**Using Nitrogen Stable Isotope Values to Track Nitrogen Cycling Over the Last 4000 Years at Cape Tuxen, Antarctic Peninsula**

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I certify that I have read this thesis and that, in my opinion, it is satisfactory in scope and quality as a thesis for the degree of Bachelor of Science in Global Environmental Science.

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*For my family and friends, who are the best support system I could ever ask for.*

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ABSTRACT

The western Antarctic Peninsula (AP) is one of the most rapidly warming regions on Earth. Retreating ice has promoted the colonization and expansion of terrestrial plant communities, including Antarctic mossbank ecosystems. Nitrogen (N) is one of the most important ecological limiting factors in high latitude regions, and thus, even small changes in N concentrations may cause dynamic shifts in the N cycle. Modern plants and mossbank cores were collected at multiple study sites across the western AP (64°09'S 60°57'W to 67°36'S 68°21'W) to characterize N abundance in Antarctic ecosystems. This includes the longest (202 cm) and oldest (~4000 years old) organic sediment core ever collected from the western AP, which is from a study site at Cape Tuxen (TUX1). Mossbank cores were measured for bulk density and organic matter, as well as total nitrogen (TN%) and carbon (TC%) by Elemental Analysis Isotope Ratio Mass Spectrometry (EA-IRMS). A species-specific approach was taken to measure foliar nitrogen and $\delta^{15}N$ in modern and subfossil leaves by EA-IRMS.

Across the five short core sites, TN% ranged from $0.17 \pm 0.04$ and $2.34 \pm 0.50$ TN%, which is slightly high compared to previous AP peat core research. The TUX1 peat core falls within these ranges, with $1.94 \pm 0.15$ TN%. TUX1 fossil leaves showed a significant positive correlation between foliar $\delta^{15}N$ and TN% (P<0.001). TUX1 data supports empirical evidence that suggests that Antarctic terrestrial N cycling is linked to marine-animal-derived sources delivered via ammonia volatilization. Declining $\delta^{15}N$ values in recent centuries may be due to declining animal populations and increasing air temperatures causing increased ammonia volatilization and isotope fractionation.

TABLE OF CONTENTS

**LIST OF TABLES**

**LIST OF FIGURES**

## LIST OF ABBREVIATIONS

AP – Antarctic Peninsula

$^{14}C$ – Radiocarbon

CIE1 – Cierva Cove study site

$\delta^{15}N$ – Delta nitrogen-15

EA-IRMS – Elemental Analysis Isotope Ratio Mass Spectrometry

N – Nitrogen

HCl – Hydrochloric acid

IRMS – Isotope ratio mass spectrometer

LEO3 – Léonie Island study site

LMG – Laurence M. Gould Antarctic research vessel

LOI – Loss-on-ignition

MS2 – Moss Island study site

OM – Organic matter

PET4 – Petermann Island study site

RAS5 – Cape Rasmussen study site

SIRFER – Stable Isotope Ratio Facility for Environmental Research

SO – Southern Ocean

TC% – Total carbon content measured as a percent

TN% – Total nitrogen content measured as a percent

TUX1 – Cape Tuxen study site

**1.0 INTRODUCTION**

**1.1 BACKGROUND**

The greening of Antarctica is occurring at a rapid pace with anthropogenic climate change (Charman et al. 2018). Environmental change in this region is driven by warming, increases in wind strength and precipitation, and extension of ice melting periods (Convey and Peck, 2019; Abram et al., 2013). According to the Intergovernmental Panel on Climate Change (IPCC) sixth assessment report, there will be global warming of over 2°C during the 21st century. An additional warming issue for Antarctica is caused by polar amplification, which is a climate change phenomenon that explains that any change in net radiation tends to lead to a greater change in temperature at the poles compared to the global average. This is especially concerning for the western Antarctic Peninsula (AP), as it is one of the most rapidly warming regions on the globe (Bromwich et al., 2013). Resulting observed changes include loss of sea ice extent and increased Southern Ocean (SO) sea surface temperature (Turner et al., 2017; Turner et al., 2020; Jiping and Curry, 2010; Anderson et al., 2021). A record-breaking temperature of 20.75°C was recorded on February 9, 2020 on



**Figure 1:** High air temperature anomaly recorded across the Antarctic continent in February 2020. Single hatching marks regions where the anomaly is <15th percentile or >85th percentile over the climatological period. Crossed hatching marks regions where the anomaly exceeds the climatological minimum or maximum (Robinson et al., 2020).

10

Seymour Island, which is located on the eastern AP (Robinson et al., 2020). Though, warm air temperature anomalies are being recorded across the entirety of the AP (Figure 1). As changes in the physical environment occur through alterations in ice cover, temperature, and habitat and food loss, ecological relationships change as well.

The SO plays a key role in maintaining various biogeochemical processes and is responsible for considerable uptake of anthropogenic nitrogen and carbon (Pan et al., 2020; Terhaar et al., 2021). The SO sees an especially significant influx of nitrogen as it borders a multitude of countries that emit large amounts of anthropogenic nitrogen, such as China and India (Pan et al., 2020). With an influx of nitrogen, rates of primary productivity may become elevated, and therefore the marine food web will be altered as a result. For instance, as phytoplankton populations grow, so will fish populations, as this will provide them with a larger food source. Marine mammals and seabirds are responsible for transporting nutrients from the SO such as nitrogen and carbon through fecal inputs onto Antarctic land environments (Henley et al., 2020). Pristine and remote ecosystems are counter-intuitively decreasing in N, and this may make them even more sensitive to transfers from realms that are N-rich (Mason et al, 2022). As a result, plant growth is driven by the animal transfer of nutrients from ocean to land.

Today, only 3% of the area of the AP is seasonally ice or snow-free (Siegert et al., 2019). With rapid ice melt comes the opportunity for the colonization of Antarctica by terrestrial plants. The dominant plant species in the region are bryophytes, with one of the most notable being species of the genus *Polytrichum*, or bog haircap moss. As these mosses grow, they can accumulate over time and form large frozen moss stacks, called

moss peat banks (Cannone et al., 2017). Antarctic moss peat banks lack a water table at

the surface and are aerobic ecosystems. Additionally, the plant material in them is well

preserved by the presence of permafrost (Yu et al., 2016). These moss banks preserve

organic matter affected by long-term environmental change as peat, and are therefore

ideal for studying past ecosystems and climate (Fenton and Smith, 1982).


## 1.2 NITROGEN CYCLING IN THE ANTARCTIC PENINSULA

Nitrogen (N) is one of the most important ecological limiting factors in high

altitude and high latitude regions (Yergeau et al., 2007). Therefore, even small changes in

N inputs and concentrations may bring about dynamic shifts in the N cycle. Although N

is the main component of Earth's atmosphere, it is limited in ecosystems as it is

unavailable to most organisms in its most abundant form, N gas (Elser et al., 2007). All

living organisms need N in order to create and repair their cells as N is required to build

amino acids, which are one of the building blocks of life.

Both indirect and direct nitrogen sources are present in the AP terrestrial and

marine environments. The primary indirect source can be mainly attributed to

wind-dispersed sediment from southernmost South America, while the principal direct

source is fecal inputs from various marine animals such as fur seals and penguins. The

Antarctic N cycle consists of microbe, soil, plant and animal pools, and is mainly driven

by microbial activity due to the relative scarcity of macroorganisms (Ortiz et al., 2020).

N becomes available into the ecosystem through decomposition of organic matter

in soil, biological fixation and deposition through wind and gravity transport (Ortiz et al.,

2020). For Antarctic soils specifically, where soil decomposition is limited (Nielsen and Wall, 2013), the primary sources of N have been found to be from $N_2$ fixation by cyanobacteria and from the precipitation of volatilized ammonium ($NH^{4+}$) from bird colonies (Yergeau et al., 2007; Cavieres et al., 2018). These processes provide N for plant and microbial uptake. In due course, N eventually returns to the soil pool through microbial and plant death, as well as animal fecal matter. N concentrations are decreased in the soil through leaching and denitrification, and are transferred to the hydrosphere and atmosphere (McNeill and Unkovich, 2007; Niu et al., 2016).

In the marine N cycle, many N transformations occur, such as in the fixed N pool of $N_2$ fixation, retained N pool of assimilation, and fixed N loss of denitrification (Pajares and Ramos, 2019). $N_2$ is taken up from the atmosphere by the ocean, and the dissolved N gas is consumed by microbes, who fix N into $NH^{4+}$, which is a crucial process for organisms that consume $NH^{4+}$. Assimilation allows for N to become integrated into the living cells of organisms (Voss et al., 2013). As consumers feed on producers, N gets transferred up each trophic level of the food web. As marine animals come up onto terrestrial ecosystems, they transfer N into the system by excreting fecal matter and by dying and decomposing (Wang et al., 2020).
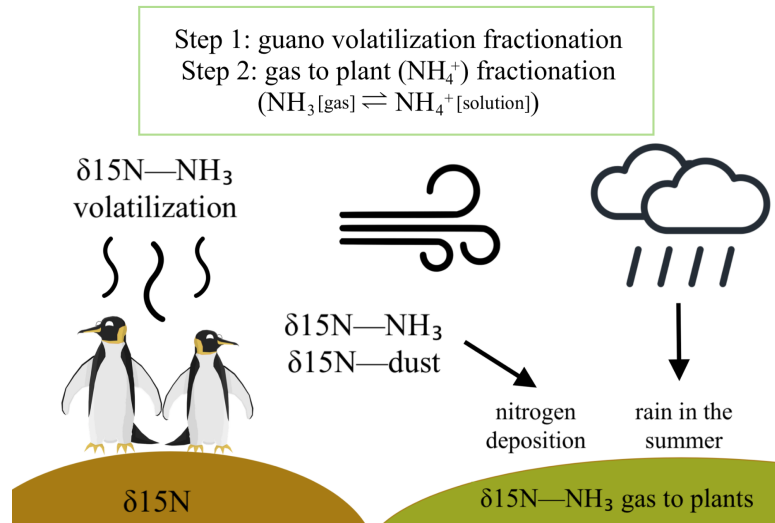
**Figure 2:** Schematic diagram of the process of $\delta^{15}N$ enrichment of Antarctic cryptogams by volatilized ammonia from penguin and seal colonies (Adapted from: Bokhorst et al., 2019).

## 1.3 TROPHIC ENRICHMENT AND $\delta^{15}N$ AS A TRACER

The heavier stable isotope of N, $^{15}N$, has been used in multiple studies as a tracer in ecosystem research (Bedard-Haughn et al., 2003; Schleppi and Wessel, 2021; O'Neill, et al., 2021). Nitrogen stable isotope ratios of $^{15}N:^{14}N$ are expressed as $\delta^{15}N$ values in delta notation (Equation 1). Values of $\delta^{15}N$ in ecosystems can be used to determine the pathways of N between different trophic levels in food webs and is especially useful in determining animal-derived N input into land environments (Bedard-Haughn et al., 2003). Previous research has shown that isotopic enrichment increases with every trophic level (Bergstrom et al., 2002). Empirical evidence records an average 2-4% increase in N with each step up the food web (Vander Zanden and Rasmussen, 2001; Post, 2002; Perkins et al., 2014; Mason et al, 2022; Stephens et al, 2022).

Through the volatilization of ammonia, where $NH^{4+}$ is converted to $NH^3$ gas and transferred into the atmosphere, $^{15}N$ from animal urea can be moved into ecosystems (Freney et al., 1983). This process is one of the most important processes in transporting marine-derived N into terrestrial environments. Soils and vegetation in close proximity to bird and seal rookeries consistently show high $\delta^{15}N$ values (Lee et al., 2009; Bokhorst et al., 2019; Wang et al., 2020). There are a multitude of other mechanisms that can affect $\delta^{15}N$ values in soils. Processes such as atmospheric wet and dry deposition and microbial activities such as mineralization, nitrification and denitrification provide $^{15}N$ enrichment in soils (Zhou et al., 2014; Makarov et al., 2021). Typically, increases in mean annual precipitation and decreases in mean annual temperature lead to a decline in $\delta^{15}N$ values in soils (Amundson et al., 2003; Craine, et al., 2015). These environmental factors and their relationship with changing N patterns are varying as a result of global change, meaning ecosystem stoichiometry is changing as well (Zhou et al., 2014).

## 1.4 RESEARCH OBJECTIVES

To better understand how N cycling has changed over time as a result of environmental change in the AP, this project follows two main research objectives, which are to:

1. Characterize N abundance in Antarctic land environments by determining nitrogen concentrations in mossbank profiles.
2. Investigate marine N effects on the Antarctic terrestrial N cycle and plant growth over time, using stable N isotope values in modern and subfossil plants.

## 2.0 METHODS

### 2.1 STUDY SITES AND FIELD SAMPLING

Multiple living plants and peat cores of frozen plant subfossils were collected from the western AP during research cruises LMG14-03 and LMG20-02 aboard the Laurence M. Gould (LMG) Antarctic research vessel in 2014 and 2020 respectively. A total of 16 different ice-free vegetated areas of the continental peninsula and nearby islands accessible by research vessel and zodiac boat were visited and selected as study sites (Table 1). Living plants were carefully collected as small, georeferenced grab samples of common plants to ensure no harm to the long-term health of the populations, and georeferenced in the field by handheld GPS. Mossbank cores were raised using a box corer and a gas-powered permafrost corer with diamond tipped teeth. Plants and cores were stored at -80°C on the LMG and shipped to the University of Hawai'i on dry ice. Five frozen moss cores ranging from 15-28 cm were collected between 64°09'S 60°57'W to 67°36'S 68°21'W (Figure 3).

Additionally, the deepest moss bank core (202 cm) ever raised from the western AP was retrieved in February 2020 from a study site at Cape Tuxen (65°16′S 64°8′W). The large ice-free, vegetated area of Cape Tuxen makes it an ideal study site for tracking long-term N changes as it is elevated and steep, which ensures little to no direct N input from marine animals like penguins and seals. However, it is located close enough to the coast (~200m) so that processes such as ammonia volatilization are occurring.

**Table 1**. The 16 total study sites and collected samples used in this study organized by latitude, with the main Cape Tuxen study site highlighted.

| Location | Site | Year | Latitude | Longitude | Modern Plants | Mossbank Cores |
|---|---|---|---|---|---|---|
| Léonie Island | LEO | 2014 | -67.598778 | -68.3565278 | 1 | 1 |
| Berthelot Islands | BER | 2020 | -65.32797 | -64.14423 | 1 | N/A |
| Cape Tuxen 1 | TUX1 | 2020 | -65.271522 | -64.121306 | 1 | 1 |
| Cape Tuxen 3 | TUX3 | 2020 | -65.261893 | -64.115905 | 1 | N/A |
| Galindez Island | GAL | 2014 | -65.2476111 | -64.25063889 | 7 | N/A |
| Cape Rasmussen | RAS | 2020 | -65.247083 | -64.085222 | 1 | 1 |
| Petermann Island | PET | 2014 | -65.1774167 | -64.1442778 | 1 | 1 |
| Hermit Island | HER | 2014 | -64.8 | -64.01777778 | 1 | N/A |
| Bonaparte Point | BON | 2014 | -64.777448 | -64.044374 | 1 | N/A |
| Litchfield Island | LIT | 2014 | -64.77025 | -64.0889167 | 1 | N/A |
| Pi Islands | PII | 2020 | -64.32389 | -62.87232 | 1 | N/A |
| Spring Point | SPR | 2020 | -64.29748 | -61.04929 | 1 | N/A |
| Charles Point | CHA | 2020 | -64.2365 | -60.99722 | 1 | N/A |
| Apéndice Island | APE | 2020 | -64.18266 | -61.026291 | 1 | N/A |
| Moss Island | MS2 | 2020 | -64.16676 | -61.04575 | 1 | 1 |
| Cierva Cove | CIE | 2014 | -64.1560833 | -60.95641667 | 1 | 1 |
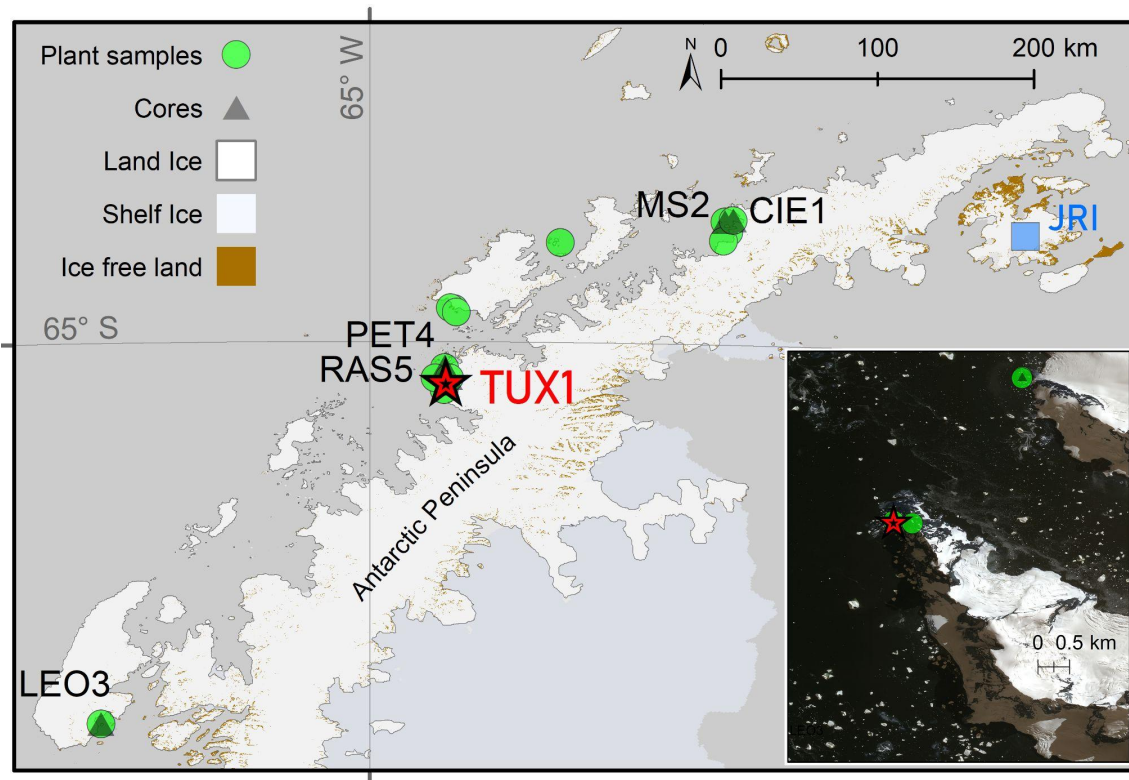
**Figure 3:** Map of the 2020 study sites along the Antarctic Peninsula and worldview2 image from summer 2020 inset map that highlights the location of the TUX1 study site. Light blue areas represent sea ice and brown areas show ice-free areas. Black triangles represent mossbank coring sites and green circles represent modern plant sampling sites.

## 2.2 NITROGEN AND δ¹⁵N OF BULK MOSSBANK PEAT

At the University of Hawai'i, frozen mossbank sediment cores were cut in half lengthwise using a band saw with a stainless steel blade. One half was archived, and the other half was sliced into one-centimeter sections. From each section, a known-volume subsample was taken with the aid of a steel borer and 0.01 mm calipers. These samples were dried at 100ºC and bulk density was calculated as the ratio of the dry weight to the fresh volume. Dried samples were then homogenized using a Retsch MM200 mixer mill with stainless steel jars and balls followed by sieving completely at 250-microns. Half of

the homogenized samples were baked at 550ºC in order to calculate loss-on-ignition

(L.O.I.) as an estimate of organic matter (OM) content (Heiri et al., 2001). Of the

remaining half of the homogenized samples, 1.5 to 2.0 mg was weighed into pure Sn

capsules and measured for total N (TN%) and total C (TC%) on a Costech ECS4010

elemental analyzer (Chambers et al., 2011).

## 2.3 CHARACTERIZATION OF SUBFOSSIL PLANTS

Subfossil plant leaf tissue from well-preserved *Polytrichum* plants was isolated

from every odd-numbered TUX1 mossbank level for a total of 101 fossil leaf samples.

Bulk mossbank material was dispersed in 18.2 MΩ ultrapure water in a petri dish and

sorted under a stereomicroscope at 0.65× magnification and subfossil remains of

*Polytrichum* were dissected and isolatted from multiple plants and the peat matrix using

forceps. At least 40 individual leaves were picked from each level to ensure

representativeness and enough material for nitrogen and isotopic measurements. The

leaves were transferred to pre-baked (490°C) and labeled glass test tubes and put through

a hot acid treatment of 1N hydrochloric (HCl) solution at 70ºC for 30 minutes to remove

exogenous debris and inorganic carbon. Sequential 18.2 MΩ ultrapure water rinses were

applied four times until a circum-neutral pH was reached. The treated leaves were

transferred into pre-baked (550°C) crucibles and dried dry at 50ºC to constant mass. A

subsample of 1.5 to 2.0 mg of cleaned, dry subfossil leaves were measured into pure Sn

capsules. Nitrogen stable isotope values were measured at the Stable Isotope Ratio

Facility for Environmental Research (SIRFER) laboratory at the University of Utah using

an isotope ratio mass spectrometer (IRMS) coupled to a Carlo Erba EA1110 and

ThermoFinnigan Conflo III. Isotopic values (Equation 1) were expressed as:

$$\delta^{15}N\ (‰) = \left( \frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000,$$

Equation 1. Expression of $\delta^{15}N$ values

where $R_{sample}$ is the $^{15}N/^{14}N$ ratio and $R_{standard}$ is air (atmospheric $N_2$). The value is

multiplied by 1000 to end with a final $\delta$ value in parts per thousand departure from the

standard, or permil (‰).


## 2.4 FOSSIL LEAF RADIOCARBON DATING

In order to see how N values varied over time, fossil leaves within the TUX1 core

were radiocarbon dated. Three levels (26, 85 and 201 cm) of the TUX1 subfossil leaves

were processed by standard Acid-Base-Acid pretreatment and hydrogen-reduction

graphitization for radiocarbon measurement. An age-depth model for the entire mossbank

profile was produced using the program, BACON. This program reconstructs Bayesian

accumulation deposits, which are an estimate of accumulation rates at each sample depth

(Wang et al., 2019). Through the measurement and comparison of $^{14}C$ to a modern

standard, an estimated date is acquired in the form of a mean "radiocarbon age" with a

corresponding standard measuring error (Blaauw and Christen, 2011).

**2.5 DATA ANALYSIS**

A total of five data analyses were run through a Pearson product-moment correlation coefficient approach to measure linear correlations between data sets. P-values and correlation coefficients were calculated for foliar $\delta^{15}N$ vs. foliar total N for 2014 modern, 2020 modern, and TUX1 fossil leaves. To explore the relationship between foliar $\delta^{15}N$ and air temperature over time, a Pearson product-moment correlation analysis was conducted using air temperature trends taken from Mulvaney et al. (2012). P-values and correlation coefficients were calculated for air temperature trends vs. TUX1 fossil $\delta^{15}N$ and foliar total N.

**3.0 RESULTS**

**3.1 MODERN PLANT LEAF NITROGEN**

Total foliar nitrogen content in modern *Polytrichum strictum* grab samples varied from 0.35 to 1.67 % N across all sites (Table 2). The Moss Island (MS2) modern plant sample saw the highest total nitrogen content. The second highest total nitrogen content was seen in the Charles (CHA) modern plant sample, with 1.25% N. All of the other sites saw a TN% value of around 0.5-0.8 % N, besides the Cape Rasmussen (RAS) sample, which saw the lowest TN% with 0.35% N. Contrastingly, total carbon content was similar across all sites (44.51–48.46% C), and averaged 45.47 ± 0.903% C.

The $\delta^{15}N$ values of *P. strictum* leaves varied from -0.8 to 14.7‰. No significant relationship was identified between TN% and $\delta^{15}N$ values (*P*=0.534). Of note is that the 2020 sites with the highest $\delta^{15}N$ values were MS2 and RAS5, which saw the highest and

lowest total nitrogen content, respectively. The $\delta^{15}N$ value in MS2 was 13.24‰, and

13.75‰ in RAS5. Of the 2020 modern samples, the *P. strictum* leaves from Cape Tuxen

(TUX1 and TUX3) had the lowest $\delta^{15}N$ values with 6.14‰ and 7.29‰ (Table 2).

**Table 2:** Foliar TN% and $\delta^{15}N$ values of modern plant samples collected during research cruises in 2014 and 2020.

| Site | Year | $\delta^{15}N$ (‰) | TN% |
|------|------|------|------|
| APE | 2020 | 12.4 | 0.45 |
| BER | 2020 | 8.5 | 0.66 |
| CHA | 2020 | 12.6 | 1.25 |
| MS2 | 2020 | 13.2 | 1.67 |
| PII | 2020 | 8.4 | 0.58 |
| RAS | 2020 | 13.8 | 0.35 |
| SPR | 2020 | 9.8 | 0.56 |
| TUX1 | 2020 | 6.1 | 0.89 |
| TUX3 | 2020 | 7.3 | 0.60 |
| CIE | 2014 | 10.3 | 1.14 |
| BON | 2014 | 7.3 | 1.01 |
| LIT | 2014 | -0.8 | 1.20 |
| HER | 2014 | 12.4 | 0.57 |
| PET | 2014 | 1.2 | 1.24 |
| LEO | 2014 | 9.9 | 0.59 |
| GAL_10L | 2014 | 9.4 | 0.70 |
| GAL_11L | 2014 | 7.2 | 0.51 |
| GAL_12L | 2014 | 9.1 | 0.84 |
| GAL_13L | 2014 | 9.6 | 1.25 |
| GAL_14L | 2014 | 14.7 | 0.80 |
| GAL_15L | 2014 | 14.7 | 0.94 |
| GAL_05L | 2014 | 8.5 | 1.38 |

## 3.2 MOSSBANK SHORT CORES

### 3.2.1 BULK DENSITY

All five of the short (15-28 cm) frozen moss cores were measured for bulk density, total N (TN%), total C (TC%) and OM content. Across all sites, the overall observed trend is the increase of bulk density towards the lower levels of the core. Though, for the Cape Rasmussen sample, there is a steep decrease in bulk density towards the bottom of the core around 15 cm. Contrary to the bulk density trend, a steady decrease in OM content with depth was observed across all sites.

### 3.2.2 NITROGEN AND C:N RATIO CONTENT

Samples from Cierva Cove (CIE1), Cape Rasmussen (RAS5), and Moss Island (MS2) all returned similar TN% trends, with increasing TN% as depth increases. CIE1 was most enriched at the bottom level, 20 cm, with 8.68% N and least enriched at 3 cm with 0.4% N. Similarly, RAS5 was most enriched at the very lowest level, 18 cm, with 3.1% N and least enriched at 3 cm with 0.01% N. MS2 was most enriched at 31 cm, with 4.15% N and least enriched at 1 cm with 0.7% N. The sample from Petermann Island (PET4) showed large variability, with a dip in TN% in the first few levels, yet still showed an overall increase in TN% as depth increased. PET4 was most enriched at 11 cm, with 3.3% N and least enriched at 4 cm with 1.12% N. The sample from Léonie Island (LEO3) showed the least variability, and followed the same trend with an overall increase in TN% as depth increased. LEO3 was most enriched at 14 cm, with 1.99% N and least enriched at 4 cm with 1.2% N. Generally, all samples were N enriched as depth increased.

24

All five core samples saw similar C:N ratio trends, with decreasing C:N as depth increases (Table 3). Additionally, most sites returned similar C:N values, all ranging around 20-58.3. However, for RAS5, the values were extremely large as the TN% was very low.

**Table 3:** Bulk density, TN%, C:N (mean ± SE) and N density values of the first 15-20 centimeter levels of cores from the study sites (Figure 3).

| Site | Depth (cm) | Bulk Density | TN% | C:N ratio | N Density (kg m^-2) |
|---|---|---|---|---|---|
| CIE1 | 0-10 | 0.09 ± 0.007 | 1.04 ± 0.171 | 58.34 ± 10.99 | 0.09 |
|  | 0-19 | 0.12 ± 0.014 | 2.34 ± 0.496 | 40.24 ± 7.62 | 0.73 |
| MS2 | 0-10 | 0.12 ± 0.004 | 1.06 ± 0.080 | 40.02 ± 3.72 | 0.13 |
|  | 0-20 | 0.13 ± 0.006 | 1.34 ± 0.091 | 32.97 ± 2.52 | 0.37 |
| PET4 | 0-10 | 0.09 ± 0.02 | 1.97 ± 0.192 | 23.25 ± 2.58 | 0.19 |
|  | 0-15 | 0.19 ± 0.04 | 1.99 ± 0.162 | 19.98 ± 2.10 | 0.56 |
| RAS5 | 0-10 | 0.15 ± 0.003 | 0.17 ± 0.036 | 745.95 ± 426.45 | 0.02 |
|  | 0-18 | 0.14 ± 0.009 | 0.66 ± 0.231 | 452.22 ± 244.85 | 0.16 |
| TUX1 | 0-10 | 0.11 ± 0.01 | 1.50 ± 0.186 | 39.43 ± 8.24 | 0.16 |
|  | 0-20 | 0.14 ± 0.01 | 1.94 ± 0.149 | 29.76 ± 4.61 | 0.57 |
| LEO3 | 0-10 | 0.08 ± 0.006 | 1.49 ± 0.072 | 26.58 ± 1.91 | 0.12 |
|  | 0-15 | 0.13 ± 0.02 | 1.58 ± 0.065 | 22.22 ± 2.08 | 0.31 |

## 3.3 CAPE TUXEN

### 3.3.1 BULK MOSSBANK PEAT

The frozen moss core collected from the Cape Tuxen (TUX1) study site was measured for bulk density, TN%, TC% and OM content. The overall observed trend is the decrease of bulk density towards the lower levels of the core. A peak in bulk density is seen at level 22, with a value of 0.24 $g/cm^3$. OM content is fairly steady throughout the core, with a few steep points of low OM content at levels 22, 163 and 198.

### 3.3.2 $\delta^{15}N$, NITROGEN AND CARBON CONTENT

Large variability is seen in TN% values throughout the entire length of the core. There is a peak in total N content in the mid-way point of the core, at level 101 with a value of 3.8% N. Values of $\delta^{15}N$ follow a similar pattern to total N content, and also see a peak in $\delta^{15}N$ content in the mid-way section of the core, with the highest $\delta^{15}N$ value being 17.4‰ at level 103. On the contrary, TC% values see small variability throughout the core. The C:N ratio averaged 27.75 across the core, with the highest C:N values being 90.8 and 94.4 at levels 1 and 2, respectively. In comparison to the five shorter cores, TUX1 sees similar nitrogen and C:N ratio values (Table 3; Figure 4).
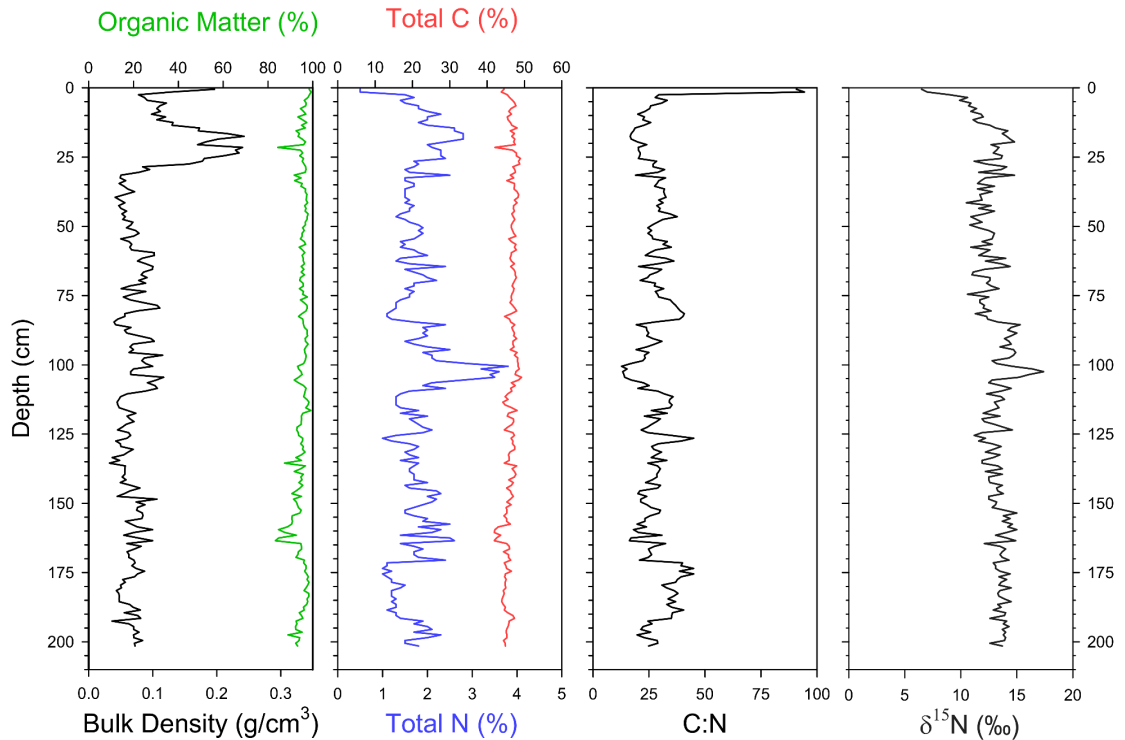
**Figure 4:** Cape Tuxen bulk mossbank core profile displaying the bulk density, organic matter, total carbon and nitrogen, C:N ratios, and $\delta^{15}$N content for every centimeter of the core.

### 3.3.3 SUBFOSSIL LEAF

A total of 97 TUX1 subfossil leaf samples from core TUX1 of the originally intended 101 samples were analyzed for TN%, TC%, and $\delta^{15}$N values. Four of the samples could not be analyzed due to insufficient leaf material at the depths of 27, 85, 123 and 125 cm. The TN% values ranged between 0.49 and 2.79% at levels 127 and 103, respectively. The TC% values ranged between 40.66 and 47.37% at levels 185 and 21, respectively. Finally, the $\delta^{15}$N values ranged between 8.1 and 16.1‰ at levels 3 and 101, respectively. A significant positive correlation was identified between TN% and $\delta^{15}$N values ($P<0.001$).

### 3.3.4 AGE-DEPTH MODEL

The age-depth model shows that the TUX1 study site core is approximately 3749 years old at its base, making it the oldest organic sediment core collected and studied from the western AP (cf Charman et al. 2018). Ages of leaves ranged from 1437 (1315-1536) and 3749 (3636-3844) years (Table 4). The age-depth model suggests a period of slower accumulation rates since 1400 cal yr BP (Figure 5).

**Table 4:** $^{14}$C-AMS measurements of *Polytrichum strictum* leaf fossil age at four intervals of TUX-1 mossbank core, listed by decreasing depth. Ages were calibrated using CALIB8.10 and the SHCal20.14c dataset.

| Site | Lab ID | Depth Dated (cm) | Material Dated | $^{14}$C (years BP) | Age (cal BP) |
|------|--------|------------------|----------------|---------------------|--------------|
| TUX 1 | SANU-69219 | 25-26 | *Polytrichum* leaves | 1587 ± 50 | 1437 (1315-1536) |
| TUX 1 | SANU-69320 | 84-85 | *Polytrichum* leaves | 2414 ± 30 | 2410 (2183-2694) |
| TUX 1 | SANU-69321 | 200-201 | *Polytrichum* leaves | 3506 ± 33 | 3749 (3636-3844) |
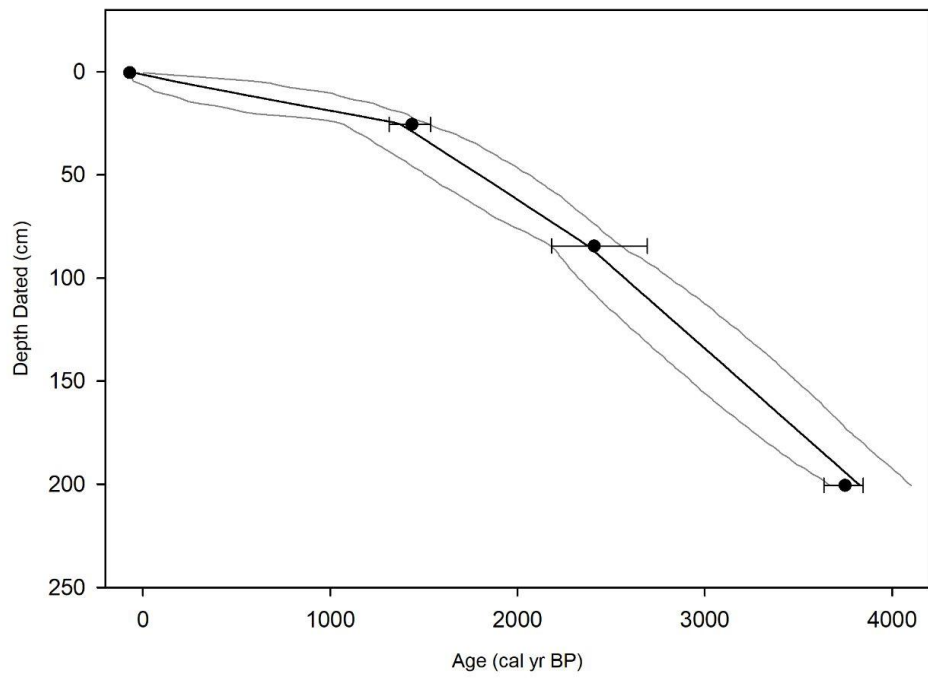
**Figure 5:** Radiocarbon age-depth curve for the Cape Tuxen mossbank core.

## 4.0 DISCUSSION

## 4.1 N VARIATIONS IN MOSSBANK CORES AND PLANTS

Across all six of the mossbank cores (Table 3), there is an overall observed trend of increased bulk density towards the lower levels of the core. This trend is affected by older frozen moss layers that have more time to decompose and compact. TN% for all mossbank cores (1.5 TN% on average) are higher than the TN% of similar research done on Arctic bryophyte peat banks (1.2 TN% on average; Loisel et al., 2014). Although the Arctic and Antarctic are polar environments, it is interesting to note that Antarctic peat banks generally see higher N content. This may be due to available N sources being different for the polar regions. For instance, the Arctic sees ammonia sources mainly from terrestrial emissions while the Antarctic from bird colonies (Wolff, 2013). OM content throughout the TUX1 core was mostly high with values ranging from 83-99% with an average of 95% OM. The slight departures in OM content with values of 83-90% are likely due to wind-blown mineral dust inputs from nearby exposures, which potentially suggests stronger wind periods in the past. Additionally, TUX1 saw the highest C:N values of 90.8 and 94.4 at levels 1 and 2, respectively. This may be owing to lichens at the surface level of the mossbank core, which tend to be of low TN% (Lindsay, 1978). For this reason, using a single-species approach to characterize N trends is necessary to avoid bias.

Modern and subfossil *Polytrichum* leaves were analyzed for TN% and $\delta^{15}N$ values. According to the calculated p-values between foliar TN% was $\delta^{15}N$, a significant relationship found was in subfossil *Polytrichum* leaves. In the Lee et al. (2009) study,

different types of plants were collected from King George Island, off the coast of the western AP, including *Polytrichum strictum*. A scatter plot was constructed to see how these *P. strictum* literature values compared to the data collected in this research (Figure 6). In comparison to the modern and subfossil plants, *P. strictum* literature values had a much larger range of foliar $\delta^{15}N$ values.
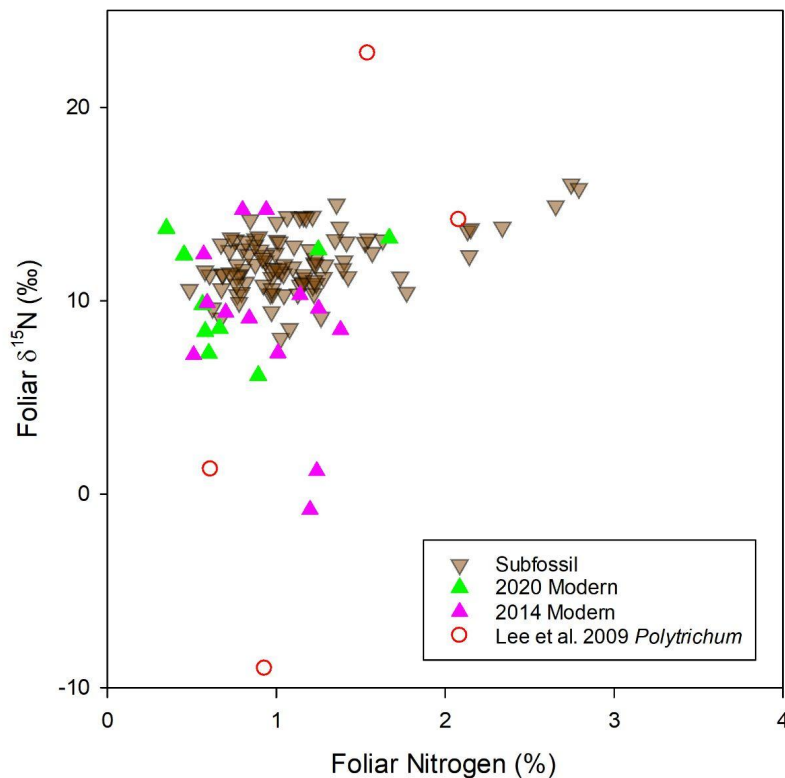


**Figure 6:** Foliar $\delta^{15}N$ (‰) vs. Foliar Nitrogen (%) Scatter Plot of TUX1 Fossil samples, 2020 and 2014 Modern samples, and Literature values taken from Lee et al. 2009.

## 4.2 N VARIABILITY WITH ENVIRONMENTAL MECHANISMS

There are a number of factors that affect $\delta^{15}N$ values in AP plants. First, trophic enrichment of directly deposited fecal matter onto terrestrial environments would increase $\delta^{15}N$ values. Moreover, higher trophic level species such as elephant or leopard seals, or changes in diet within the same trophic levels could also increase $\delta^{15}N$ values

31

(Stephens et al, 2022). However, for TUX1, the steep and elevated location deems it

unlikely as a site for large marine animals, such as elephant seals, to be able to reach.

Testing for fecal biomarkers at TUX1 would aid in proving this.
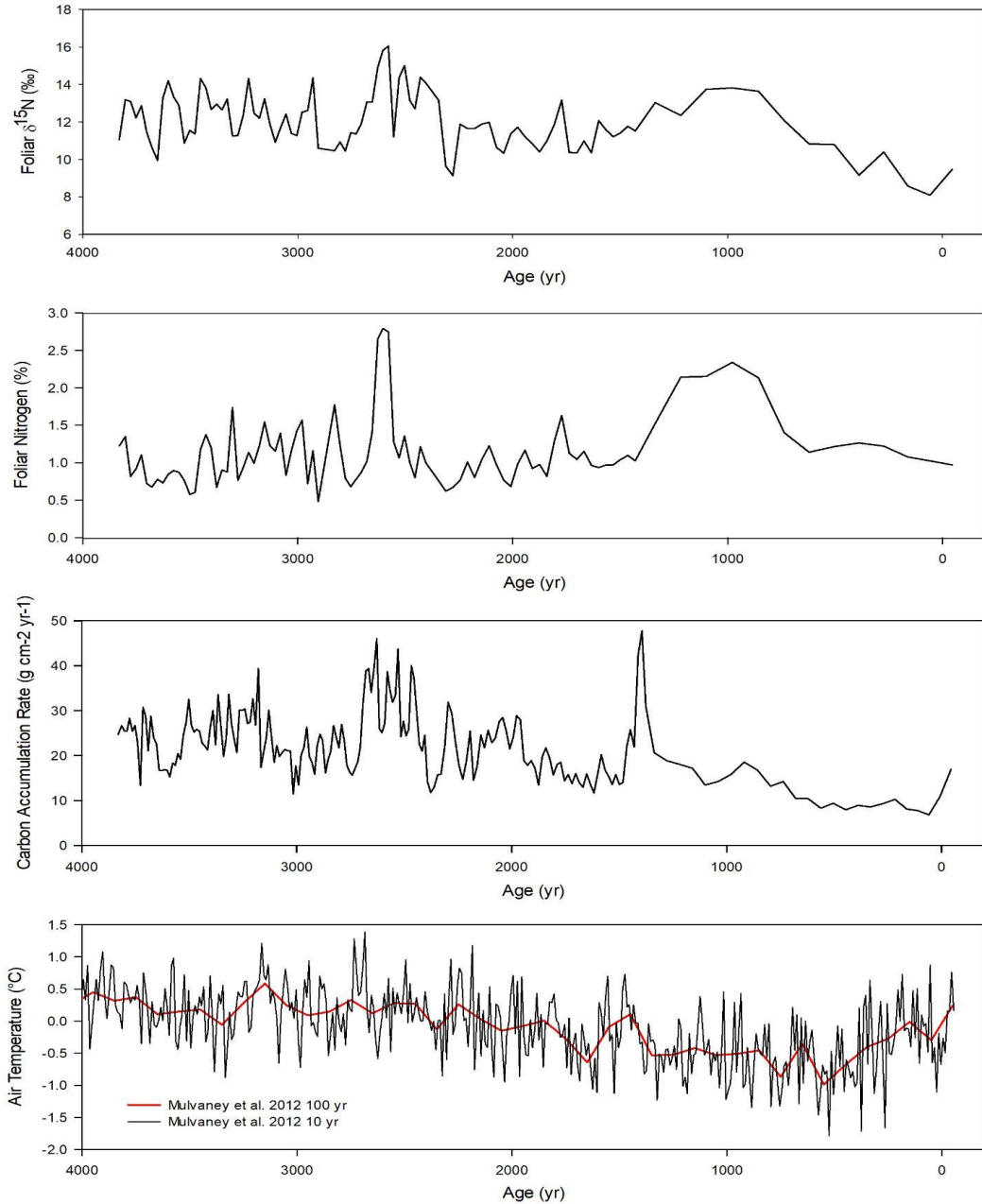


**Figure 7:** Foliar TUX1 TN% and $\delta^{15}N$ values, carbon accumulation rates, and air temperature trends (Mulvaney et al., 2012) across a 4000 year period.

Next, another mechanism that may lead to increased $\delta^{15}N$ values are upward,

wind-blown $^{15}N$-enriched solid fecal dust from the coast or nearby land seabird nests.

Though, this is unlikely as no relationship is seen between bulk TN% and OM

fluctuations (Figure 4). If dust inputs were an important source of N to plants at the study

site, it would be expected that mossbank levels with lower OM content would have

greater N content. This is not the case as low OM at levels 22 and 160 have subfossil

foliar N contents that are near or below average.

Lastly, the most likely mechanism that explains the $\delta^{15}N$ values in foliar TUX1 is

ammonia volatilization. This is consistent with previous research conducted on external

N sources in Antarctic terrestrial ecosystems that are isolated from direct animal

influence (Bokhorst et al., 2007; Bokhorst et al., 2019). In Bokhorst et al. (2019), it was

determined that volatilized $NH_3$ from penguin and seal rookeries are a significant N

source for Antarctic plants.

Periods of lower $\delta^{15}N$ values found in TUX1 fossil samples are most likely owing

to increases in the rate of ammonia volatilization. In general, increased rates of the

volatilization of ammonia occurs with high soil pH, high moisture content, and warm

temperatures (Ernst and Massey, 1960; He et al., 1999). From air temperature trends

evident in the James Ross Island (JRI) ice core (Fig. 3; Mulvaney et al. 2012), it is clear

that Antarctic air temperatures have been steadily increasing over the last few decades.

This warming corresponds with the relatively recent decrease in $\delta^{15}N$ values, consistent

with an increase in volatilization since ~700 years ago. Carbon accumulation rates see a

similar trend to air temperature, which is seen especially in the most recent spike in the two trends around ~0 years (Figure 7). This suggests primary productivity has increased with air temperature in most recent years and plants are getting more N from environmental processes and mechanisms.

An explanation for the greater presence of $\delta^{15}N$ in the past may be owing to more sizable animal populations. Around 2500 to 2800 cal bp, there is a peak in $\delta^{15}N$, TN% and carbon accumulation, as well as the highest air temperature in the JRI record. At this point in time, it seems that air temperatures were warm, there were periods of high volatilization along with substantial animal presence.

In the last few centuries, Antarctic mammal and bird populations have seen a general decrease, as well as their major food sources such as Antarctic krill (Weimerskirch et al., 2003; Trivelpiece et al., 2011; Barbosa et al., 2012; Krüger et al., 2021). Most notably, in the nineteenth century, Antarctic fur seals were almost hunted to extinction (Hucke-Gaete et al., 2004). This period from the year 1800 to 1900 corresponds to the TN% values around ~200 years ago, as this was a period of relatively low TN% values. Therefore, decreases in available urea may have led to a decrease in N concentrations as well.

Few studies of previous, long-term research of Antarctic animal populations on the same scale of TUX1 have been conducted, which makes it difficult to reach a solid conclusion. Nevertheless, new studies have proved more accurate methods to study factors affecting $\delta^{15}N$ values such as trophic interactions, with the usage of trophic discrimination factors values in isotopic assessments (Stephens et al, 2022). Studies to

34

reconstruct animal populations over time have also been done (Sun et al, 2013), however, more similar research should be conducted. Implementations of such new methods would allow for a modern understanding of why N concentrations are fluctuating in recent decades and centuries.

## 4.3 GLOBAL DECLINING N PATTERNS

Recent research has proposed that there is a global decline of N availability in terrestrial ecosystems including remote polar environments (Mason et al., 2022). Declining N availability for plants could potentially lead to a constraining of the ability for plants to uptake atmospheric $CO_2$ (Meyerholt et al., 2020). This is concerning as terrestrial ecosystems are among the world's largest carbon sinks, with plants removing around one-fifth of atmospheric carbon every year (Keenan and Williams, 2018). For Antarctica as well as globally, this may mean that uptake of anthropogenic carbon emissions by plants will be slowed down, and as a result, air temperatures will rise even quicker than they are already, and Antarctic ice will melt quicker thereby.

Data from Cape Tuxen shows a decrease in N content in plant leaf tissue over the last 20 decades. Similarly to the multiple foliar N trends highlighted in Mason et al., 2022, TUX1 fossil leaves are seeing lower TN% and $\delta^{15}N$ in the last few centuries, with the most dramatic decline during the most recent century at the top of the mossbank core (Figure 7). For the western AP, this may mean a heavier reliance on the main source for available N for plants, which are animals such as seabirds and fur seals (Otero et al., 2018; Dai et al., 2020).

35

## 5.0 CONCLUSION

This study used modern plants, mossbank cores, and subfossil plant leaves to better understand long-term nitrogen cycling in the Antarctic Peninsula. The deepest and oldest mossbank yet cored in the AP at Cape Tuxen has provided new and valuable information about nitrogen cycling in the western AP over the last few millennia. In comparison to five shorter mossbank cores (15-28 cm) collected along the western AP, TUX1 has seen a very similar N trend in the first 20 cm levels. However, towards the lower levels of the core, large fluctuations of N concentrations have occurred and N concentrations see a peak at the mid-way point of the core. A similar but more intense trend in $\delta^{15}N$ values is seen in the TUX1 fossil leaves. These fluctuations occurred during the past ~1500-4000 years, and the likely mechanism driving these fluctuations is environmental controls on ammonia volatilization. It is clear that TN% and $\delta^{15}N$ values have been highly dynamic in the AP throughout history. One possible explanation may be due to declining animal populations, which have led to the decline in available urea and guano to drive the volatilization of ammonia. Depleting $\delta^{15}N$ values suggest volatilization has increased with increasing air temperature over recent decades.

The data presented in this study suggest that future research should include additional long-term studies in the Antarctic region. It would be interesting to see how TN% and $\delta^{15}N$ values from other sites compare in terms of a similar time period of ~4000 years. In future studies, it would be worthwhile to test the TUX1 mossbank core samples for fecal biomarker data. Fecal biomarkers could be used to identify groups of animals responsible for inputs (Harrault et al., 2019) and discovering a lack of fecal material

would provide further evidence for the importance of indirect inputs via the ammonia volatilization pathway. Along with this, long-term research on factors affecting N concentrations in Antarctic environments would help to reach a solid understanding of N fluctuations over time. For instance, bringing together detailed marine animal monitoring efforts with more extensive terrestrial N measurements would allow for the making of a more solid conclusion on how N trends are changing in comparison. Research on TUX1 soil pH and moisture content fluctuations, including the measurement of $\delta^{13}C$ values in subfossil leaf tissue would also be helpful to understand how weather and climate affect both animal populations and N pathways to plants.

**APPENDIX A:** TUX-1 Bulk Peat Data

| Depth | Bulk Density (g/cm³) | OM (%) | TC% | TN% | C:N | δ¹⁵N |
|---|---|---|---|---|---|---|
| 1 | 0.1964 | 98.4 | 44.5 | 0.5 | 90.8 | 6.5 |
| 2 | 0.1285 | 99.2 | 43.8 | 0.5 | 94.4 | 7.0 |
| 3 | 0.0779 | 98.5 | 45.4 | 1.5 | 29.4 | 9.0 |
| 4 | 0.0868 | 97.8 | 46.0 | 1.7 | 27.8 | 10.6 |
| 5 | 0.0914 | 96.2 | 46.8 | 1.4 | 33.1 | 9.9 |
| 6 | 0.1212 | 97.0 | 47.4 | 1.5 | 30.7 | 10.9 |
| 7 | 0.1110 | 96.9 | 47.7 | 1.8 | 25.8 | 10.7 |
| 8 | 0.1063 | 94.5 | 46.4 | 1.8 | 25.3 | 11.4 |
| 9 | 0.1119 | 95.9 | 45.8 | 2.0 | 23.2 | 10.9 |
| 10 | 0.0981 | 96.9 | 46.5 | 2.3 | 20.0 | 11.8 |
| 11 | 0.1199 | 93.3 | 45.4 | 2.0 | 23.0 | 12.0 |
| 12 | 0.1063 | 95.4 | 45.6 | 2.0 | 22.3 | 11.1 |
| 13 | 0.1317 | 97.3 | 46.2 | 1.8 | 25.8 | 11.5 |
| 14 | 0.1299 | 95.0 | 46.6 | 2.0 | 22.8 | 12.6 |
| 15 | 0.1731 | 96.6 | 48.0 | 2.6 | 18.8 | 13.1 |
| 16 | 0.1711 | 92.6 | 46.2 | 2.6 | 18.1 | 14.2 |
| 17 | 0.2160 | 94.1 | 47.3 | 2.8 | 17.1 | 13.7 |
| 18 | 0.2426 | 93.4 | 46.6 | 2.8 | 16.6 | 14.1 |
| 19 | 0.2023 | 95.2 | 47.4 | 2.8 | 17.1 | 14.4 |
| 20 | 0.1828 | 96.7 | 47.1 | 2.4 | 19.9 | 14.8 |
| 21 | 0.1700 | 95.9 | 47.5 | 2.0 | 24.0 | 12.7 |
| 22 | 0.2402 | 84.4 | 42.1 | 2.1 | 20.2 | 13.4 |
| 23 | 0.2291 | 94.5 | 46.8 | 2.3 | 20.3 | 13.2 |
| 24 | 0.2348 | 95.5 | 47.8 | 2.3 | 21.1 | 12.9 |
| 25 | 0.2114 | 94.2 | 47.8 | 2.3 | 20.9 | 13.7 |
| 26 | 0.1806 | 95.9 | 48.9 | 2.4 | 20.3 | 13.6 |
| 27 | 0.1775 | 95.3 | 48.4 | 1.7 | 28.4 | 11.2 |
| 28 | 0.1562 | 96.1 | 48.7 | 1.8 | 26.9 | 12.3 |

| 29 | 0.0841 | 96.9 | 46.9 | 1.7 | 26.9 | 14.1 |
|----|--------|------|------|-----|------|------|
| 30 | 0.0950 | 96.9 | 47.4 | 1.5 | 32.0 | 13.6 |
| 31 | 0.0785 | 96.7 | 47.6 | 1.6 | 29.0 | 11.6 |
| 32 | 0.0504 | 91.7 | 46.2 | 2.5 | 19.0 | 14.8 |
| 33 | 0.0490 | 94.8 | 47.1 | 1.5 | 32.4 | 12.2 |
| 34 | 0.0576 | 91.9 | 45.3 | 1.5 | 29.4 | 11.8 |
| 35 | 0.0473 | 95.3 | 47.3 | 1.7 | 28.6 | 11.5 |
| 36 | 0.0551 | 94.7 | 47.3 | 1.7 | 27.5 | 13.0 |
| 37 | 0.0607 | 96.8 | 47.2 | 1.5 | 31.9 | 11.5 |
| 38 | 0.0715 | 96.6 | 48.0 | 1.5 | 31.6 | 12.8 |
| 39 | 0.0560 | 97.4 | 48.4 | 1.5 | 32.0 | 11.7 |
| 40 | 0.0412 | 97.2 | 48.3 | 1.5 | 32.6 | 11.8 |
| 41 | 0.0489 | 97.1 | 47.3 | 1.6 | 29.4 | 11.9 |
| 42 | 0.0563 | 97.7 | 48.0 | 1.5 | 31.3 | 10.5 |
| 43 | 0.0469 | 96.4 | 47.1 | 1.7 | 28.5 | 12.7 |
| 44 | 0.0503 | 97.0 | 47.0 | 1.6 | 30.0 | 11.6 |
| 45 | 0.0591 | 96.6 | 47.3 | 1.6 | 29.3 | 13.0 |
| 46 | 0.0517 | 97.9 | 46.6 | 1.4 | 34.4 | 12.1 |
| 47 | 0.0570 | 97.5 | 47.0 | 1.3 | 37.6 | 10.9 |
| 48 | 0.0531 | 97.4 | 47.4 | 1.5 | 31.2 | 11.4 |
| 49 | 0.0689 | 96.6 | 46.9 | 1.6 | 28.8 | 11.9 |
| 50 | 0.0657 | 96.7 | 46.5 | 1.8 | 26.5 | 10.8 |
| 51 | 0.0590 | 95.5 | 46.5 | 1.9 | 24.5 | 11.6 |
| 52 | 0.0733 | 96.2 | 46.8 | 1.8 | 26.2 | 12.5 |
| 53 | 0.0784 | 95.2 | 47.1 | 1.9 | 24.5 | 13.0 |
| 54 | 0.0703 | 95.2 | 47.7 | 1.8 | 26.4 | 12.9 |
| 55 | 0.0500 | 94.5 | 45.8 | 1.7 | 26.7 | 12.8 |
| 56 | 0.0629 | 96.2 | 46.5 | 1.4 | 33.2 | 11.9 |
| 57 | 0.0672 | 96.8 | 47.7 | 1.5 | 31.3 | 12.8 |
| 58 | 0.0641 | 93.9 | 47.3 | 1.4 | 35.0 | 10.9 |
| 59 | 0.0669 | 95.4 | 47.8 | 1.7 | 28.0 | 12.6 |
| 60 | 0.1022 | 96.4 | 46.5 | 1.8 | 25.4 | 12.1 |

| | | | | | |
|---|---|---|---|---|---|
| 61 | 0.1026 | 95.3 | 46.4 | 2.0 | 23.4 | 11.6 |
| 62 | 0.0836 | 95.7 | 46.1 | 1.4 | 32.5 | 14.0 |
| 63 | 0.0762 | 95.8 | 46.5 | 1.3 | 36.1 | 12.2 |
| 64 | 0.0890 | 96.3 | 47.3 | 1.6 | 29.1 | 13.6 |
| 65 | 0.1002 | 94.8 | 46.3 | 2.4 | 20.4 | 14.4 |
| 66 | 0.0994 | 96.1 | 47.1 | 1.5 | 30.7 | 12.1 |
| 67 | 0.0856 | 94.8 | 47.5 | 1.7 | 28.7 | 11.1 |
| 68 | 0.0818 | 96.3 | 47.5 | 1.9 | 25.4 | 11.0 |
| 69 | 0.0910 | 94.5 | 47.8 | 2.0 | 24.4 | 12.6 |
| 70 | 0.0780 | 94.2 | 47.4 | 2.2 | 21.1 | 12.6 |
| 71 | 0.0888 | 95.6 | 47.0 | 1.7 | 27.9 | 12.3 |
| 72 | 0.0642 | 95.8 | 46.7 | 1.7 | 27.4 | 12.7 |
| 73 | 0.0507 | 94.0 | 47.2 | 1.5 | 31.6 | 13.4 |
| 74 | 0.0893 | 95.9 | 47.0 | 1.7 | 27.9 | 12.1 |
| 75 | 0.0686 | 95.5 | 46.6 | 1.6 | 28.8 | 10.6 |
| 76 | 0.0540 | 97.6 | 46.4 | 1.6 | 29.4 | 12.5 |
| 77 | 0.0646 | 94.5 | 46.6 | 1.4 | 34.5 | 11.7 |
| 78 | 0.0850 | 96.1 | 46.1 | 1.3 | 35.6 | 11.7 |
| 79 | 0.1065 | 97.4 | 46.8 | 1.3 | 36.9 | 12.1 |
| 80 | 0.1110 | 97.5 | 47.4 | 1.3 | 37.9 | 12.0 |
| 81 | 0.0757 | 97.0 | 47.9 | 1.2 | 39.0 | 12.7 |
| 82 | 0.0563 | 95.2 | 46.5 | 1.1 | 40.8 | 11.3 |
| 83 | 0.0563 | 93.6 | 44.7 | 1.1 | 40.2 | 12.3 |
| 84 | 0.0452 | 95.5 | 46.0 | 1.2 | 38.7 | 12.4 |
| 85 | 0.0394 | 95.7 | 46.3 | 1.7 | 27.7 | 13.3 |
| 86 | 0.0419 | 95.9 | 47.4 | 2.4 | 19.4 | 15.3 |
| 87 | 0.0658 | 96.3 | 46.6 | 1.9 | 23.9 | 14.5 |
| 88 | 0.0559 | 97.5 | 46.9 | 2.0 | 24.0 | 14.2 |
| 89 | 0.0594 | 97.4 | 47.3 | 1.9 | 24.9 | 15.0 |
| 90 | 0.0783 | 97.7 | 47.1 | 2.0 | 24.0 | 14.5 |
| 91 | 0.0972 | 96.6 | 47.9 | 1.8 | 26.7 | 13.9 |
| 92 | 0.1024 | 96.8 | 46.9 | 1.5 | 30.8 | 14.3 |

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|---|---|---|---|---|---|
| 93 | 0.0688 | 97.9 | 46.9 | 1.7 | 27.5 | 14.5 |
| 94 | 0.0646 | 96.9 | 47.2 | 2.0 | 24.0 | 13.5 |
| 95 | 0.0699 | 96.3 | 46.2 | 2.5 | 19.3 | 14.7 |
| 96 | 0.0629 | 96.5 | 48.0 | 1.9 | 25.0 | 14.9 |
| 97 | 0.1155 | 97.0 | 47.3 | 2.1 | 23.0 | 14.7 |
| 98 | 0.0868 | 96.9 | 48.2 | 2.1 | 23.3 | 14.3 |
| 99 | 0.0829 | 96.5 | 48.1 | 2.2 | 22.3 | 12.8 |
| 100 | 0.0890 | 95.9 | 48.3 | 2.9 | 16.9 | 13.2 |
| 101 | 0.0999 | 93.3 | 48.3 | 3.8 | 12.8 | 14.6 |
| 102 | 0.0699 | 93.7 | 48.6 | 3.2 | 15.2 | 16.4 |
| 103 | 0.0656 | 94.8 | 47.7 | 3.6 | 13.3 | 17.4 |
| 104 | 0.0657 | 95.2 | 47.5 | 3.4 | 13.8 | 16.1 |
| 105 | 0.1168 | 93.7 | 49.2 | 3.5 | 14.2 | 15.2 |
| 106 | 0.1057 | 91.7 | 48.4 | 2.8 | 17.1 | 12.8 |
| 107 | 0.0916 | 93.6 | 46.5 | 2.1 | 22.5 | 12.5 |
| 108 | 0.1035 | 95.9 | 47.5 | 1.9 | 25.1 | 13.6 |
| 109 | 0.1071 | 97.0 | 46.3 | 2.4 | 20.1 | 14.5 |
| 110 | 0.0884 | 96.6 | 46.6 | 1.6 | 28.9 | 13.6 |
| 111 | 0.0600 | 96.3 | 45.5 | 1.4 | 31.8 | 12.3 |
| 112 | 0.0497 | 95.9 | 44.8 | 1.3 | 35.8 | 13.6 |
| 113 | 0.0471 | 97.4 | 45.6 | 1.3 | 34.3 | 13.9 |
| 114 | 0.0442 | 98.3 | 44.2 | 1.3 | 34.0 | 13.0 |
| 115 | 0.0455 | 97.8 | 44.8 | 1.3 | 35.3 | 13.2 |
| 116 | 0.0478 | 96.8 | 46.6 | 1.4 | 34.4 | 13.4 |
| 117 | 0.0607 | 99.1 | 48.0 | 1.8 | 26.1 | 12.7 |
| 118 | 0.0736 | 95.6 | 45.7 | 1.4 | 33.1 | 12.0 |
| 119 | 0.0598 | 94.9 | 45.4 | 2.0 | 23.0 | 13.5 |
| 120 | 0.0642 | 95.0 | 47.0 | 1.6 | 30.1 | 11.9 |
| 121 | 0.0708 | 94.8 | 47.1 | 1.7 | 28.4 | 12.1 |
| 122 | 0.0583 | 94.8 | 46.7 | 1.8 | 26.2 | 13.0 |
| 123 | 0.0523 | 93.0 | 45.5 | 1.9 | 24.3 | 13.8 |
| 124 | 0.0452 | 92.8 | 44.6 | 2.1 | 21.5 | 14.6 |

| | | | | | |
|---|---|---|---|---|---|
| 125 | 0.0623 | 93.5 | 46.9 | 1.9 | 24.5 | 11.9 |
| 126 | 0.0654 | 93.7 | 47.3 | 1.3 | 35.0 | 11.2 |
| 127 | 0.0597 | 95.5 | 46.4 | 1.0 | 45.0 | 12.2 |
| 128 | 0.0423 | 95.4 | 46.9 | 1.2 | 39.5 | 11.6 |
| 129 | 0.0493 | 94.6 | 46.8 | 1.6 | 29.2 | 12.8 |
| 130 | 0.0502 | 95.8 | 47.4 | 1.8 | 26.2 | 13.6 |
| 131 | 0.0694 | 95.4 | 47.4 | 1.7 | 27.2 | 12.9 |
| 132 | 0.0614 | 96.6 | 46.1 | 1.5 | 30.6 | 12.2 |
| 133 | 0.0548 | 94.9 | 45.7 | 1.6 | 28.2 | 13.5 |
| 134 | 0.0366 | 92.5 | 45.9 | 1.8 | 26.0 | 12.9 |
| 135 | 0.0482 | 94.9 | 45.9 | 1.4 | 33.0 | 11.9 |
| 136 | 0.0322 | 87.4 | 44.6 | 1.8 | 24.5 | 11.9 |
| 137 | 0.0570 | 96.7 | 47.9 | 1.7 | 28.8 | 13.3 |
| 138 | 0.0565 | 94.6 | 46.7 | 1.6 | 30.1 | 13.7 |
| 139 | 0.0564 | 91.8 | 47.3 | 1.6 | 29.4 | 12.2 |
| 140 | 0.0564 | 95.8 | 47.7 | 1.7 | 28.5 | 13.7 |
| 141 | 0.0523 | 94.7 | 47.3 | 1.7 | 28.6 | 12.5 |
| 142 | 0.0582 | 95.2 | 45.8 | 1.7 | 26.5 | 12.5 |
| 143 | 0.0491 | 93.8 | 47.0 | 2.0 | 23.5 | 12.6 |
| 144 | 0.0655 | 95.5 | 46.5 | 1.5 | 30.2 | 13.7 |
| 145 | 0.0799 | 94.3 | 45.2 | 1.6 | 28.9 | 13.2 |
| 146 | 0.0645 | 92.5 | 46.2 | 2.2 | 20.9 | 13.3 |
| 147 | 0.0556 | 90.7 | 46.5 | 2.3 | 20.1 | 13.8 |
| 148 | 0.0444 | 94.9 | 47.0 | 2.0 | 24.0 | 12.5 |
| 149 | 0.1064 | 91.4 | 46.2 | 2.2 | 21.4 | 12.5 |
| 150 | 0.0740 | 92.7 | 45.3 | 2.1 | 21.4 | 13.2 |
| 151 | 0.0878 | 93.1 | 46.4 | 1.9 | 24.1 | 13.1 |
| 152 | 0.0761 | 93.5 | 45.1 | 1.7 | 25.9 | 12.8 |
| 153 | 0.0748 | 94.8 | 45.3 | 1.5 | 30.2 | 13.9 |
| 154 | 0.0839 | 94.2 | 45.3 | 1.5 | 29.5 | 15.0 |
| 155 | 0.0844 | 90.8 | 44.5 | 1.7 | 25.5 | 13.8 |
| 156 | 0.0831 | 90.6 | 45.2 | 2.0 | 23.2 | 14.4 |

| | | | | | |
|---|---|---|---|---|---|
| 157 | 0.0572 | 90.9 | 45.2 | 1.9 | 23.2 | 13.7 |
| 158 | 0.0665 | 90.6 | 46.2 | 2.5 | 19.7 | 14.6 |
| 159 | 0.0757 | 88.7 | 43.0 | 1.8 | 23.9 | 14.2 |
| 160 | 0.0998 | 84.7 | 42.1 | 2.3 | 18.1 | 15.0 |
| 161 | 0.0707 | 87.5 | 41.9 | 2.1 | 20.3 | 14.1 |
| 162 | 0.0547 | 92.6 | 43.6 | 1.4 | 30.8 | 13.1 |
| 163 | 0.0773 | 84.8 | 42.5 | 2.5 | 17.0 | 14.1 |
| 164 | 0.1000 | 83.3 | 41.9 | 2.6 | 16.3 | 14.9 |
| 165 | 0.0594 | 94.6 | 45.2 | 1.4 | 32.4 | 12.1 |
| 166 | 0.0818 | 94.9 | 45.9 | 1.7 | 27.5 | 13.5 |
| 167 | 0.0712 | 95.0 | 46.0 | 1.9 | 24.8 | 14.0 |
| 168 | 0.0598 | 93.6 | 44.4 | 1.7 | 25.4 | 13.7 |
| 169 | 0.0629 | 93.4 | 45.7 | 1.7 | 26.2 | 13.5 |
| 170 | 0.0624 | 92.5 | 45.7 | 1.8 | 24.7 | 13.7 |
| 171 | 0.0704 | 96.2 | 46.3 | 2.4 | 20.8 | 14.3 |
| 172 | 0.0724 | 95.9 | 44.6 | 1.1 | 40.0 | 12.9 |
| 173 | 0.0673 | 97.0 | 45.0 | 1.1 | 39.3 | 13.1 |
| 174 | 0.0739 | 97.1 | 45.2 | 1.0 | 44.9 | 13.1 |
| 175 | 0.0872 | 96.4 | 46.5 | 1.2 | 38.6 | 13.5 |
| 176 | 0.0762 | 97.2 | 44.9 | 1.0 | 45.0 | 14.4 |
| 177 | 0.0713 | 98.0 | 44.7 | 1.1 | 39.4 | 13.4 |
| 178 | 0.0531 | 97.4 | 45.1 | 1.2 | 37.7 | 14.1 |
| 179 | 0.0570 | 98.3 | 44.8 | 1.2 | 36.9 | 13.6 |
| 180 | 0.0497 | 97.7 | 44.8 | 1.5 | 30.8 | 13.4 |
| 181 | 0.0509 | 97.0 | 45.0 | 1.4 | 32.9 | 14.5 |
| 182 | 0.0431 | 96.1 | 44.3 | 1.2 | 36.2 | 13.5 |
| 183 | 0.0468 | 98.2 | 44.6 | 1.2 | 38.0 | 13.3 |
| 184 | 0.0477 | 98.3 | 44.3 | 1.2 | 36.0 | 13.4 |
| 185 | 0.0473 | 97.4 | 44.0 | 1.3 | 33.5 | 13.9 |
| 186 | 0.0477 | 97.8 | 43.9 | 1.2 | 36.9 | 14.5 |
| 187 | 0.0637 | 97.3 | 44.3 | 1.3 | 33.0 | 13.3 |
| 188 | 0.0693 | 95.8 | 44.9 | 1.3 | 35.2 | 13.6 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 189 | 0.0807 | 96.2 | 44.6 | 1.1 | 40.5 | 12.9 |
| 190 | 0.0556 | 94.0 | 45.5 | 1.3 | 35.5 | 14.0 |
| 191 | 0.0765 | 94.9 | 46.9 | 1.3 | 35.2 | 13.9 |
| 192 | 0.0811 | 95.6 | 47.3 | 1.4 | 35.0 | 12.6 |
| 193 | 0.0365 | 92.5 | 45.9 | 1.9 | 24.5 | 14.1 |
| 194 | 0.0626 | 92.9 | 45.8 | 1.7 | 26.4 | 13.8 |
| 195 | 0.0702 | 92.3 | 45.6 | 2.0 | 22.4 | 14.3 |
| 196 | 0.0702 | 92.4 | 45.2 | 2.1 | 21.4 | 13.7 |
| 197 | 0.0784 | 95.2 | 45.1 | 1.7 | 25.8 | 14.0 |
| 198 | 0.0700 | 89.0 | 45.3 | 2.3 | 19.7 | 13.8 |
| 199 | 0.0704 | 94.1 | 45.3 | 2.0 | 22.9 | 14.0 |
| 200 | 0.0841 | 93.9 | 44.4 | 1.5 | 28.7 | 13.9 |
| 201 | 0.0715 | 92.4 | 44.8 | 1.5 | 28.9 | 12.6 |
| 202 | 0.0722 | 93.2 | 44.9 | 1.8 | 24.9 | 13.7 |

**APPENDIX B:** TUX-1 Subfossil *Polytrichum* Leaf Data

| Depth | $\delta^{15}N$ (‰) | TN% | $\delta^{13}C$ (‰) | TC% | C:N |
|---|---|---|---|---|---|
| 1 | 9.5 | 0.97 | -28.9 | 46.42 | 47.8 |
| 3 | 8.1 | 1.03 | -28.5 | 44.98 | 43.8 |
| 5 | 8.6 | 1.08 | -27.9 | 44.92 | 41.7 |
| 7 | 10.4 | 1.22 | -27.7 | 45.16 | 36.9 |
| 9 | 9.2 | 1.26 | -26.4 | 43.45 | 34.4 |
| 11 | 10.8 | 1.22 | -26.4 | 44.12 | 36.3 |
| 13 | 10.8 | 1.14 | -26.1 | 44.94 | 39.4 |
| 15 | 12.1 | 1.40 | -26.9 | 45.96 | 32.8 |
| 17 | 13.6 | 2.13 | -26.6 | 45.11 | 21.1 |
| 19 | 13.8 | 2.34 | -25.8 | 45.37 | 19.4 |
| 21 | 13.7 | 2.15 | -27.2 | 47.37 | 22.0 |
| 23 | 12.4 | 2.14 | -27.4 | 44.72 | 20.9 |
| 25 | 13.0 | 1.53 | -26.5 | 44.87 | 29.4 |
| 27 | | | -25.5 | 43.74 | |
| 29 | 11.5 | 1.03 | -26.6 | 43.14 | 42.0 |

| | | | | | |
|---|---|---|---|---|---|
| 31 | 11.8 | 1.10 | -27.1 | 42.19 | 38.5 |
| 33 | 11.4 | 1.04 | -26.0 | 45.57 | 43.7 |
| 35 | 11.2 | 0.97 | -26.8 | 44.65 | 45.9 |
| 37 | 11.6 | 0.97 | -27.0 | 44.96 | 46.4 |
| 39 | 12.1 | 0.93 | -27.4 | 42.11 | 45.0 |
| 41 | 10.4 | 0.96 | -25.9 | 44.83 | 46.5 |
| 43 | 11.0 | 1.15 | -26.9 | 45.05 | 39.1 |
| 45 | 10.3 | 1.05 | -26.0 | 44.35 | 42.4 |
| 47 | 10.4 | 1.13 | -26.8 | 43.03 | 38.2 |
| 49 | 13.2 | 1.63 | -27.2 | 42.49 | 26.1 |
| 51 | 11.9 | 1.29 | -26.6 | 42.83 | 33.2 |
| 53 | 11.0 | 0.82 | -25.5 | 44.92 | 54.9 |
| 55 | 10.4 | 0.98 | -27.0 | 44.07 | 45.1 |
| 57 | 10.8 | 0.92 | -27.3 | 44.08 | 47.7 |
| 59 | 11.2 | 1.17 | -26.7 | 42.25 | 36.2 |
| 61 | 11.7 | 0.98 | -26.5 | 43.13 | 43.9 |
| 63 | 11.4 | 0.68 | -25.4 | 42.19 | 61.9 |
| 65 | 10.3 | 0.77 | -26.1 | 44.22 | 57.5 |
| 67 | 10.6 | 0.97 | -26.4 | 42.22 | 43.3 |
| 69 | 12.0 | 1.23 | -25.8 | 44.61 | 36.4 |
| 71 | 11.9 | 1.05 | -25.5 | 44.22 | 42.3 |
| 73 | 11.6 | 0.80 | -25.9 | 43.05 | 53.6 |
| 75 | 11.7 | 1.01 | -26.3 | 41.37 | 41.0 |
| 77 | 11.9 | 0.77 | -25.7 | 42.11 | 55.0 |
| 79 | 9.1 | 0.67 | -25.9 | 43.79 | 65.2 |
| 81 | 9.6 | 0.62 | -25.5 | 43.08 | 69.2 |
| 83 | 13.2 | 0.76 | -25.8 | 42.89 | 56.7 |
| 85 | | | | | |
| 87 | 14.1 | 1.00 | -25.3 | 41.53 | 41.5 |
| 89 | 14.4 | 1.21 | -26.3 | 43.64 | 36.0 |
| 91 | 12.7 | 0.80 | -24.9 | 43.61 | 54.4 |
| 93 | 13.1 | 1.00 | -24.3 | 42.55 | 42.4 |
| 95 | 15.0 | 1.36 | -25.4 | 42.12 | 31.0 |
| 97 | 14.4 | 1.06 | -25.8 | 41.44 | 38.9 |
| 99 | 11.2 | 1.28 | -25.6 | 45.11 | 35.3 |
| 101 | 16.0 | 2.75 | -26.4 | 44.51 | 16.2 |
| 103 | 15.8 | 2.79 | -25.5 | 45.93 | 16.4 |
| 105 | 14.9 | 2.65 | -26.3 | 44.65 | 16.8 |
| 107 | 13.1 | 1.41 | -26.4 | 44.33 | 31.3 |
| 109 | 13.1 | 1.02 | -26.0 | 41.70 | 41.0 |

| | | | | | |
|---|---|---|---|---|---|
| 111 | 11.9 | 0.88 | -26.0 | 42.88 | 49.0 |
| 113 | 11.4 | 0.78 | -25.1 | 43.05 | 55.2 |
| 115 | 11.4 | 0.68 | -26.0 | 41.54 | 61.1 |
| 117 | 10.4 | 0.79 | -26.5 | 42.96 | 54.1 |
| 119 | 10.9 | 1.24 | -26.6 | 43.42 | 35.2 |
| 121 | 10.5 | 1.77 | -27.0 | 43.34 | 24.5 |
| 123 | | | | | |
| 125 | | | | | |
| 127 | 10.6 | 0.49 | -25.6 | 42.27 | 87.0 |
| 129 | 14.4 | 1.16 | -25.4 | 42.98 | 37.0 |
| 131 | 12.6 | 0.72 | -24.9 | 43.23 | 59.8 |
| 133 | 12.5 | 1.57 | -26.1 | 44.80 | 28.6 |
| 135 | 11.3 | 1.42 | -27.0 | 42.03 | 29.5 |
| 137 | 11.4 | 1.16 | -24.9 | 44.31 | 38.1 |
| 139 | 12.4 | 0.84 | -25.0 | 44.17 | 52.9 |
| 141 | 11.7 | 1.39 | -25.1 | 45.18 | 32.4 |
| 143 | 10.9 | 1.16 | -24.6 | 44.07 | 38.1 |
| 145 | 11.9 | 1.23 | -25.3 | 44.70 | 36.4 |
| 147 | 13.2 | 1.54 | -25.6 | 43.94 | 28.5 |
| 149 | 12.2 | 1.23 | -24.2 | 44.36 | 36.0 |
| 151 | 12.5 | 0.99 | -24.3 | 43.95 | 44.2 |
| 153 | 14.3 | 1.14 | -24.2 | 43.53 | 38.3 |
| 155 | 12.4 | 0.94 | -23.9 | 43.36 | 46.2 |
| 157 | 11.3 | 0.77 | -24.8 | 44.12 | 57.6 |
| 159 | 11.3 | 1.73 | -24.9 | 43.91 | 25.3 |
| 161 | 13.2 | 0.88 | -24.7 | 44.52 | 50.9 |
| 163 | 12.6 | 0.90 | -24.2 | 42.05 | 46.5 |
| 165 | 13.0 | 0.67 | -25.3 | 44.85 | 66.7 |
| 167 | 12.7 | 1.20 | -24.3 | 45.36 | 37.9 |
| 169 | 13.8 | 1.37 | -24.5 | 46.52 | 33.8 |
| 171 | 14.3 | 1.18 | -25.0 | 42.43 | 36.1 |
| 173 | 11.4 | 0.60 | -22.9 | 43.08 | 71.3 |
| 175 | 11.6 | 0.58 | -23.4 | 42.72 | 74.0 |
| 177 | 10.9 | 0.76 | -23.2 | 44.15 | 57.8 |
| 179 | 12.9 | 0.87 | -23.7 | 42.31 | 48.5 |
| 181 | 13.3 | 0.90 | -24.0 | 42.79 | 47.8 |
| 183 | 14.2 | 0.84 | -23.9 | 42.47 | 50.3 |

| 185 | 13.3 | 0.73 | -23.7 | 40.66 | 55.6 |
| 187 | 9.9 | 0.78 | -23.3 | 42.65 | 54.7 |
| 189 | 10.6 | 0.67 | -23.8 | 44.05 | 65.3 |
| 191 | 11.5 | 0.73 | -23.1 | 42.77 | 58.9 |
| 193 | 12.9 | 1.10 | -25.1 | 44.08 | 39.9 |
| 195 | 12.2 | 0.92 | -24.5 | 43.26 | 47.2 |
| 197 | 13.1 | 0.82 | -24.8 | 42.57 | 52.0 |
| 199 | 13.2 | 1.35 | -25.0 | 42.20 | 31.3 |
| 201 | 11.1 | 1.22 | -24.6 | 44.18 | 36.1 |

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