMSE are shown for all null models in comparison to their respective bulk $\delta^{15}N$ records. Bold marks significant correlations at $p < 0.1$.

Lake Core	Null Model	ε	δi	Null Model 1 *r*	Null Model 1 *p*	Null Model 2 *r*	Null Model 2 *p*	Null Model 1 RMSE (‰)	Null Model 2 RMSE (‰)
Lonesome (LSM09-2)	1	1.489	1.130	0.89	**0.0003**	0.03	0.9416	0.21	0.59
Lonesome (LSM08-2)	1	1.489	1.910	0.15	0.4217	0.17	0.3526	0.36	0.43
North (NOR09-2)	2	1.055	1.826	0.56	0.1962	0.96	**0.0007**	0.28	0.1
North (NOR08-2)	2	1.924	1.605	0.74	**0.0000**	-0.24	0.2661	0.23	0.67
Ramshead	1	1.346	1.340	0.75	**0.0003**	-0.52	**0.0258**	0.5	0.92
Amphitheater	1	1.561	1.749	0.43	**0.0273**	0.02	0.9173	0.97	0.34
Holly	2	1.145	1.120	-0.52	**0.0704**	0.39	0.1945	0.43	0.42

Table 3. Comparison of regime shifts detected for the bulk and diagenesis corrected $\delta^{15}N$ records. Note the use of the diagenesis corrected record produces a more consistent upcore offset in $\delta^{15}N$ (Δ) (~1 to 2‰) as well a more consistent onset of decline (~1960-1970), both of which are consistent with the known regional record of N emissions and $\delta^{15}N$ in atmospheric deposition

	Bulk Record		Diagenesis corrected Record		
	$\Delta\ \delta^{15}N$	Onset of $\delta^{15}N$ decline	$\Delta\ \delta^{15}N$	Onset of $\delta^{15}N$ decline	Percent attributable to diagenesis
Lonesome (LSM09-2)	3.15	1960	0.97	1960	69
North (NOR09-2)	1.83	1926	1.02	1960	44
Average	2.49	1943	1.00	1960	57
Std. Dev	0.93	24	0.04	0	
Ramshead	3.07	1955	2.22	1973	28
Amphitheater	3.38	1866	1.93	1974	43
Holly	2.44	1995	1.41	1967	42
Average	2.96	1939	1.85	1971	38
Std. Dev	0.48	66	0.41	4	

Figure Captions

Figure 1. Conceptual null models showing the effects of diagenesis on sedimentary records of $\delta^{15}N$, %N, and the C:N ratio in the absence of any environmental change (black line). Dashed and dotted lines show the directional offset from the null model due to increases in N deposition (dash), increases in productivity (dot), and increases in vascular plant material (dash-dot).

Figure 2 Lake sediment records for Lonesome Lake, Wind River Range Wyoming (LSM08-2, LSM09-2).

Figure 3 Lake sediment records for North Lake, Wind River Range Wyoming (NOR08-2, NOR09-2). NOR08-2 is shown against a depth profile as surface sediment ages are poorly constrained and compressed in the age representation.

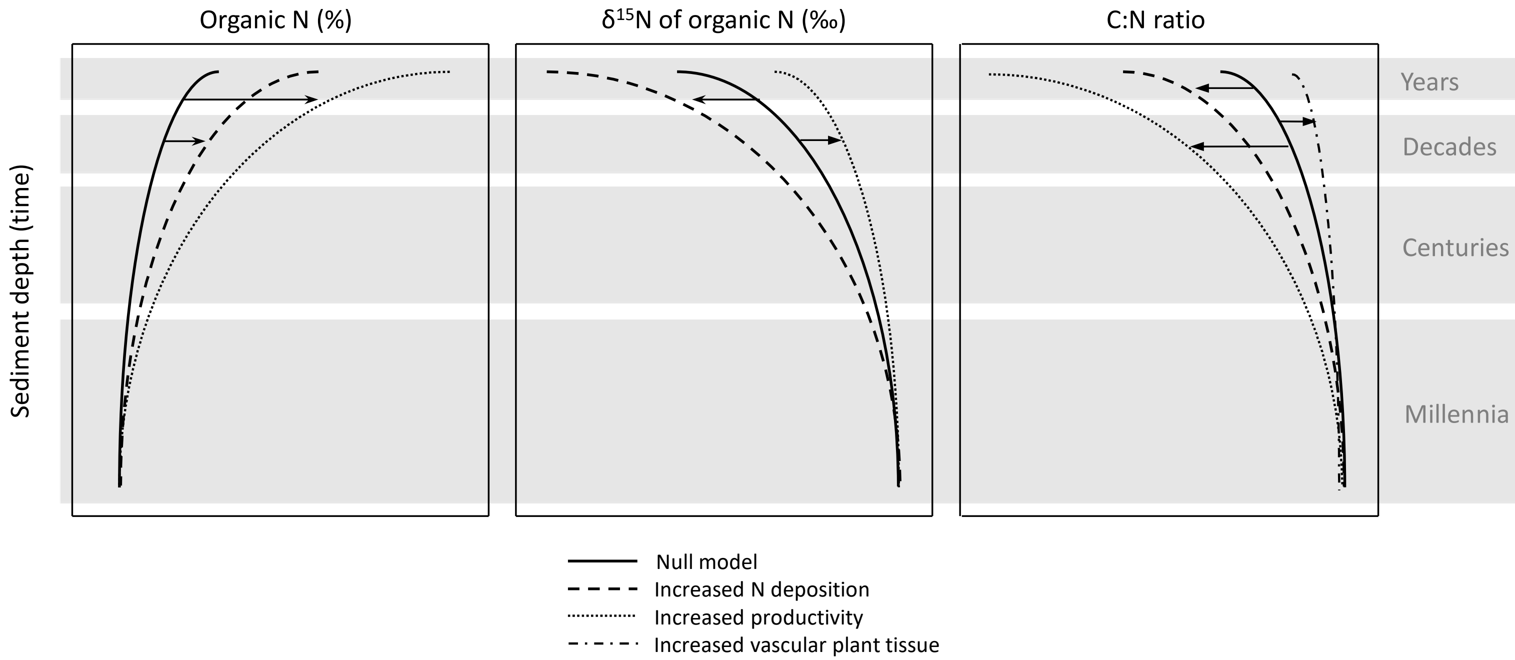
Figure 4 Lake sediment records for Ramshead Lake, Teton Range, Wyoming

Figure 5 Lake sediment records for Amphitheater Lake, Teton Range, Wyoming

Figure 6 Lake sediment records for Holly Lake, Teton Range, Wyoming

Figure 7: An illustration showing the bulk $\delta^{15}N$ sediment record (solid black line), the diagenesis corrected $\delta^{15}N$ record (solid gray line), and the Fremont Glacier isotope record (dotted line). The diagenesis corrected record reproduces inflections recorded in the glacier record better than the bulk sediment $\delta^{15}N$ record alone.

Figure 1



Organic N (%)
δ15N of organic N (‰)
C:N ratio
Sediment depth (time)
Years
Decades
Centuries
Millennia
Null model
Increased N deposition
Increased productivity
Increased vascular plant tissue

Figure 2

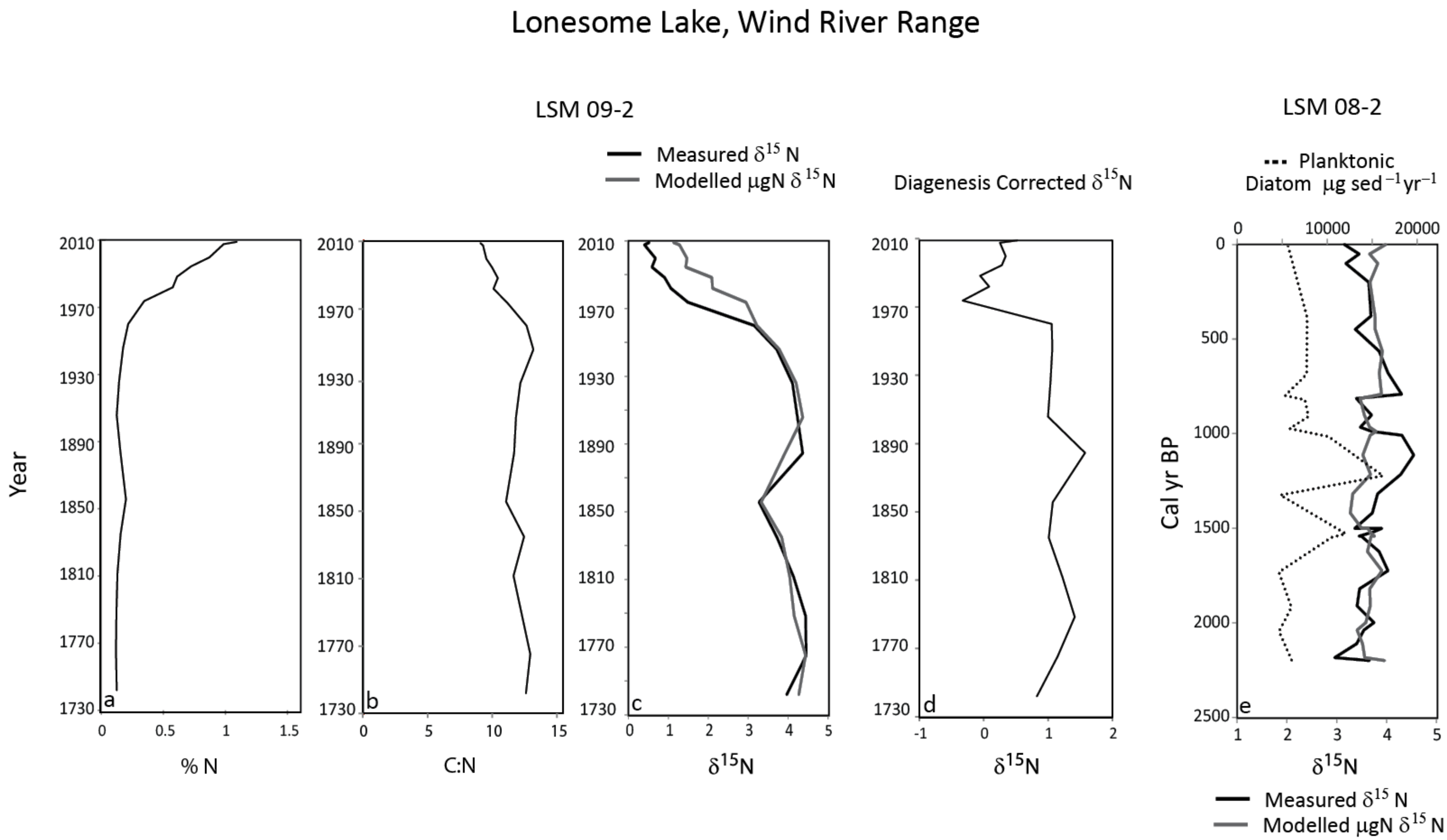

Lonesome Lake, Wind River Range
LSM 09-2
LSM 08-2
Measured δ15 N
Modelled µgN δ 15 N
Diagenesis Corrected δ15N
Planktonic Diatom µg sed−1yr−1
Year
Cal yr BP
% N
C:N
δ15N
a
b
c
d
e

Figure 3

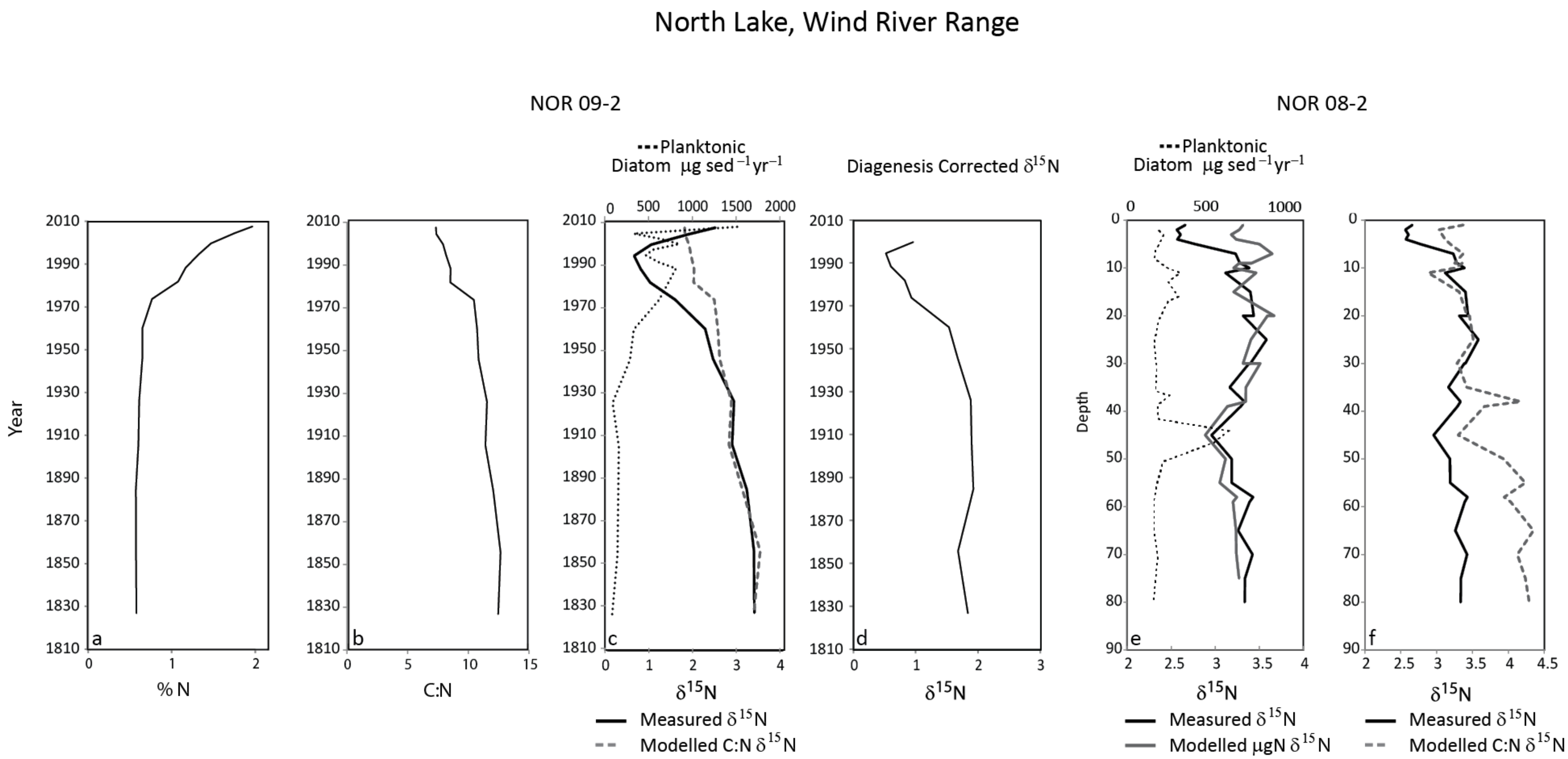

North Lake, Wind River Range
NOR 09-2
NOR 08-2
Planktonic Diatom µg sed⁻¹yr⁻¹
Diagenesis Corrected δ15N
Planktonic Diatom µg sed⁻¹yr⁻¹
Year
Depth
a
b
c
d
e
f
% N
C:N
δ15N
δ15N
δ15N
δ15N
Measured δ15N
Modelled C:N δ15N
Measured δ15N
Modelled µgN δ15N
Measured δ15N
Modelled C:N δ15N

Figure 4

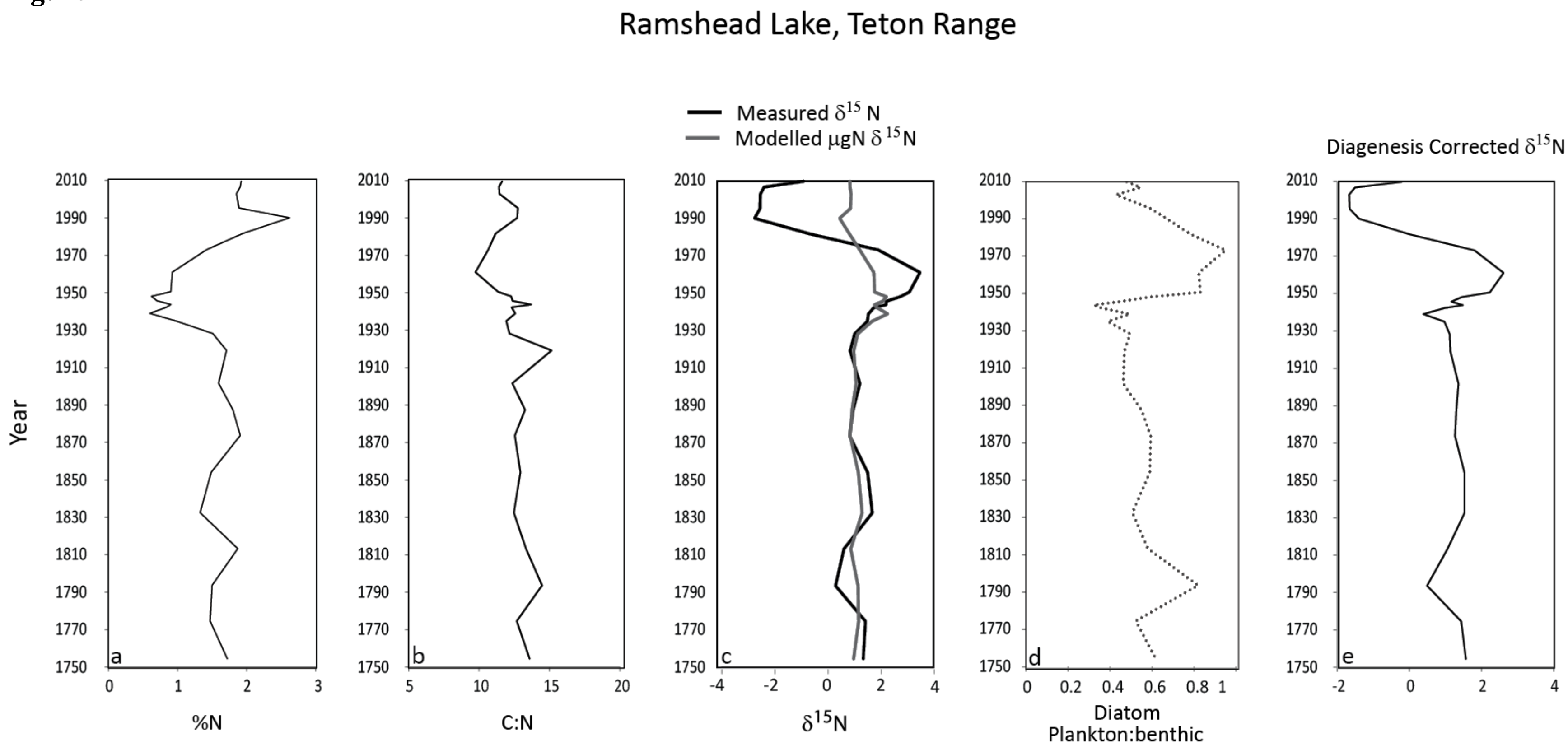

Ramshead Lake, Teton Range
Measured δ15 N
Modelled μgN δ 15N
Diagenesis Corrected δ15N
Year
a
b
c
d
e
%N
C:N
δ15N
Diatom
Plankton:benthic

Figure 5

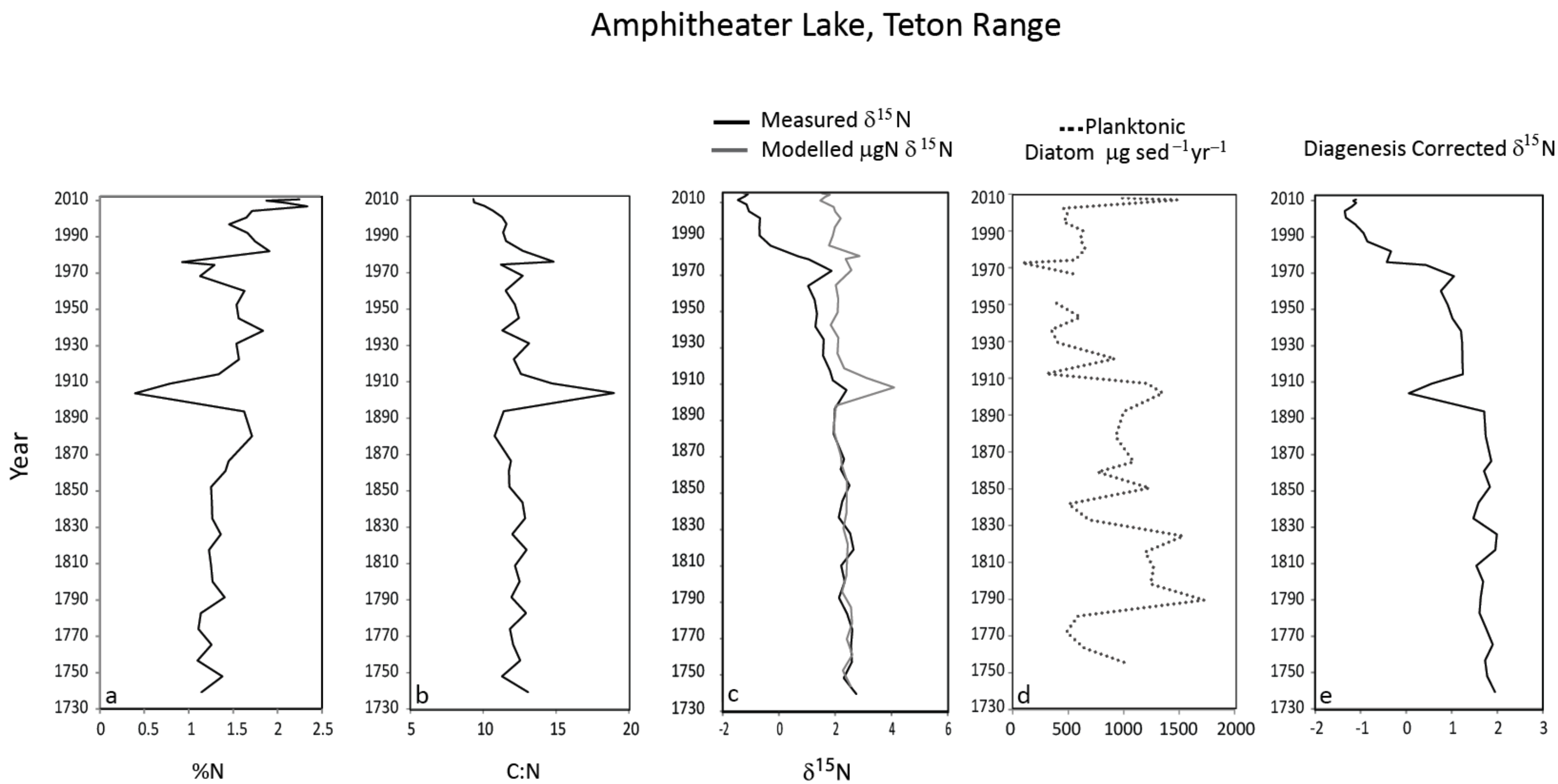

Amphitheater Lake, Teton Range
Measured δ15N
Modelled µgN δ 15N
Planktonic
Diatom µg sed −1yr−1
Diagenesis Corrected δ15N
Year
a
b
c
d
e
%N
C:N
δ15N

Figure 6

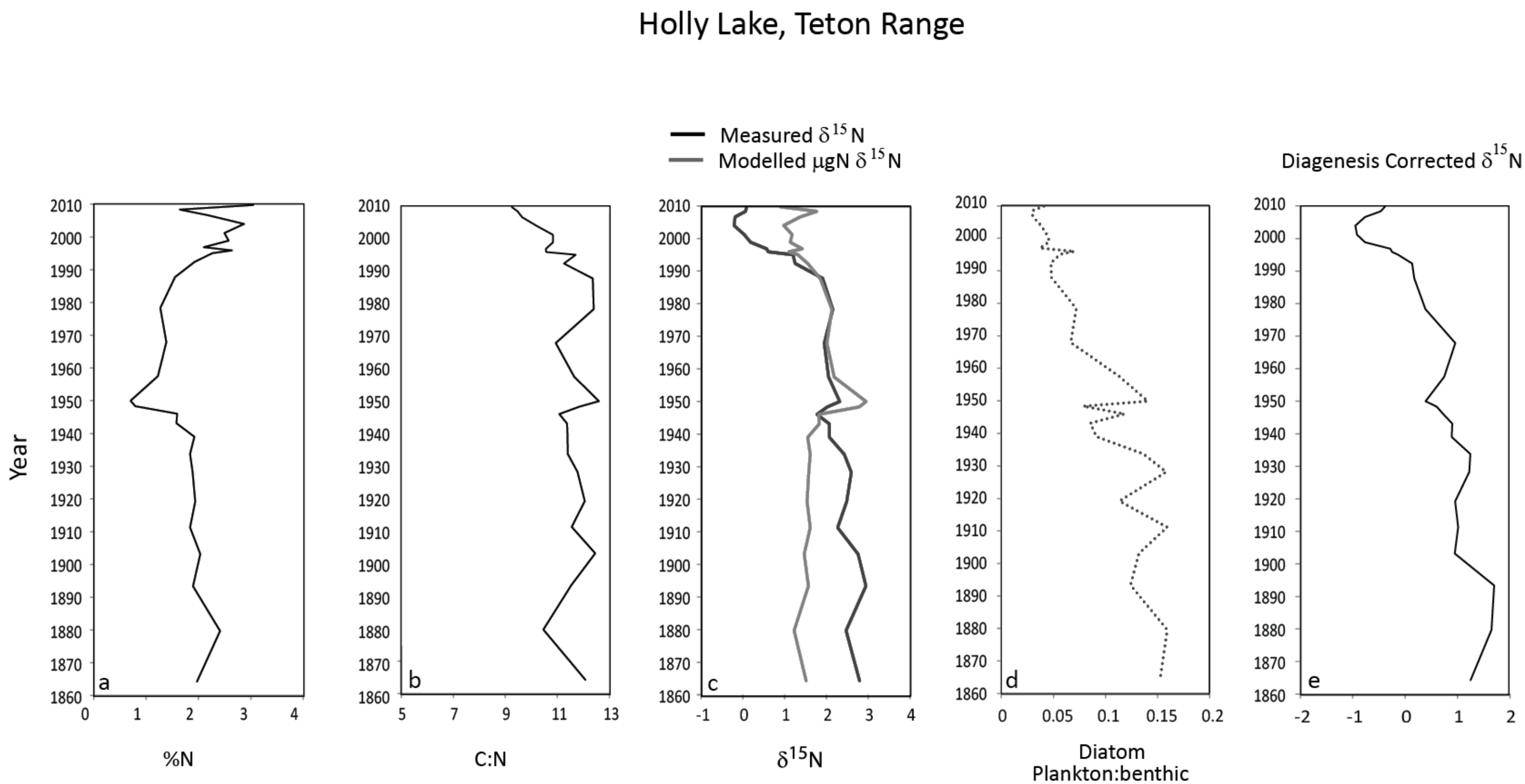
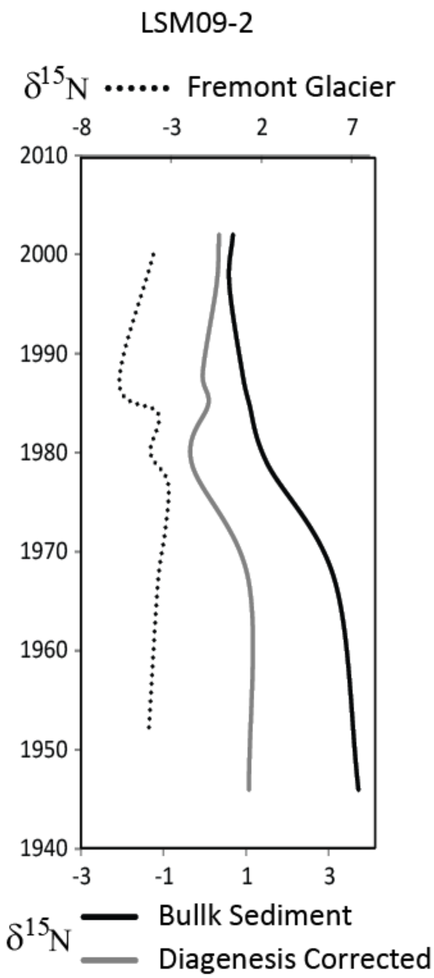

Holly Lake, Teton Range
Measured δ15N
Modelled µgN δ15N
Diagenesis Corrected δ15N
Year
2010
2000
1990
1980
1970
1960
1950
1940
1930
1920
1910
1900
1890
1880
1870
1860
a
b
c
d
e
0 1 2 3 4
5 7 9 11 13
-1 0 1 2 3 4
0 0.05 0.1 0.15 0.2
-2 -1 0 1 2
%N
C:N
δ15N
Diatom
Plankton:benthic

Figure 7


LSM09-2
δ15N Fremont Glacier
-8
-3
2
7
2010
2000
1990
1980
1970
1960
1950
1940
-3
-1
1
3
δ15N
Bullk Sediment
Diagenesis Corrected