Population trends in an Atlantic puffin (*Fratercula arctica*) colony determined from a ~500-year sediment core

by

Maliya Elizabeth Cassels

A Thesis submitted to the Department of Graduate Studies of

Memorial University of Newfoundland

In partial fulfillment of the requirements of the degree of

MASTER OF SCIENCE

Department of Biology

Memorial University of Newfoundland

May 2025

St. John’s Newfoundland and Labrador

Abstract

The global population of Atlantic puffin (*Fratercula arctica*) is declining. This decline has been linked to numerous anthropogenic impacts. However, untangling these impacts from fluctuations due to colony dynamics is complicated by the lack of historical population data. Paleoecological reconstructions based on chemical and biological signatures in sediment cores taken from seabird colonies have been successfully used to infer historical trends in nesting seabird numbers for several seabird species, but not for Atlantic puffin. This research uses diatom assemblages, stable isotopes, metal(loid)s, sterols and stanols, and chlorophyll *a* to reconstruct an Atlantic puffin colony located in the western North Atlantic near Fogo Island, Newfoundland. The analysis shows that numbers of Atlantic Puffins nesting at this colony remained relatively stable from ~1450 CE, and began increasing in ~1966 CE, with a sharp and rapid population increase suggested from the 1990's to present. The five proxies used had good congruence with one another. This corresponds with other evidence that Atlantic puffin populations in Newfoundland are stable or increasing, in contrast to colonies elsewhere in their range. The apparent increase at this colony also coincided with several significant changes in conditions, including the collapse of the cod fishing industry in Newfoundland.

General Summary

The global population of Atlantic puffin (*Fratercula arctica*) is declining due to disturbance by humans. However, there is a lack of historical population data for most puffin breeding colonies. This research uses sedimentary diatoms, stable isotopes, metal(loid)s, sterols and stanols, and chlorophyll *a* to reconstruct an Atlantic puffin colony near Fogo Island, Newfoundland. Numbers of Atlantic puffins nesting at this colony remained relatively stable from ~1450 CE, and began increasing in ~1966 CE, with a rapid increase suggested from the 1990’s to present. This corresponds with other evidence that Atlantic puffin populations in Newfoundland are stable or increasing, in contrast to colonies elsewhere in their range. The apparent increase at this colony coincided with several significant changes in the region, including the collapse of the cod fishing industry in Newfoundland.

Acknowledgements

Firstly, I would like to respectfully acknowledge and thank the peoples on whose land I am fortunate enough to live and work. The island of Newfoundland, where I collected these data, is the ancestral homeland of the Mi’kmaq and Beothuk. I also recognize the Inuit of Nunatsiavut and NunatuKavut and the Innu of Nitassinan, and their ancestors, as the original people of Labrador. I wrote much of this thesis in Nanaimo, British Columbia, in the heart of the Salish Sea, on the past and present territory of Snuneymuxw First Nation.

I would like to thank my supervisor Dr. Kathryn Hargan. Thank you for all your guidance, assistance, and patience. My fellow Paleo lab-members: Molly Morrissey, Veronica Smith, Courtney White, Johanna Bosch, Madeline Sceviour, Ben Taylor, Alex Zvezdin, Katie Hong-Kiu Lau, and Ishraq Rahman. Thank you for your camaraderie, help in the field and lab, and for making a newcomer to St. John’s during a pandemic feel welcome.

I also thank Dr. Pierre-Paul Bitton for his assistance in reaching the Little Fogo Islands, and Dr. Bill Montevecchi for letting me join a field trip to Musgrave Harbour and the Penguin Islands. Also thank you to Taylor Brown, Dr. Sabina Wilhelm, and the CPAWS Puffin Patrol for help in procuring puffin guano. I thank my committee members, Dr. Andrew Lang and Dr. Bill Montevecchi, for guidance throughout the project and draft edits.

Lastly, I would like to thank my family for their love and support, my partner Chris for his endless encouragement, and of course my best buddy Nathan for keeping my spirits up while writing.

Co-authorship statement

This thesis conforms to the Traditional Format outlined by the School of Graduate Studies. I was the lead author for all chapters. My thesis supervisor, Dr. Kathryn Hargan, provided support during the field work, lab work, statistical analyses, interpretation, and writing and editing.

I was responsible for collecting and processing sediment samples, including diatom isolations, and preparing samples for stable isotope analysis, statistical analyses, and preparation of the manuscript. Evan Langille at Memorial University of Newfoundland conducted the lipids analysis.

COVID-19 Mitigation statement

The COVID-19 pandemic had an impact on this research project. The timeline for laboratory work and subsequent report writing was set back, as the closure of educational institutions meant that the research team had limited access to resources. To mitigate the effects of the pandemic on the research project, the research team explored alternative data collection methods and adjusted the project timeline accordingly.

Table of Contents

Abstract 1
General Summary 2
Acknowledgements 3
List of Tables 7
List of Figures 8
List of Appendices 10
List of Abbreviations 11
Chapter 1: General Introduction 1
  1.1 Seabirds 1
  1.2 Paleoecology 3
  1.3 Thesis objectives & overview 7
  1.4 Site Description: Little Fogo Islands, Newfoundland 9
Chapter 2: Methods 11
  2.1 Study area 11
  2.2 Sample collection 14
  2.3 Sediment core chronologies 14
  2.4 Seabird proxies 15
  2.5 Data analysis 22
Chapter 3: Results 24
  3.1 Sediment core chronologies 24
  3.2 Puffin guano 26
  3.3 Water chemistry 27
  3.4 Seabird sediment proxies 27
    3.4.1 Metal(loid)s & biogenic enrichment factors 27
    3.4.2 % Carbon and % Nitrogen 32
    3.4.3 Chlorophyll *a* 34
    3.4.4 Stable nitrogen and carbon isotopes 34
    3.4.5 Organic $\delta^{13}C$ and % C 36
    3.4.6 Diatom assemblages 38
    3.4.7 Lipids 43
Chapter 4: Discussion 48
  4.1 Data summary and multi-proxy population reconstruction 48

4.2 Summary of the proxy changes through the cores 51
4.3 History of the region 56
4.4 Sea surface temperature (SST) 56
4.5 Puffin diet and prey availability in Newfoundland 57
4.6 Bycatch 59
4.7 Hunting 59
4.8 Conditions for puffins in the 20th century 60
4.9 Study limitations 61
4.10 Future research 62
References 64
Appendix 1 1
Appendix 2 2
Appendix 3 3
Appendix 4 1

List of Tables

Table 3.1. Lead-210 and radiocarbon dating of the puffin impact core sediments.

Table 3.2. Lead-210 and radiocarbon dating of the mainland reference pond sediments.

Table 3.3. $\delta^{13}C$ and $\delta^{15}N$ values, %C and %N of Atlantic puffin guano

Table 3.4. Metal(loid) concentrations in puffin guano, surface sediments from the mainland reference pond, and biogenic enrichment (BE) factors

Table 3.5. Generalized additive model results for each proxy, including k-indices, p-values, and range of years where a significant non-zero derivative indicating an increase/decrease was found for chlorophyll *a*, $\delta^{15}N$, and the ratio of seabird lipids.

List of Figures

Figure 2.1. Locations and photos of the mainland reference pond and the puffin impact pond.

Figure 3.1. Classical age-depth modeling with *Clam* (Blaauw, 2010), incorporating ^{210}Pb and ^{14}C dating for the puffin impact core (a) and the reference core showing both a linear fit (b) and a smooth spline fit (c).

Figure 3.2. Concentrations of seabird-associated metals and metalloids, corrected to titanium, through time for the puffin impact core and the mainland reference core, with breakpoints of change for the puffin impact core, determined by CONISS and broken stick analysis.

Figure 3.3. CONISS of all metal(loid)s in the puffin impact core and broken stick analysis of metal(loid)s.

Figure 3.4. Generalized additive model of a) Zinc and b) Cadmium concentrations relative to titanium for the puffin impact core.

Figure 3.5. Percent nitrogen for the puffin impact core and the reference core.

Figure 3.6. Percent carbon (total) for the puffin impact core and the reference core.

Figure 3.7. δ^{15}N, δ^{13}C, and chlorophyll *a* for the puffin impact core and mainland reference core.

Figure 3.8. Generalized additive model of a) chlorophyll *a* and b) δ^{15}N for the puffin impact core.

Figure 3.9. Organic δ^{13}C values in the puffin impact core and reference core.

Figure 3.10. Percent organic carbon in the puffin impact core and the reference core.

Figure 3.11. Percent relative abundance of diatoms in the puffin impact core, showing breakpoints of change in species assemblage according to nested constrained hierarchical clustering analysis.

Figure 3.12. CONISS of all diatoms in the puffin impact core and broken stick analysis of diatoms.

Figure 3.13. Principal component analysis biplot of axis 1 and 2, showing the diatom taxa that are characteristic throughout the puffin core.

Figure 3.14. Percent relative abundance of diatoms in the Musgrave Harbour Reference core, showing breakpoints of change in species assemblage according to nested constrained hierarchical clustering analysis.

Figure 3.15. CONISS of all diatoms in the Musgrave Harbour reference core and broken stick analysis of diatom assemblages.

Figure 3.16. Sterols and stanols and percent organic carbon for the puffin impact and reference cores.

Figure 3.17. The seabird ratio for the puffin impact core fitted with a generalized additive model showing a period of significant decrease and increase.

Figure 3.18. Mean sterol and stanol concentrations in puffin guano collected from fledglings in Witless Bay, NL.

Figure 3.19. Summary of chlorophyll *a*, $\delta^{15}N$ (‰), seabird ratio, and seabird-associated metal(loid)s (Cd and Zn).

Figure 3.20. Generalized additive model of the mean Z score.

List of Appendices

Appendix 1. Site characteristics for the puffin impact pond, mainland reference, and Fogo Island reference ponds.

Appendix 2. Water chemistry for the puffin impact pond and the Fogo Island reference pond.

Appendix 3. Reporting detection limits (RDL) for metal(loid)s in sediments and puffin guano

Appendix 4. Complete geochemical analysis results for puffin impact core and mainland reference core.

List of Abbreviations

AMS	Accelerator mass spectrometry
ca.	circa
CE	Common era
Chl *a*	Chlorophyll *a*
C/N	Carbon to nitrogen ratio
Clam	classical age-modeling
CONISS	Constrained incremental sum of squares
CRS	Constant rate of supply
CWS	Canadian Wildlife Service
DCM	Dichloromethane
DO	Dissolved oxygen
DOC	Dissolved organic carbon
ECCC	Environment and Climate Change Canada
GAM	Generalized additive model
GC-MS	Gas chromatography mass spectrometry
LOESS	Locally estimated scatterplot smoothing
PCA	Principal component analysis
RDL	Reporting detection limit
VRS	Visible Reflectance Spectroscopy

Chapter 1: General Introduction

1.1 Seabirds

Global seabird populations are undergoing dramatic declines. Almost half of species are declining and 31% of species are globally threatened (Dias et al., 2019). Threats to seabird populations are increasing due to climate change and increasing fishing pressure causing bycatch mortality and a decline in prey stocks (Dias et al., 2019). Seabird breeding colonies are an important vector for marine-derived nutrients to terrestrial ecosystems and play a key role in global nutrient cycling (Doughty et al., 2016; Otero et al., 2018; De La Peña-Lastra, 2021). Breeding seabirds shape the terrestrial ecosystem at their colonies both by depositing nutrients (e.g., Bokhorst et al., 2019) and through burrowing activities (Orwin et al., 2016). They also function as sentinel species and changes in seabird populations can indicate unobserved changes in marine food webs (e.g., Velarde et al., 2019). However, there are few long-term monitoring data available on the dynamics of seabird colonies under various environmental conditions (Bonebrake et al., 2010). Understanding the long-term population history of seabird nesting colonies can help clarify colony dynamics and the drivers of population change.

Atlantic puffin (*Fratercula arctica*) are medium-sized (length 26-29 cm) seabirds that are members of the family Alcidae (Lowther et al., 2002). Puffins live throughout the North Atlantic Ocean, spending winters at sea and breeding in the summer in colonies from Labrador to Maine and from Greenland to northern France (Harris and Wanless, 2012). Recent genetic evidence suggests there are four distinct subpopulations of Atlantic puffin, with the western Atlantic birds forming their own semi-isolated population (Kersten et al., 2021). Large aggregations of puffins form on islands during the breeding season, where they nest in burrows or rock crevices (Lowther et al., 2002). Atlantic puffins have high breeding site fidelity, with immature puffins prospecting at several islands before their first nesting season at 4-5 years of age. Once they select a nesting site, they will return to it every season and it is thought to be rare for an adult bird to move to a different colony (Harris, 1983). Puffins are pursuit-diving pelagic feeders and feed on fish and marine invertebrates (Burger and Simpson, 1986). During the breeding season, parents forage within 20-100 km of the colony (Harris and Wanless, 2012).

Up to 90% of the global puffin population breeds in Europe, mostly in Iceland. Of the North American population, ~50% breed on the islands in Witless Bay, Newfoundland, in the middle of their western Atlantic range (Harris and Wanless, 2012). Atlantic Puffins were upgraded to Vulnerable on the International Union for Conservation of Nature (IUCN) Red List in 2018, due to their declining global numbers (Birdlife International, 2018). Most of these declines have occurred in the eastern Atlantic, where the majority of the global population breeds (Fauchald et al., 2015). The European population is calculated to be declining overall at a rate of 50–79% over three generations (65 years) (Birdlife International, 2018). The specific factors influencing this decline depend on the colony, although it is likely largely due to a lack of immature survival and recruitment caused by declining forage fish stocks (Miles et al., 2015).

Puffin colonies in the western North Atlantic seem to be generally faring better than their European counterparts. North America's largest Atlantic puffin colony on Great Island, Witless Bay, NL increased between 1979 and 1994 due to favourable breeding conditions, and the most recent estimate shows a large increase in breeding pairs (Wilhelm, 2023). However, colonies at the southern end of the North American species distribution, in the Gulf of Maine, have experienced very poor chick survival in recent years due to warm waters creating a lack of suitable prey during the breeding season (Kress et al., 2016).

Anthropogenic impacts on seabirds are increasing and there is a lack of long-term monitoring data (Montevecchi, 2023). According to Bonebrake et al. (2010), only 15% of studies examining population declines used data older than 100 years and only 42% used continuous monitoring data (defined as studies that described a population trend over a 10-year period at minimum using annual estimates). A lack of long-term monitoring can make it unclear whether observed seabird population trends are due to human impacts, are a response to underlying changes in the marine food web, and/or are a result of natural population fluctuations. Long-term monitoring data can help elucidate and predict how a species or a population would vary with changing environmental conditions, including understanding how it could change under future climate scenarios (Wood et al., 2015). Untangling long-term population cycles from human impacts can have important implications for management and policy decisions (Bonebrake et al., 2010).

1.2 Paleoecology

Paleoecological methods can help fill in gaps in seabird population monitoring data. Seabirds transport substances including lipids, nutrients, and contaminants from their marine feeding grounds to land, depositing these mostly in the form of guano (Doughty et al., 2016; Otero et al., 2018; De La Peña-Lastra, 2021). These substances flow downhill and accumulate in lakes and ponds, which preserve a historical record of seabird inputs in their sediments. Additionally, nutrients alter the aquatic flora and fauna that these aquatic ecosystems can support (De La Peña-Lastra, 2021). By taking a sediment core from the bottom of a basin and analyzing direct and indirect chemical and biological proxies related to seabird presence, it is possible to estimate the history of seabird inputs into the basin. Seabirds are especially well-suited to these types of studies because 95 % are colonial (Danchin and Wagner, 1997) and their inputs concentrate in a small area, allowing for estimates of colony changes from changes in the concentration of seabird-associated proxies collected in the basin (Duda et al., 2021).

Duda et al. (2020a) used stable nitrogen isotopes ($\delta^{15}N$), subfossil diatoms, chlorophyll *a*, metals, chironomids, and sterols and stanols in sediment cores taken from ponds to reconstruct the history of a Leach's storm-petrel (*Hydrobates leucorhous*) colony on Baccalieu Island, NL. They found dramatic population fluctuations since the year 270 CE, with the colony consistently being much smaller in the past and fluctuating markedly in the absence of anthropogenic disturbances, before undergoing a sharp decline since the 1980s. This greatly expands the timeline for monitoring of this colony and implies a need to better understand inter-colony recruitment and the factors which influence changes in colony size. A similar set of proxies was used to trace the last ~5800 years of a Leach's storm-petrel colony on Grand Colombier Island, St Pierre et Miquelon (Duda et al., 2020b). These indices showed a history of population fluctuations before a drastic decrease in population size since colonization by Europeans circa 1816, reducing this colony to only 16% of the maximum historical carrying capacity shown in the sediment record.

Sedimentary proxies for seabirds are geochemical and biological indicators of seabird inputs. Direct proxies, such as stable nitrogen isotopes, lipids and metal(loid)s, originate from seabird guano, whereas indirect proxies, such as diatom assemblages, are due to changes in the ecosystem (e.g., water quality) caused by seabird presence. Often independent proxies of seabird abundance are concurrently used to provide multiple lines of evidence for changes in a seabird population overtime. Radioisotopes with known half-lives (e.g., ^{210}Pb and ^{14}C) are used to date sediment cores. ^{210}Pb accumulates in lake basins continuously over time from precipitation and dust. It has a half-life of 22.3 years and can be used to accurately date sediments to several hundred years in the past. ^{14}C is used to verify ages beyond the range of ^{210}Pb. $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios, which track the use of leaded gasoline (Gallant et al., 2020) can also be measured to verify ages given by the $^{210}Pb/^{14}C$ dating model.

Stable carbon and nitrogen isotopes ($\delta^{13}C$ and $\delta^{15}N$) are used to estimate the amount of ornithogenic nitrogen and carbon inputs to the impact pond. On average, it is estimated that ^{15}N is enriched by ~3.4‰ with every trophic level step due to preferential use of the lighter ^{14}N isotope during metabolic processes (Minagawa and Wada, 1984). Since seabirds feed at a high trophic level, they have a higher ratio of $^{15}N/^{14}N$ in their tissues than their prey or the background environment. Reported $\delta^{15}N$ values for Atlantic puffin tissues range from 11.68 to 15.18‰ and $\delta^{13}C$ values range from roughly -21.95 to -17.7‰, with variation depending on the tissue type, measurement methods, season, location, and diet of the birds (Hedd et al., 2010; Jenkins et al., 2020; Pratte et al., 2017; Thompson et al., 1999). While guano is expected to be the largest source of seabird nutrient inputs into terrestrial ecosystems (Grant et al., 2022), currently no studies have specifically reported stable isotope carbon and nitrogen values for Atlantic puffin guano. Changes in bulk $\delta^{15}N$ values can indicate either an increased/decreased seabird population, a shift in the birds' diet, or a shift in the $\delta^{15}N$ values in the underlying marine food web. Therefore, stable isotope results will be compared with several other seabird proxies. $\delta^{13}C$ values do not accumulate predictably in trophic levels; however, it can be indicative of feeding habitat or source of carbon to a consumer. Several studies have indicated that $\delta^{13}C$ values increase as seabird colony size increases due to deposition of guano (e.g., Liu et al., 2013; Conroy et al., 2015; Cheng et al., 2021). However, the opposite trend has been seen in some cases. For example, Duda et al. (2020b) found that burrowing by Leach's storm-petrels caused a decrease in $\delta^{13}C$ as the colony increase, due to the addition of inorganic materials to the pond.

Concentration of chlorophyll *a* and its diagenetic products measures past phytoplankton productivity in pond sediments (Michelutti and Smol, 2016), which can be indicative of nitrogen and phosphorus inputs. Seabird guano has high phosphorus and nitrogen concentrations (De La Peña-Lastra, 2021); therefore, chlorophyll *a* is often used as an indirect proxy for seabird nutrient inputs (Duda et al., 2021).

Seabirds accumulate metals and metalloids from their marine diets and deposit these onto their breeding grounds (De La Peña-Lastra, 2022). For example, Mallory et al. (2015) found that soils from islands with seaduck colonies had higher concentrations of K, Ca, Cu, Se, and Zn than islands without colonies. Duda et al. (2020a) used Cd and Zn concentrations in a sediment core to track Leach's storm petrel abundance at a colony near Newfoundland over approximately 1700 years. Additionally, research examining and comparing the blood concentrations of metals in seabirds typical for a region can help elucidate the predicted metals that may be high in guano and deposited into the environment (e.g., Grant, et al., 2022; Shoji et al., 2019). Furthermore, bioenrichment factors are helpful in determining the metals that a particular seabird species or colony is elevating within the environment. For example, Brimble et al. (2009) calculated bioenrichment factors for northern fulmars (*Fulmarus glacialis*) by comparing the concentrations within guano with concentrations in the background surface sediment not influenced by seabirds. They concluded that P, Cd, K, Zn, and As were seabird-associated because these elements were more concentrated in fulmar guano than in the background sediments.

Animal-derived zoosterols and plant-derived phytosterols are relatively stable in sediments, and therefore changes in these can be used to trace the source of sterol inputs through a sediment core (Gallant et al., 2024). Seabird guano can contain high concentrations of cholesterol (Cheng et al., 2016; Hargan et al., 2019). Sitosterol is found in terrestrial and aquatic plants and phytoplankton. The “seabird ratio” of [cholesterol]/([cholesterol] + [sitosterol]) showed significant enrichment of cholesterol in pond sediments closest to a nesting colony of northern fulmars in the High Arctic and was significantly correlated with ornithogenic δ15N enrichment of sediment (Cheng et al., 2016). This “seabird sterol index” provides a direct measure of seabird presence and, when measured in sediment cores, can be used to infer population trends through time.

Diatoms (Class Bacillariophyceae) are microscopic, single-celled eukaryotic algae found in most wet habitats worldwide (Smol and Stoermer, 2010). Diatom species have specific environmental preferences and their short life spans enable them to respond rapidly to environmental changes. As well, their silicious valves often preserve well in lake sediments over long time scales. These features make them the most commonly used indicator to track past changes in water quality through sediment cores (Smol and Stoermer, 2010; Duda et al., 2021). Shifts in diatom species assemblage can reflect changes in pond pH, nutrient concentrations, and conductivity (e.g., Reavie and Smol, 2001; Rühland et al., 2015) - all water chemistry variables influenced by seabirds and thus they can aid in reconstructing past changes in seabird breeding colonies. Typically, with increasing influence of a seabird colony, the diatom assemblage of nearby ponds will shift from taxa preferring low nutrients to those which thrive in high nutrient water (Duda et al., 2021).

1.3 Thesis objectives & overview

This thesis explores the population trend in breeding Atlantic puffins at a colony in the Little Fogo Islands over the last ~500 years. The thesis objective is to use chemical and biological proxies for seabirds to track changes in puffin abundance at this site and compare trends in these proxies to those in a sediment core taken from a pond with no known seabird influence. The proxies chosen were: subfossil diatoms, $\delta^{15}N$ values, chlorophyll *a*, lipids, and metal(loid)s. $\delta^{13}C$ values, organic $\delta^{13}C$ values, % nitrogen, % total carbon, and % organic carbon were also measured and compared, but these are less closely associated with seabirds. Chapter 2 includes a description of the study site and sample collection methods, and the methods used to isolate the proxies of seabird abundance. Chapter 3 outlines the results including pond water chemistry and analysis of sediment proxies for both the reference and seabird-impacted cores. Chapter 4 is a discussion of our findings in the context of significant events in the history of the North Atlantic, including the cod fishery moratorium and the collapse of the capelin stock, which both occurred in the early 1990s. To my knowledge, no long-term monitoring data exists for my study site, the Little Fogo Islands puffin colony, and sediment cores have not been used to study the history of an Atlantic puffin colony. This project combines several seabird-associated proxies to reconstruct this population, adding to knowledge about the life cycle of puffin colonies and the long-term population dynamics of this specific colony. Additionally, I compared changes within a seabird-impact core to changes in a sediment core taken from a reference pond, which is not located near a seabird colony and has no known history of marine inputs. This type of comparison has been, for example, used to track $\delta^{15}N$ inputs from double-crested cormorants (*Nannopterum auritum*) nesting on islands in Eastern Ontario (Stewart et al., 2019). Hargan et al. (2017) compared cores from ponds at increasing distances to a thick-billed murre (*Uria lomvia*) colony in the Arctic and found that $\delta^{15}N$, nutrients, and major ions were elevated in ponds nearer the colony, but that shifts in other proxies, such in diatom assemblage, were linked more to climatic changes. To help untangle any changes in the seabird core that may be due to environmental shifts, I compared the proxies from the impact pond core to the same proxies isolated from a non-seabird-impacted pond sediment core.

1.4 Site Description: Little Fogo Islands, Newfoundland

The Little Fogo Islands are a small archipelago approximately 7 km north of Fogo Island, off the northeast coast of Newfoundland. Little information exists about the history of human use of this archipelago; however, the history of nearby Fogo Island is well documented. The Beothuk used the area in the summer months for fishing and harvesting seabirds and their eggs, and a few burial sites have been uncovered on Fogo Island, however it does not appear they settled here year-round (Kristensen, 2011). Beginning in the early 1500s, boats from Europe travelled back and forth to the area in the summer to exploit the then-abundant Atlantic cod (*Gadus morhua*). They were not permitted to settle permanently, however, and the first official permanent villages on Fogo Island were established in the 1700s. Settlers came from England, Ireland, and the Southern Bays of Newfoundland, drawn by the cod and seal fisheries (Shorefast Website, 2022).

The Little Fogo Islands fall within the 3K Northwest Atlantic Fisheries Organization (NAFO) fishing zone (part of the Newfoundland Shelf). Historically, Atlantic Cod was the main fishery in the area, with significant fisheries for other groundfish such as redfish, flounder, and turbot. Before the 1950s the fishery was conducted mostly inshore with small boats, using gillnets or jigging. In the 1950s, technological and geographic expansion of the fishery, arrival of large foreign offshore trawling vessels, and the expansion of the otter trawl fleet resulted in a dramatic increase in groundfish landings in the region (Government of Canada, 2022). The traditional inshore fishery on Fogo Island struggled to compete with large offshore commercial operations and inshore groundfish stocks had declined noticeably by the late 1960s (McCay, 1979). Intensive commercial fishing continued throughout the 1980s. For the 2J3KL cod stock, landings increased from approximately 151,750 tons in 1980 to 238,000 tons in 1989. A moratorium was implemented on the Newfoundland cod fishery in July 1992 due to substantial declines in stock biomass. Fisheries for several other groundfish species and Atlantic salmon (*Salmo salar*) were also closed in following years (Government of Canada, 2022). Prior to the cod moratorium, the Little Fogo Islands were the site of a seasonal fishing community and visited regularly by people from Fogo Island. With the abrupt closure of the groundfish fishery in 1992, boat traffic, fishing pressure, and general human use of these islands decreased suddenly.

Chapter 2: Methods

2.1 Study area

The Little Fogo Islands is a small archipelago, which lies approximately 7 km north of Fogo Island, off the northeastern coast of the island of Newfoundland (Appendix 1). Historically, the larger islands contained homes and fishing cabins, many of which have fallen into disuse since the moratorium on the cod fishery in 1991. The Little Fogo Islands and the surrounding area are classified as part of the North Shore Forest ecoregion. These islands, however, are not forested. Soils in this region are characterized as dark with a high organic content (Protected Areas Association of Newfoundland and Labrador, 2008). The islands in this archipelago with nesting puffins are bounded by sheer cliffs and have grassy, hummocky soil, honeycombed by burrows. The most recent available survey from 2014 estimated a total of 15,370 nesting pairs on six puffin-occupied islands (Canadian Wildlife Service, unpubl. data, 2014). This may be an underestimation of the total number of puffins nesting in this archipelago, as only the main nesting islands were surveyed. Of the islands visited only one, Puffin Island (49.8104N, -54.111E), has a pond which is suitable for sediment coring (referred to here as the "puffin impact pond"). Puffin Island measures approximately 200 x 90 m and is also home to cliff-nesting Razorbills (*Alca torda*). The 2014 survey estimated that 4,089 puffin breeding pairs breed on this island (Canadian Wildlife Service, unpubl. data, 2014). The puffin impact pond is 14 cm deep and lies in a valley between two hills riddled with puffin burrows. The nearest puffin burrow is approximately 10 m from the pond.

I selected a pond with no seabird inputs to serve as a "reference pond" to monitor other ongoing stressors that aquatic ecosystems may be responding to, for example, climatic warming. This reference pond is located on mainland Newfoundland near Musgrave Harbour, roughly 42 km from the puffin impact pond (Figure 2.1). This pond receives minimal bird inputs and is not the site of any known nesting seabirds. The reference pond is 5 m deep and falls within the same North Shore Forest ecoregion as the impact pond. For comparison, water samples were also taken from a third pond on Fogo Island, approximately 10 km from the puffin impact pond. Geological information for these sites is given in Appendix 1.

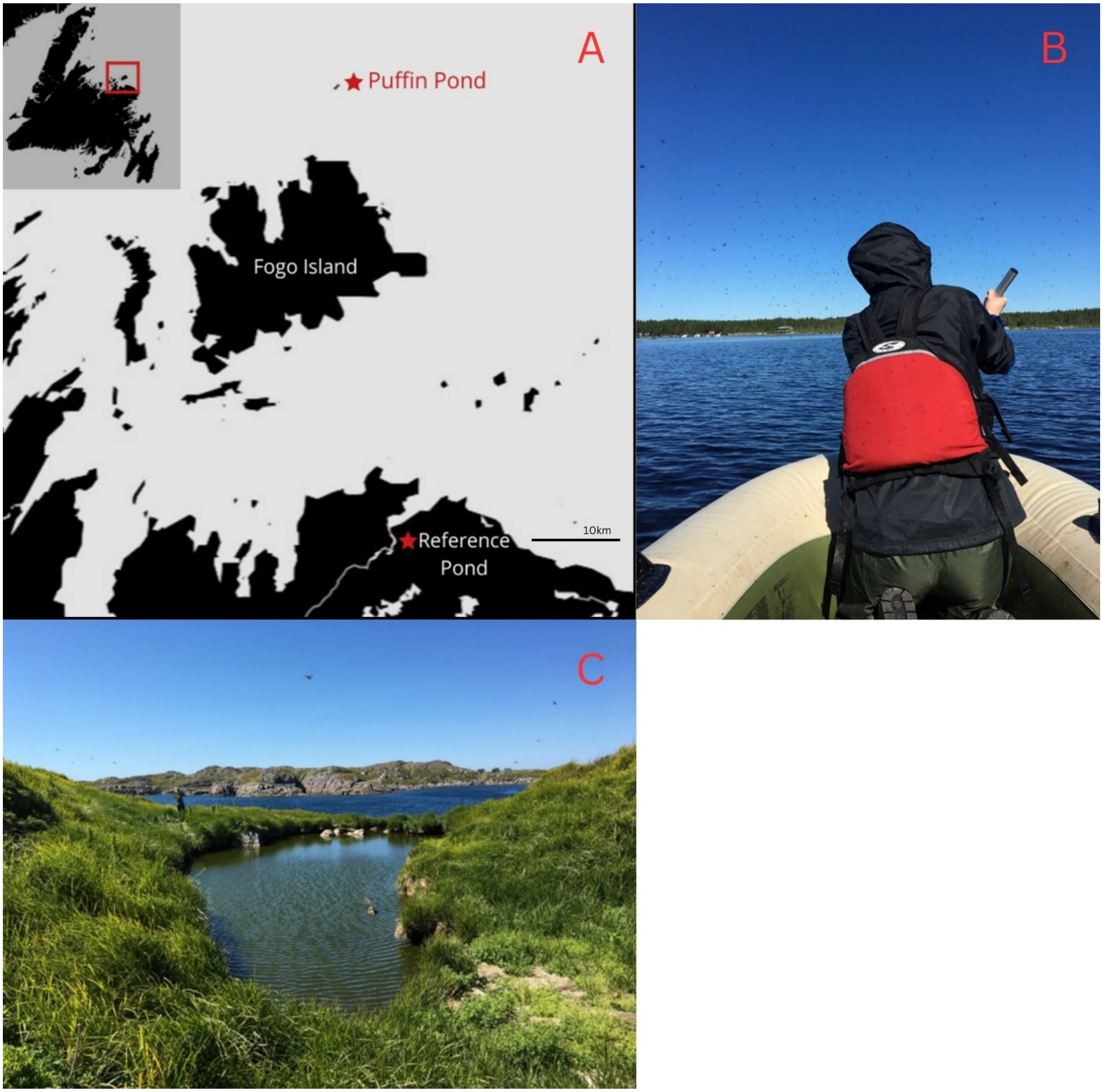


Figure 2.2 a) Locations of the mainland Reference Pond and the Puffin Impact Pond (inset: Island of Newfoundland, Canada); b) Mainland reference pond near Musgrave Harbour; c) Puffin impact pond in the Little Fogo Islands.

2.2 Sample collection

I used a push corer (Glew and Smol, 2016) with a 1 m long, 76 mm diameter plexiglass tube to collect a sediment core from the impact pond (33 cm long) and the reference pond (42 cm long). This is a standard method in paleolimnology for taking sediment cores from shallow lakes (Glew and Smol, 2016). Cores were sectioned every 0.5 cm immediately following collection using a high-resolution extruder (Glew, 1988) and sections were placed into Whirl-Pak® bags. Samples were transported from the field in coolers before being stored frozen at -20ºC. Every interval from the reference core and every second interval from the puffin impact core was freeze dried. Dried samples were kept in Ziploc® bags to keep out excess moisture. Cores and water samples were collected in July and August of 2021.

2.3 Sediment core chronologies

Samples of dry sediment were sealed in polypropylene tubes with epoxy resin and stored for at least 2 weeks before counting to ensure equilibrium between ^{226}Ra and ^{214}Bi. ^{210}Pb was analyzed at Queen's University (Kingston, ON) using an Ortec High Purity Germanium Gamma Spectrometer (Oak Ridge, TN, USA) and ages were estimated using the Constant Rate of Supply Model (Appleby and Oldfield, 1978). Certified Reference Materials obtained from the International Atomic Energy Association (Vienna, Austria) were used for efficiency corrections and results were analyzed using ScienTissiME (Barry's Bay, ON).

Radiocarbon (^{14}C) was used to verify ages from the bottom of the cores, as extrapolation from ^{210}Pb becomes less accurate in deeper sediments due to changes in sedimentation rate. Radiocarbon dating was carried out at the A.E. Lalonde AMS Laboratory, University of Ottawa (Ottawa, ON). One bulk sediment radiocarbon sample from 33 cm depth was measured for the puffin impact core, and one bulk sediment sample at 13.25 cm depth for the reference core. An acid pretreatment was performed on the bulk sediment samples, per standard protocol at the A.E.

Lalonde AMS Laboratory (Crann et al., 2017). Using the *clam* package in R (Blaauw, 2010), for the puffin core, dates were extrapolated using a linear fit from the ^{210}Pb date at depth 10.25 cm to the radiocarbon date at depth 33.25 cm. For the reference core, a smooth spline fit was found to more smoothly extrapolate dates from the ^{210}Pb date at 8.25 cm to the radiocarbon date at 13.25 cm.

2.4 Seabird proxies

Water chemistry analysis

To assess which nutrients and metals were elevated in the puffin impact pond water relative to the surrounding non-impacted ponds, 500 mL of water was taken from both the puffin impact pond and from a pond on Fogo Island. Water from the mainland reference pond was not sampled due to logistical constraints. Samples were sent to Avalon Laboratories (St. John's, NL), which is certified by the Canadian Association for Laboratory Accreditation Inc. (CALA). Water was analyzed for metals using inductively coupled plasma mass spectrometry (ICP/MS), total Kjeldahl nitrogen (TKN) using colorimetric analysis, and dissolved carbon concentration via infrared spectrometry. Sample preparation methods followed standard procedures (Standard Methods, 2018). Limits of detection are given in Appendix 3.

Metal(loid)s

Dried and ground sediment (~1 g) was weighed into plastic scintillation vials. Guano from 12 puffin fledglings caught by the Canadian Parks and Wilderness Society Puffin Patrol in Witless Bay, NL was dried at 60°C for 24 hours. Guano was combined (according to Table 3.3) to give 1 g for three analyses which was weighed into a plastic scintillation vial. Analyses were carried out by SGS Canada in Lakefield, Ontario (nationally accredited with CALA). Prior to analysis, sediment samples were pulverized in an agate bowl and subjected to an *aqua regia* digestion to extract environmentally relevant metals while preserving the silicate matrix. ICP/MS was used to analyze 30 metals. Limits of detection (RDL) are given in Appendix 3. Quality assurance and quality control were ensured by running certified reference material, internal standards, blanks, and duplicates after every batch of 20 samples.

Biogenic enrichment (BE) factors were calculated as follows:

BE = [metal(loid) in guano]/[metal(loid) in surface sediment of mainland reference pond]
A value greater than 1 indicates that concentration of the element is higher in the guano compared to the background geology (Brimble et al., 2009). Where the value for the surface sediment of the reference pond was less than the reporting detection limit (RDL), factors were calculated as suggested by Hornung and Reed (1990), as follows: BE = [metal(loid)]/(RDL/(2^(1/2))).
Metal(loid) concentrations in the pond sediments were also normalized to titanium to account for changes in concentrations through time due to erosion (Duda et al., 2021).

Elemental analysis and stable carbon and nitrogen isotopes

Stable isotope and elemental analysis of $\delta^{15}N$ and $\delta^{13}C$, and %N and %C for the puffin impact pond, reference pond sediments, and puffin guano was carried out at the Earth Resources Research and Analysis Facility (TERRA) at Memorial University of Newfoundland (St. John's, NL). Samples were weighed on a microbalance into 7x7 mm tin cups and analyzed with a Carlo Erba elemental analyzer (EA) coupled to a Delta V Plus isotope ratio mass spectrometer (IRMS) (Thermo Scientific, Germany) via a ConFlo III interface. The combustion reactor (chromium oxide and silvered cobaltous oxide) was held at 1050 ºC, while the reduction reactor (Cu) was at

600 ºC. For elemental analysis, a calibration curve for % C and % N was prepared using acetanilide. For isotopic analysis, scale calibration for $\delta^{13}C$ was performed with $CaCO_3$ ($\delta^{13}C$ = -40.11 ± 0.15‰) and D-fructose ($\delta^{13}C$ = -10.53 ± 0.11‰). Scale calibration for $\delta^{15}N$ was performed using IAEA-N-2 ((NH4)2SO4; $\delta^{15}N$ = +20.32 ± 0.09‰) and USGS25 ((NH4)2SO4; $\delta^{15}N$ = -30.25 ± 0.38‰). A high organic sediment (B2151: 7.45 ± 0.14 %C; 0.52 ± 0.02 %N; $\delta^{13}C$ = -28.90 ± 0.10‰; $\delta^{15}N$ = 4.35 ± 0.20‰) was analysed several times during a run as a quality control sample (Elemental Microanalysis Ltd., Okehampton, UK). Isotope data were normalized using previously calibrated internal standards, and analytical precision was ±0.2‰.

Additional samples were analyzed at the Ján Veizer Stable Isotope Laboratory at the University of Ottawa (Ottawa, ON) on a Vario EL Cube elemental analyzer (Elementar, Germany) interfaced to a Delta Advantage IRMS via a Conflo IV interface (Thermo Scientific, Germany). Samples and standards were flash combusted at about 1800ºC (via Dumas combustion). For elemental analysis, a calibration curve for % C and % N was prepared using nicotinamide (59.01% of C and 22.94% of N) and caffeine (49.48% of C and 28.85% of N). Internal standards were ($\delta^{15}N$, $\delta^{13}C$ in ‰): Nicotinamide (0.07,-22.95), mix of ammonium sulphate + sucrose (16.58,-11.94), caffeine (-16.61,-34.46), blind standard: glutamic acid (-3.98, -28.53). All $\delta^{15}N$ values were normalized to internal standards, calibrated to international standards IAEA-N1 (+0.4‰), IAEA-N2 (+20.3‰), USGS-40 (-4.52‰) and USGS-41 (47.57‰). All $\delta^{13}C$ was normalized to internal standards, calibrated to international standards IAEA-CH-6 (-10.4‰), NBS-22 (-29.91‰), USGS-40 (-26.24‰) and USGS-41 (37.76‰). Analytical precision was based on an internal standard (L-glutamic acid) which was not used for calibration and usually has a better than 0.2‰ precision. L-glutamic acid was the blind standard for both isotopes and elemental analysis. Isotope results are reported in delta (δ) notation where δ

= ((R_{sample} -$R_{standard}$)/$R_{standard}$)) ∗ 1000; R = ratio of the abundance of the heavy to light isotope; $R_{standard}$ = Vienna Peedee Belemnite (for $\delta^{13}C$) and atmospheric nitrogen (for $\delta^{15}N$).

$\delta^{13}C$ values and organic $\delta^{13}C$ values from 1840 CE onwards were corrected for the Suess effect, the historic depletion of ^{13}C in atmospheric CO_2 because of fossil fuel burning, according to values given in Graven et al. (2017). Because isotope values for atmospheric CO_2 are not available for the years 2018-2021, the correction value from 2017 was used for these years.

Organic $\delta^{13}C$ values and percent carbon

Acidified samples were analyzed to measure $\delta^{13}C$ and %C from organic carbon. Samples were prepared by hydrochloric acid fumigation, following methods described in Komada et al. (2008). I weighed 20-50 g of dried sediment from each interval for both the puffin impact and reference into glass scintillation vials. A few drops of distilled water were added to dampen the sediment. Samples were then placed in a glass desiccator with 80 mL HCl for 48 hrs. Samples were removed from the desiccator and 15 mL distilled water was added to each vial. Samples were soaked for 24 hrs before water was pipetted off. This rinsing process was repeated 4 times. Rinsed samples were dried in a 70-80ºC oven for 24 hrs. Organic carbon samples were analyzed for $\delta^{13}C$ and %C using an EA-IRMS, as above.

Chlorophyll a

Visible Reflectance Spectroscopy (VRS) was used to measure sedimentary chlorophyll *a* and its main diagenetic products (i.e., chlorophyll *a* + all chlorophyll *a* isomers + pheophytin-*a* + pheophorbide-*a*), hereafter referred to as chlorophyll *a*, as a means of reconstructing changes in whole-lake production (Michelutti et al., 2010). Freeze-dried sediment (100 mg per interval) was sieved through a 125-µm screen onto weigh-paper to equalize sediment grain size. Sediment-filled vials were run through a Model 6500 series Rapid Content Analyzer (FOSS NIRSystems Inc.). The visible portion of the electromagnetic spectrum was used to infer chlorophyll *a* and its derivatives. Details of this method and the equation used to infer chlorophyll *a* and its derivatives are given in Michelutti et al. (2010). Every second (even) centimeter was measured for the puffin impact core and every centimeter from 0-14.25 cm was measured for the reference core.

Diatoms

I performed diatom analysis at Memorial University of Newfoundland (MUN). Diatom preparation followed methodology used in the Paleoecological Environmental Assessment and Research Laboratory (PEARL) at Queen's University (Kingston, ON), as described in Rühland et al. (1999). This protocol is a modification of the methods outlined in Battarbee et al. (2001). To isolate diatoms, sediments were digested using a 1:1 (molecular weight) mixture of nitric and sulfuric acids. The samples were placed in an 80°C water bath for ~6 hours to digest the organic matrix. Samples were rinsed with deionized water daily until they reached a neutral pH (5-7 rinses). Slurries were plated onto microscope coverslips and, once dry, mounted onto microscope slides using Meltmount™ 1.704 (Cargille-Sacher Laboratories Inc., Cedar Grove, NJ, USA). Identifications were made using a light microscope under oil immersion at 1000x magnification. A minimum of 400 valves per sample were identified using diatom identification guides in Krammer and Lange-Bertalot (1991), Camburn and Charles (2000), and Spaulding et al. (2021). Identifications were made to species where possible. Percent relative abundances were calculated for all taxa in each sedimentary interval.

Lipids – sterols and stanols

Sedimentary sterols and stanols were measured using methods adapted from Hargan et al. (2019). Our analysis targeted sterols and stanols that are proxies for seabirds, humans, and vegetation. Seabird inputs were tracked using cholesterol (cholest-5-en-3β-ol), a sterol present in cell membranes of vertebrates, and its microbially-reduced product, cholestanol (5α-cholestan-3β-ol). Plants were tracked with sitosterol (β-sitosterol) and its microbially reduced forms stigmastanol (5α-stigmastan-3β-ol) and campesterol. Coprostanol and epicoprastanol tracked human inputs to the ponds.

To extract lipids, 100 mg of copper (Fisher) and 10 mL dichloromethane (DCM) was added to ashed 15 mL glass scintillation vials and sonicated for 10 min. The DCM was discarded after sonication. This step was repeated 3 times total. Clean copper was then air-dried, and 100 mg of freeze-dried sediment or guano was added to each vial. Every 1 cm from 0 to 10 cm was extracted for the reference core and every 4 cm for the puffin impact core. Three guano samples were analyzed. Samples were aggregated from various birds to obtain enough material to analyse, as detailed in Table 3.3.

Each sample was spiked with 100 µL of 50 ppm (3α)-Allopregnanolone. Method blanks containing only copper were spiked with 50 ppm 9 standard mix. Samples were evaporated dry and refrigerated for 12 h at 4ºC. To extract lipids from samples, 10 mL of 10 % Ethyl acetate and 90 % Dichloromethane (DCM high-grade Optima ® brand) was added to each vial and samples were sonicated for 10 minutes. The solvent mixture was pipetted into 50 mL centrifuge tubes and this step was repeated twice more. Samples were centrifuged at 3000 rpm for 20 minutes and then transferred to solvent washed Turbovap tubes and evaporated to 2 mL under a gentle nitrogen stream. The remaining sample was transferred to a SPE column with 1.0 g of Si

(Millipore), which was prior pre-conditioned with 6 mL of DCM. The Turbovap tube was rinsed with 0.3 mL DCM which was transferred to the columns, and samples were then eluted with a total of 40 mL DCM. All DCM was removed from the columns under vacuum pressure. The samples were transferred to solvent-washed Turbovap tubes and evaporated to 1 mL under a gentle nitrogen stream. The 1 mL samples were transferred to GC vials and evaporated to dryness under a gentle nitrogen stream. At this step, 100 µL of internal standard, 50 ppm (3α)-Allopregnanolone, was also evaporated dry. Once dry, 100 µL of 99 % N,O-bis(trimethylsilyl)trifluoroacetamide) + 1 % trimethylchlorosilane was added and samples were vortexed and then heated at 70ºC for 2 hrs. Samples were cooled for 15 min and 890 µL of Toluene (high-grade Optima® brand) and 10 µL of 250 ppm p-terphenyl-d_{14} (brand) were added to each sample. Samples were vortexed and analysed on the GC-MS.

Lipid analyses were carried out using an Agilent Technologies 6890 GC (G1530A) coupled to an Agilent Technologies 5973A MSD (G1098A) using an HP5MS-UI column from Agilent Technologies (19091S-433-UI; 30 m x 250 µm x 0.25 µm). Helium was the carrier gas at a constant flow of 1 mL min^{-1}, resulting in a pressure of 10.5 PSI. Injections were performed using an Agilent Technologies 7683 series injector in triplicate for each sample, with a 1.0 µL injection volume. Injections were made using a pulsed split-less mode with the injector heater set at 280°C, and injection pulse pressure of 16.26 PSI for 1.0 min. The oven was maintained at 100°C for 1 min, followed by a ramp of 12°C/min to 265°C, followed by a ramp of 0.5°C to 275°C then 20°C/min to 320°C and held for 2 min. The total runtime was 39.00 min. The MSD was operated in selected ion monitoring (SIM) mode with a collision energy of -70 eV, the transfer line was heated to 280°C. All quantifier ions were monitored with a dwell time of 100 ms while the qualifiers were measured for 40 ms. The low mass filtering setting was used (+/-

0.7-0.9 m/z). Lipid values are reported in mg L^{-1} and μg g^{-1} of dry weight sediment and were corrected to the internal standard, (3α)-Allopregnanolone added to each sample when applicable. All sterols and stanols were corrected to organic carbon by multiplying with the organic carbon content of each sample. Sterol and stanol values are reported in μg $(gOC)^{-1}$.

2.5 Data analysis

Breakpoints of changes in diatom assemblage and metal(loid) concentrations were determined using constrained hierarchical clustering analysis (CONISS) and the number of significant clusters was determined using a broken stick model in the *tidypaleo* package in R (Dunnington, 2022). A principal component analysis of diatom taxa and depth in the core was completed using the *factoextra* package (Kassambara 2020). Generalized additive models (GAMs) were fitted to the data for $\delta^{13}C$ values, % C, chl *a*, $\delta^{15}N$ values, % N, lipids, and metal(oid)s using the *mgcv* package (Wood, 2011).

The abundance of *S. construens*, $\delta^{15}N$ values, cadmium and zinc, and chlorophyll *a* data were combined to estimate the mean ornithogenic influence throughout the cores. Proxies were standardized using a Z-score, according to $Z = (x-\mu)/\sigma$; where x is a raw value, μ is the proxy mean, and σ is the proxy standard deviation. These Z scores were then averaged and plotted to give an overall trend in the core through time (Duda et al., 2020). Because data were sometimes collected on alternating intervals (i.e. stable isotopes and chl *a* were collected from even intervals and metal(loid)s from odd intervals), it was necessary to fill in missing values before averaging all the proxies. These values were filled in using linear interpolation in the *imputeTS* package (Moritz and Bartz-Beielstein, 2017). The reference and impact cores were compared to account for changes in the proxies through time not due to seabird influence. All analyses were carried out and figures created in R (R Core Team, 2020).

Chapter 3: Results

3.1 Sediment core chronologies

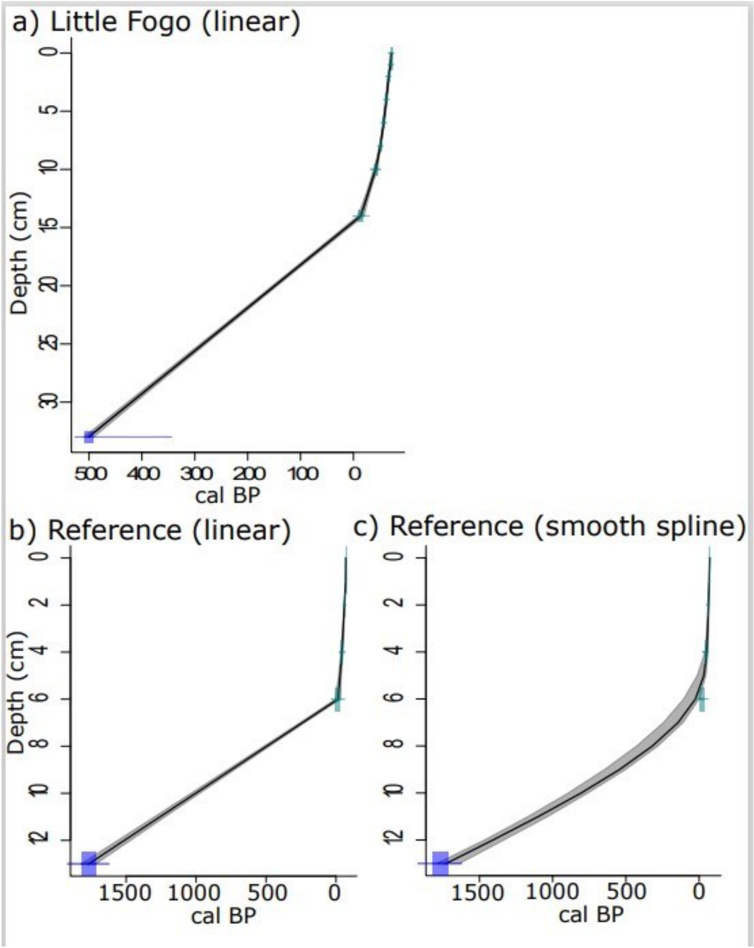
Lead-210 activity reached background levels (determined using ^{214}Pb) at 22.25 cm for the puffin impact core and 8.25 cm for the reference core. Bulk sediment from the bottom of the puffin impact core at 33.25 cm radiocarbon dated to 1515 CE (Table 3.1). The reference core converged with the age of bottom of the puffin core at around 9 cm depth (Table 3.2). Using the *clam* package in R (Blaauw, 2010), ages were derived with a linear fit for the impact core and a smooth spline fit for the reference core (Fig. 3.1).

Table 3.1. ^{210}Pb and radiocarbon (^{14}C) dating of the puffin impact core sediments. ^{210}Pb dates were estimated using the Constant Rate of Supply (CRS) model. The ^{14}C date was calibrated using the IntCal20 calibration curve (Reimer et al., 2020).

Midpoint (cm)	Year (CE)	Age (before 2021CE)	Error	Dating Method
1	2021.59	0	0	^{210}Pb
0.25	2021.13	0.46	0.06	^{210}Pb
2.25	2017.17	4.42	0.43	^{210}Pb
4.25	2012.75	8.83	0.66	^{210}Pb
6.25	2007.69	13.9	0.9	^{210}Pb
8.25	2001.36	20.23	1.2	^{210}Pb
10.25	1992.45	29.14	1.66	^{210}Pb
14.25	1964.68	56.91	3.4	^{210}Pb
18.25	1928.63	92.96	8.54	^{210}Pb
22.25	1892.28	129.31	12.25	^{210}Pb
33.25	1515	506	11	^{14}C

Table 3.2. Lead-210 and radiocarbon dating of the mainland reference pond sediments. ^{210}Pb dates were estimated using the Constant Rate of Supply (CRS) model. The ^{14}C date was calibrated using the IntCal20 calibration curve (Reimer et al., 2020).

Midpoint (cm)	Year (CE)	Age (before 2021 CE)	Error	Dating Method
0	2021.49	0	0	^{210}Pb
0.25	2020.85	0.64	0.11	^{210}Pb
2.25	2010.65	10.84	1.7	^{210}Pb
4.25	1993.43	28.06	4.03	^{210}Pb
6.25	1965.33	56.16	9.26	^{210}Pb
8.25	1909.64	111.85	26.64	^{210}Pb
13.25	93	1928	21	^{14}C


a) Little Fogo (linear)

b) Reference (linear)

c) Reference (smooth spline)

Figure 3.1 Classical age-depth modeling with *Clam* (Blaauw, 2010), incorporating ^{210}Pb and ^{14}C dating for the puffin impact core (a) and the reference core showing both a linear fit (b) and a smooth spline fit (c).

3.2 Puffin guano

Puffin guano had δ^{13}C values ranging from -23.62‰ to -19.94‰ and δ^{15}N values ranging from 11.80‰ to 13.58‰. Percent C values ranged from 14.33% to 16.14% and %N from 29.87% to 34.39% (Table 3.3).

Table 3.3. $\delta^{13}C$ and $\delta^{15}N$ values, % C and % N of Atlantic puffin guano from fledglings stranded at Witless Bay, NL in the summer of 2021. Samples from several puffins were pooled to provide enough guano for analysis (# of puffins) and 3 replicates of each of these pooled samples were analyzed (n). All 3 replicates for % C and % N analysis had the exact same values, resulting in no standard deviation.

sample	# of puffins	n	mean $\delta^{13}C$ (‰)	SD $\delta^{13}C$	mean $\delta^{15}N$ (‰)	SD $\delta^{15}N$	mean % C	SD % C	mean % N	SD % N
1	2	3	-20.59	0.05	11.80	0.17	14.33	0	30.49	0
2	1	3	-19.94	0.07	11.83	0.20	15.46	0	29.78	0
3	8	3	-23.62	0.03	13.58	0.12	16.14	0	34.39	0

3.3 Water chemistry

The Fogo Island reference pond had a phosphorus concentration less than the detection limit of 0.2 mg/L, whereas the impact puffin pond had a phosphorus concentration of 3.6 mg/L. The reference pond had a Total Kjeldahl Nitrogen (TKN) concentration of 1.05 mg/L, while the impact pond had a concentration of 4.12 mg/L. The impact pond water was also elevated relative to the reference pond in elements including aluminum (68.1 µg/L vs <30 µg/L), arsenic (8.1 µg/L vs. <5 µg/L), potassium (116 mg/L vs. <0.8 mg/L), and magnesium (326 mg/L vs. 1.5 mg/L). However, the water of both ponds had zinc concentrations below the reporting detection limit (100 µg/L). Complete water chemistry results are presented in Appendix 2.

3.4 Seabird sediment proxies

3.4.1 Metal(loid)s & biogenic enrichment factors

Ten metal(loid)s were enriched in guano relative to the reference core (Table 3.4). P, As, Cd, Se, K, Mg, and Zn all increased over the 20th century, with rapid increases from the early

1990s onwards until the surface of the core, ~2021. Sediments in the mainland reference pond; however, maintained low concentrations of these metal(loid)s throughout the record (Fig 3.2). Constrained hierarchical cluster analysis (CONISS) and broken stick analysis of all metal(loid)s in the puffin impact core indicated a significant change in metals between 1985 and 1996 (11.25 cm and 9.25 cm depth) and between 1612 and 1666 (25.25 cm and 27.25 cm depth) (Figure 3.3). A GAM of Cd and Zn show a significant increase from 1816-2021 CE (k-index=0.33; $p<2e-16$) and 1854-2021 CE (k-index=0.53; $p=0.01$), respectively (Fig 3.4).

Table 3.4. Metal(loid) concentrations in puffin guano and in surface sediments from the mainland reference pond (MHRef). Elements with a biogenic enrichment (BE) factor greater than one are elevated in puffin guano relative to reference pond sediment.

Metal(loid)	**Mean guano** (*n*=3) (µg/g)	**MHRef** (µg/g)	**BE factor**
Na	9333.33	72.00	129.63
P	33333.33	580.00	57.47
Ca	37433.33	720.00	51.99
K	19666.67	400.00	49.17
Sr	166.33	5.20	31.99
Zn	246.67	41.00	6.02
Se	2.60	0.49	5.25
Cd	0.52	0.23	2.28
Mg	6100.00	2900.00	2.10
As	5.80	3.50	1.66
Ag	0.71	0.71	1.00
Sb	4.24	4.24	1.00
Cu	5.40	5.70	0.95
Sn	0.42	0.90	0.47
Mo	0.23	0.80	0.29
Tl	0.01	0.05	0.28

Cr	4.33	25.00	0.17
Ba	2.43	17.00	0.14
Bi	0.06	0.52	0.12
Li	1.41	13.00	0.11
Ni	2.21	22.00	0.10
Fe	1106.67	14000.00	0.08
V	0.90	16.00	0.06
Mn	20.67	440.00	0.05
Ti	9.77	290.00	0.03
Co	0.19	6.60	0.03
Be	0.01	0.57	0.02
Y	0.10	4.30	0.02
Al	148.33	7700.00	0.02
U	0.10	7.00	0.01
Pb	NA	13.00	
Hg	NA	0.98	

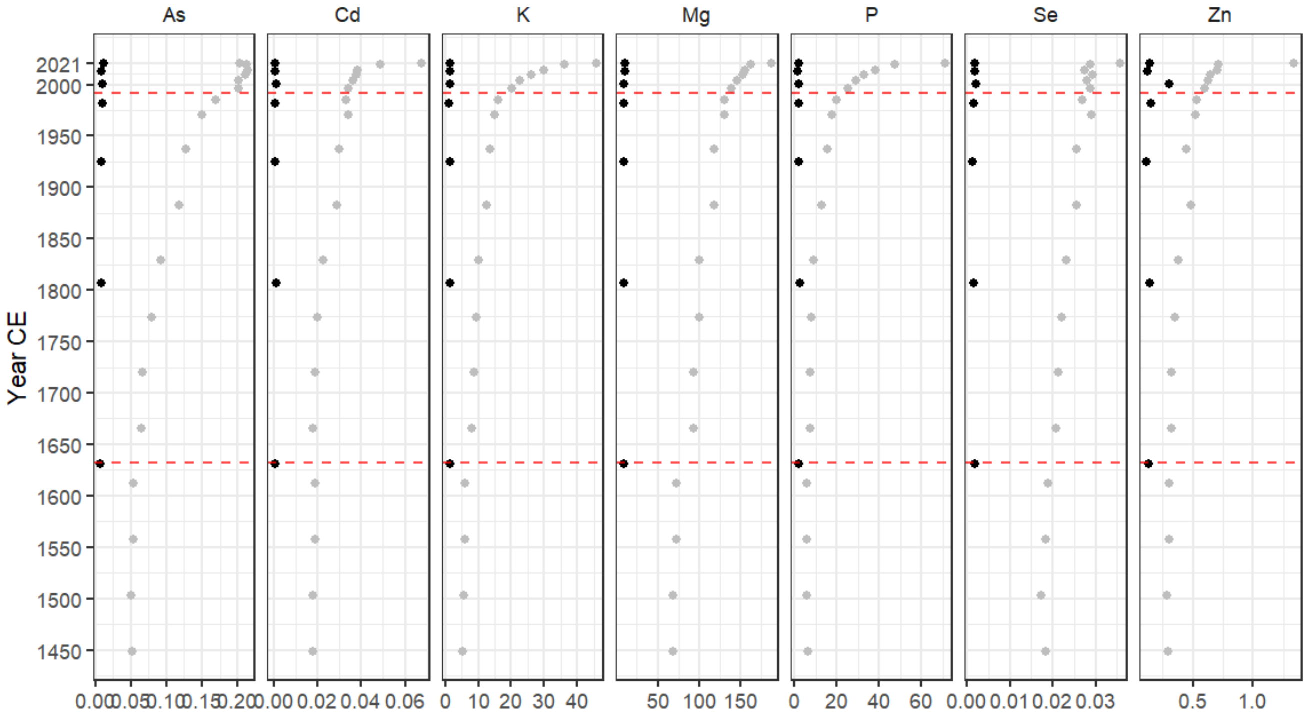


Figure 3.2 Seabird-associated metals and metalloids, divided by the concentration of titanium, through time for the puffin impact core (grey) and the mainland reference core (black). Red lines indicate significant breakpoints of change for the puffin impact core, determined by CONISS and broken stick analysis of all metal(loid)s in the core (Fig 3.3).

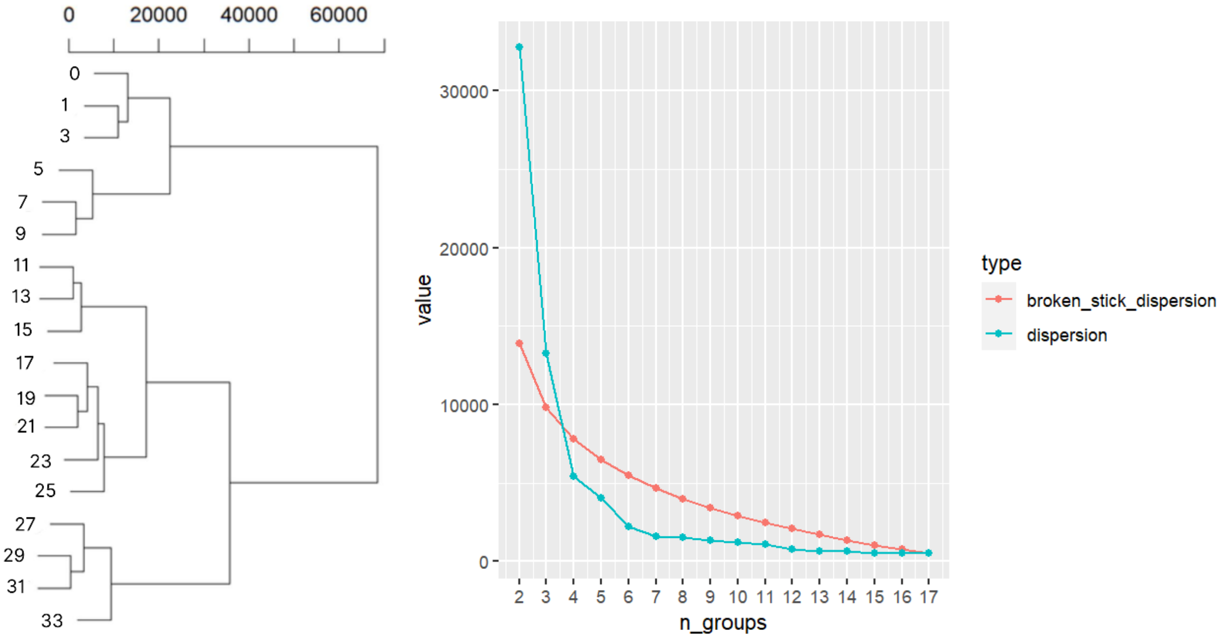


Figure 3.3 Constrained hierarchical cluster analysis (CONISS) of all metal(loid)s in the puffin impact core (left) and broken stick analysis of metal(loid)s (right). On the left, numbers refer to core depths.

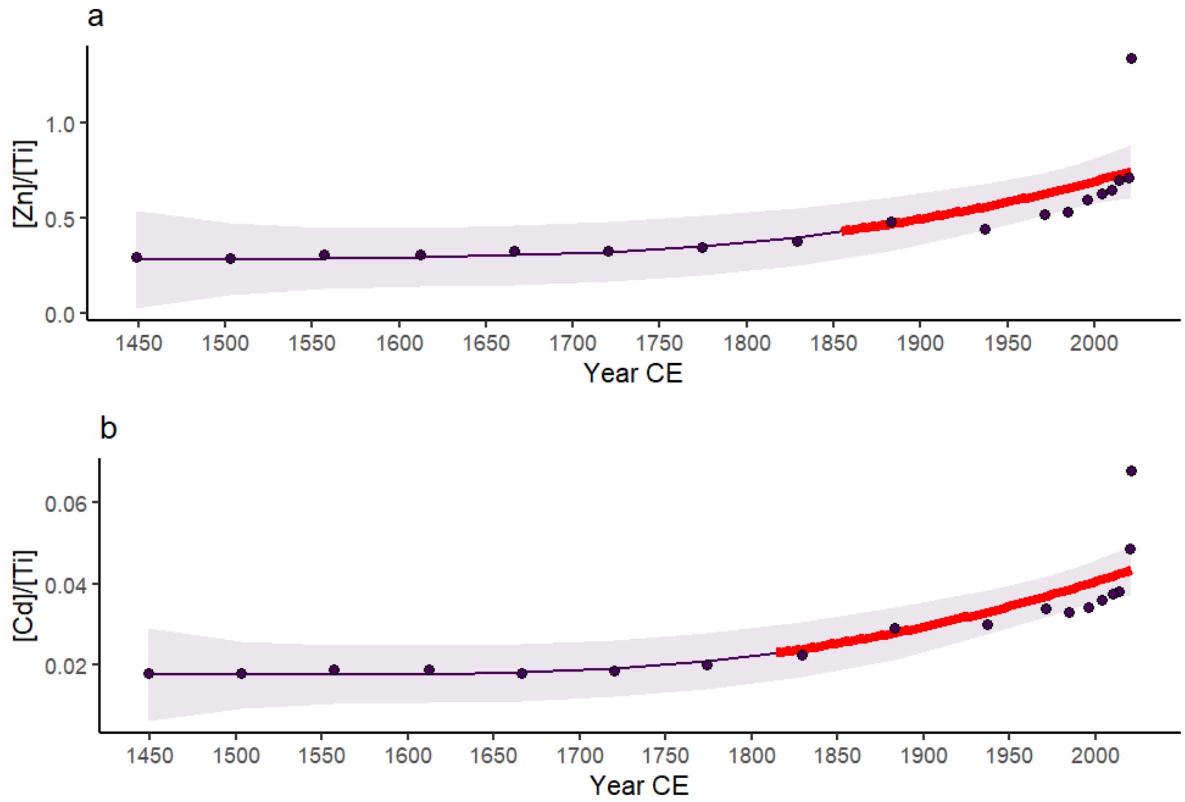


Figure 3.4. a) Zinc and b) Cadmium concentrations relative to titanium for the puffin impact core. A generalized additive model is fitted to the points (smoothing selection method=GCV). Shaded area shows 97.5 % confidence interval, red is an area of significant increase.

3.4.2 % Carbon and % Nitrogen

The mean %N in the reference core was 0.52 % (*n*=10). The mean % N in the impact core was 1.7 % (*n*=17). Neither showed an obvious change through time (Fig. 3.5). The mean % C in the reference core was 6.6 % (*n*=10) and 29.4 % (*n*=17) in the impact core. Neither core showed an obvious change through time (Fig. 3.6).

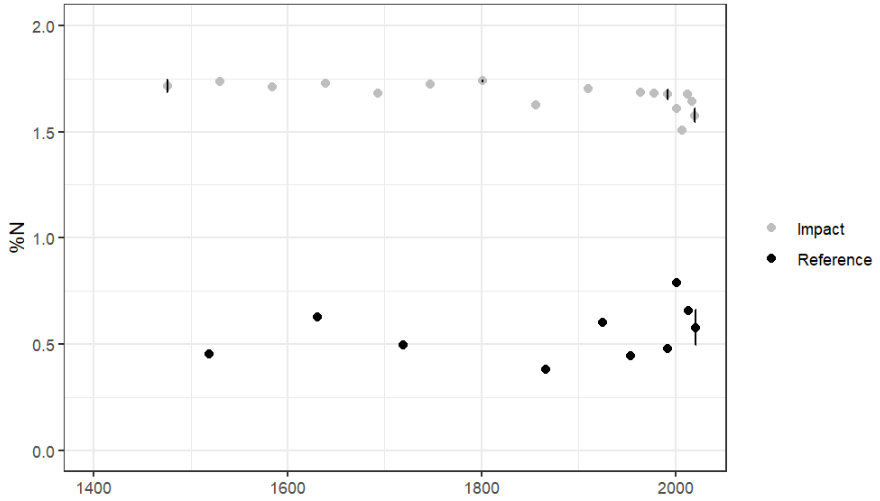


Figure 3.5. Percent nitrogen for the puffin impact core and the reference core. Error bars represent standard deviation of replicated samples (*n*=3).

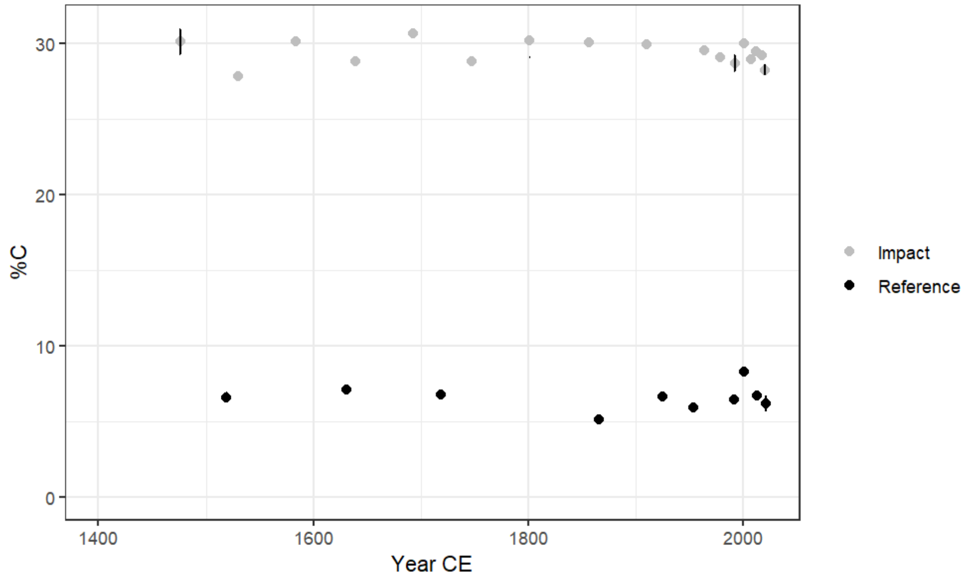


Figure 3.6. Percent carbon (total) for the puffin impact core and the reference core. Error bars represent standard deviation of replicated samples (*n*=3).

3.4.3 Chlorophyll *a*

Concentrations of chlorophyll *a* increased in the puffin impact pond throughout the 20th century, with a rapid increase beginning in the 1960s and continuing to the surface of the core, ~2021 (Fig. 3.7). Chlorophyll *a* in the mainland reference core remained at low concentrations throughout the sediment record (Fig 3.7).

3.4.4 Stable nitrogen and carbon isotopes

δ^{15}N values increased in the puffin impact pond throughout the 20th century, with a rapid increase in the 1990s (max = 13.8‰, min = 10.1‰, mean = 11.4‰, *n*=17) (Fig. 3.7). δ^{15}N values in the mainland reference core remained at low concentrations throughout the sediment record (max = 3.8‰, min = 0.34‰, mean = 1.6‰, *n*=10).

δ^{13}C values were lower in the impact core (max = -29.4‰, min = -31.1‰, mean = -30.5, *n*=17) than the mainland reference core (max = -27.4‰, min = -28.3‰, mean = -27.9‰, *n*=10) (Fig. 3.7).

A generalized additive model fitted to the δ^{15}N values and chl *a* (Fig 3.8) shows concentrations increased in the puffin impact pond beginning in the mid 20th century, with a period of slight decrease in δ^{15}N values from approximately 1864-1929 (Table 3.5).

Table 3.5 Generalized additive model results for each proxy, including k-indices, p-values, and range of years where a significant non-zero derivative indicating an increase/decrease was found for chlorophyll *a* (mg/g dry wt.), $\delta^{15}N$ (‰), and the ratio of seabird lipids. The k-index and p-value of each proxy are used to assess the dimensionality of the basis functions used in the GAM. Low p-value (k-index<1) may indicate that k is too low.

Proxy	K index	P value	Years of sig increase	Years of sig decrease
$\delta^{15}N$	1.06	0.55	1951-2020	1864-1929
Chl *a*	1.03	0.54	1960-2021	N/A
Seabird index of sterols & stanols	1.18	0.99	1900 – 2021	1450 to 1525
Cd	0.33	<2e-16	1816-2021	N/A
Zn	0.53	0.01	1854-2021	N/A

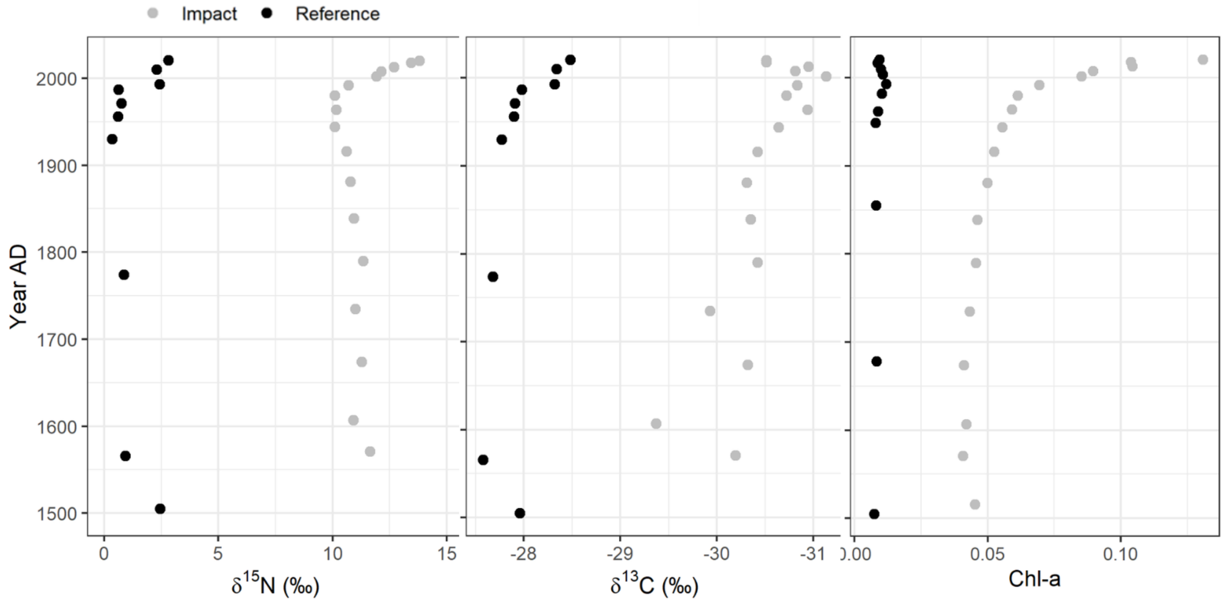


Figure 3.7. $\delta^{15}N$ (‰), $\delta^{13}C$ (‰), and chlorophyll *a* for the puffin impact core (grey circles) and mainland reference core (black circles). $\delta^{13}C$ (‰) values are corrected for the Suess Effect from 1840 to present.

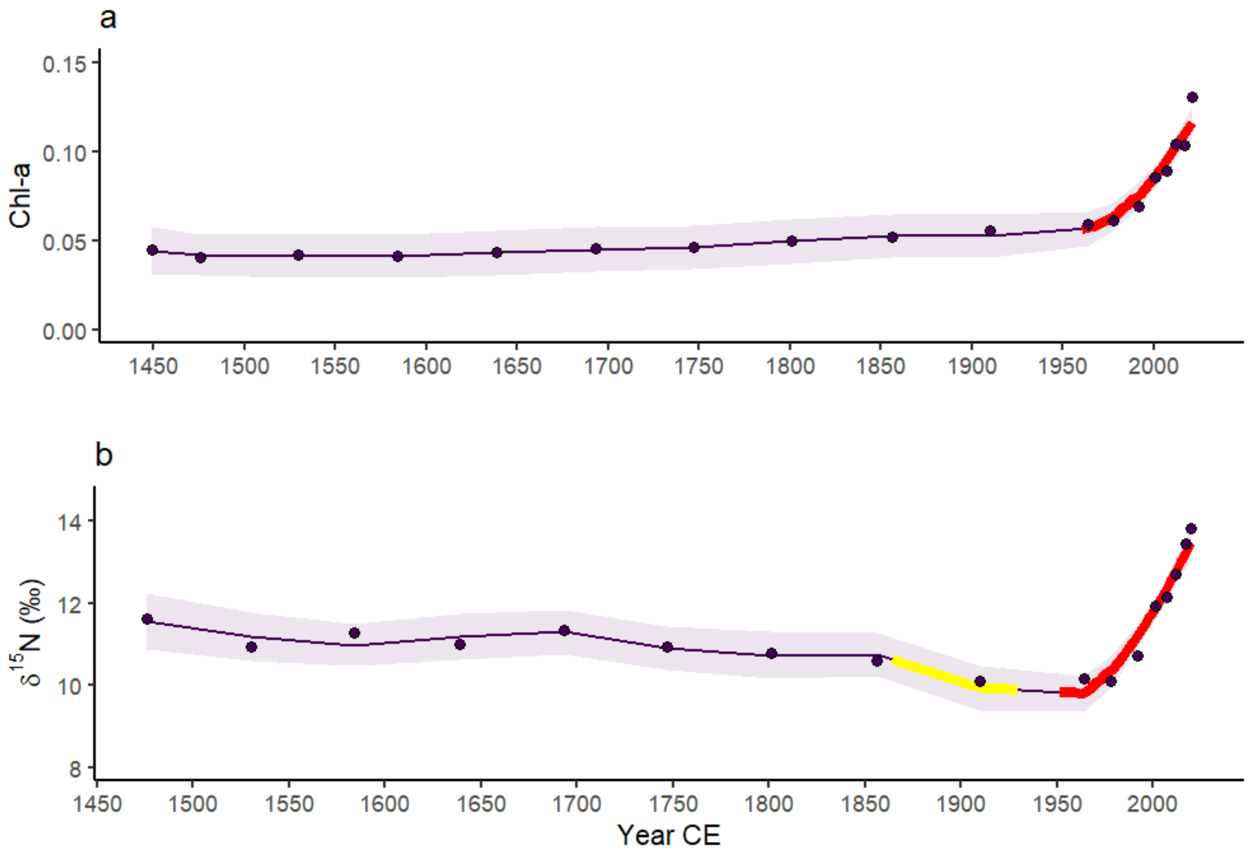


Figure 3.8. a) Chlorophyll *a* and b) δ^{15}N (‰) for the puffin impact core. A generalized additive model is fitted to the points (smoothing selection method=GCV). Shaded area shows 97.5 % confidence interval, yellow is areas of significant decrease, red is an area of significant increase.

3.4.5 Organic δ^{13}C and % C

Organic δ^{13}C was lower in the impact core (max = -28.4‰, min = -29.5‰, mean = -29.0‰, *n*=17) than the mainland reference core (max = -27.7‰, min = -28.2‰, mean = -27.8‰, *n*=10) (Fig. 3.9). The percent organic carbon was lower in the mainland reference core (mean = 6.7‰, *n*=10) than in the puffin impact core (mean = 51.0‰, *n*=10) (Fig 3.10). The difference in δ^{13}C values between the impact and reference core was smaller for organic δ^{13}C values (i.e. acidified) than untreated δ^{13}C values.

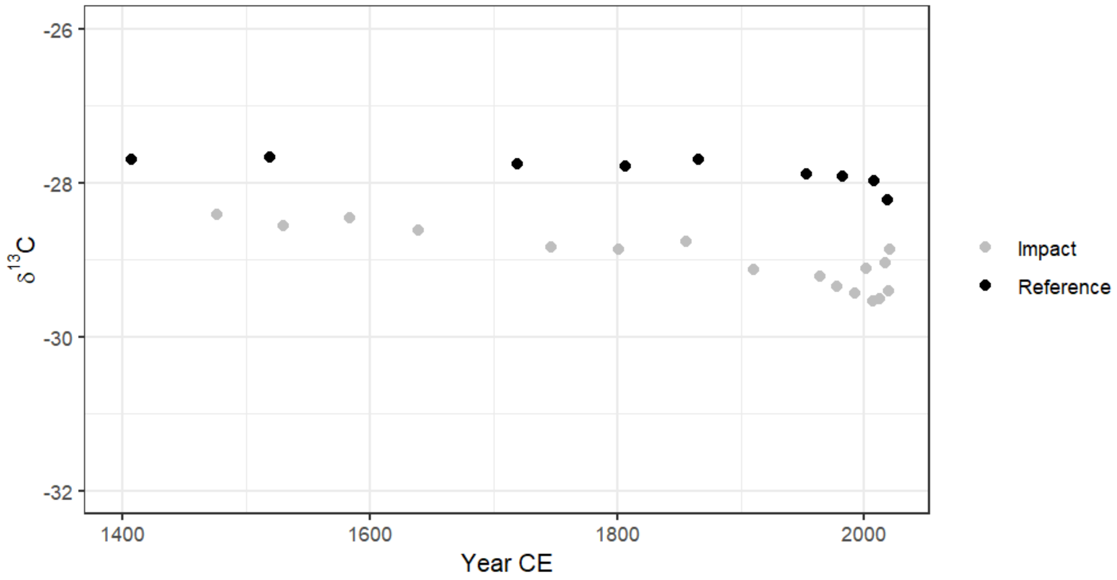


Figure 3.9. Organic (i.e. acidified sediment) $\delta^{13}C$ (‰) values in the puffin impact core (grey circles) and reference core (black circles). $\delta^{13}C$ (‰) values are corrected for the Suess Effect which yields an increasing correction factor from 1840 to present.

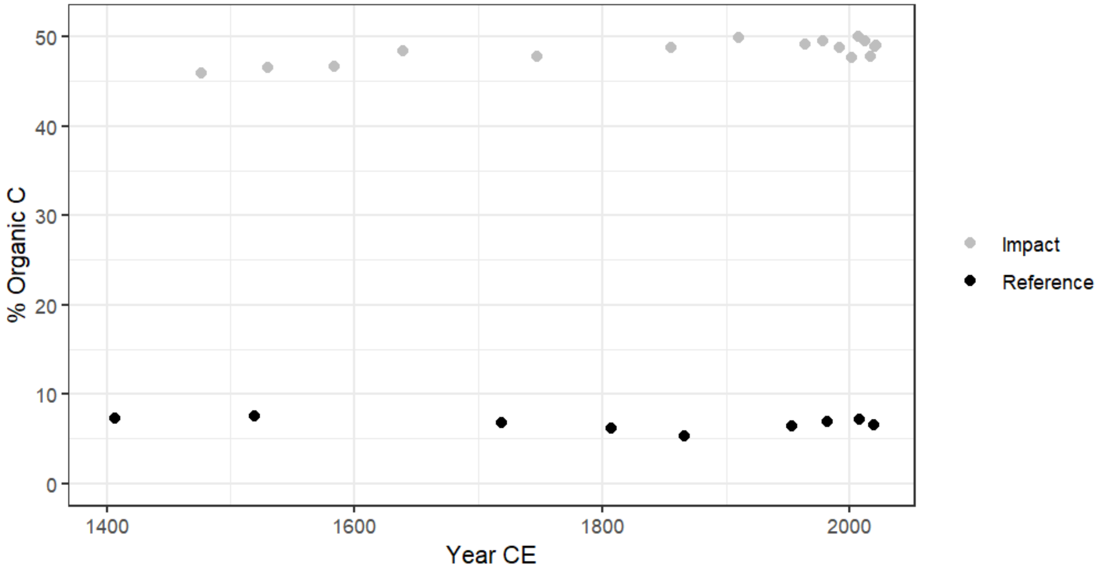


Figure 3.10. Percent organic carbon in the puffin impact core (grey circles) and the reference core (black circles).

3.4.6 Diatom assemblages

Diatom species assemblages in the puffin impact core were dominated by *Navicula cincta* and *Staurosira construens* var. *venter* (Fig. 3.11). A total of 16 species were identified in the core from the impact pond, with only 7 taxa with greater than 5 % relative abundance through the sediment core (Fig. 3.11). *N. cincta* was the most abundant taxon at the bottom of the core, with 45-50 % relative abundance between ~1450 and ~1625 CE. *N. cincta* is a widespread benthic diatom, which tends to live in waters with moderate to high levels of conductivity and elevated concentrations of chloride, sodium, and sulfate (Spaulding et al., 2021). After ~2000 CE, benthic *S. construens* var. *venter* became the dominant taxon with 40-70 % relative abundance. CONISS of all diatoms in the impact core and broken stick analysis identified 4 significant groups occurring between the base of the core and 2021 (Fig. 3.12). A principal component analysis (PCA) of the puffin impact core (Fig 3.13) shows the taxa or assemblages that are characteristic regions of the core or particular depths (e.g., 16.25 cm).

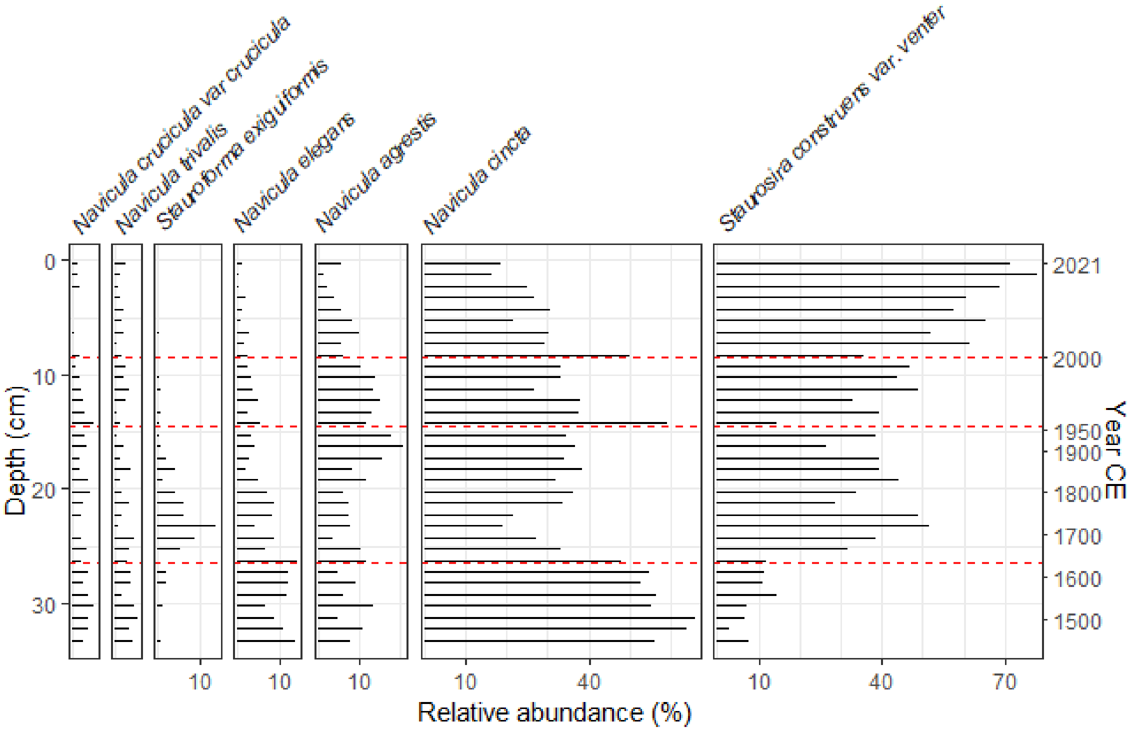


Figure 3.11. Percent relative abundance of diatoms in the puffin impact core. Only taxa with >5 % relative abundance are shown. Red lines indicate breakpoints of change in species assemblage according to nested constrained hierarchical clustering analysis. *Navicula cincta* (second from right) and *Staurosira construens* var. *venter* (far right) were the two most abundant taxa.

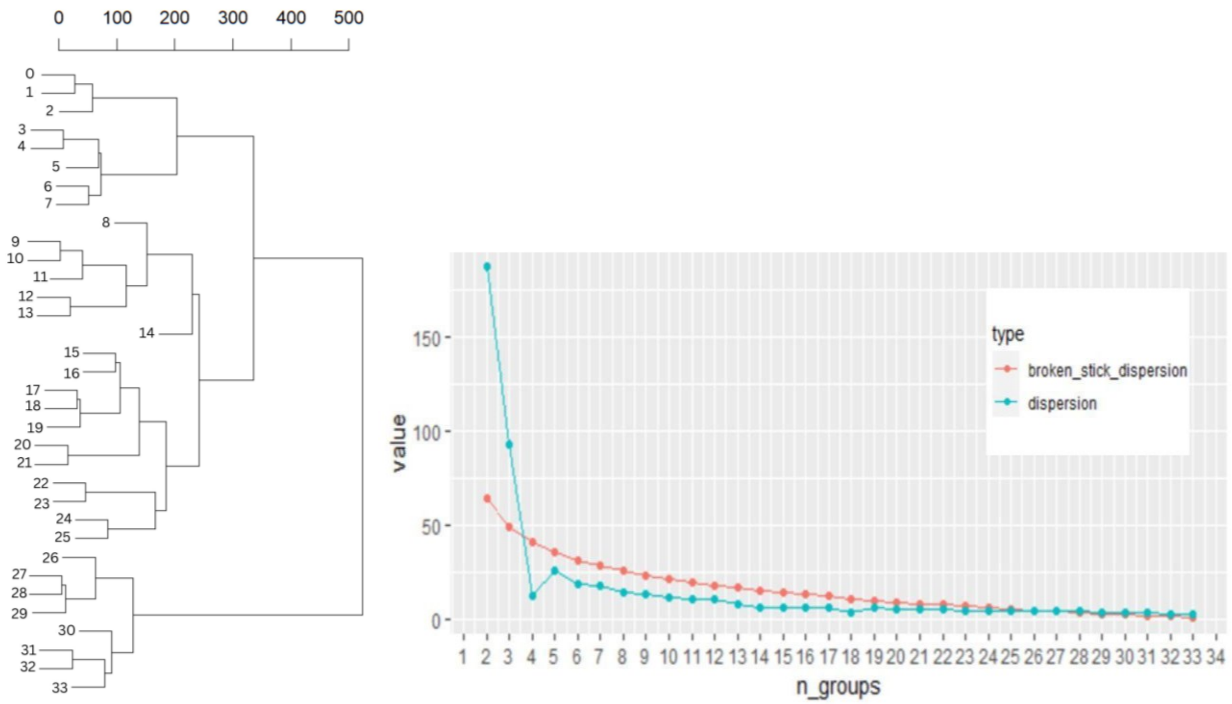


Figure 3.12. Constrained hierarchical cluster analysis (CONISS) of all diatoms in the puffin impact core and broken stick analysis of diatoms.

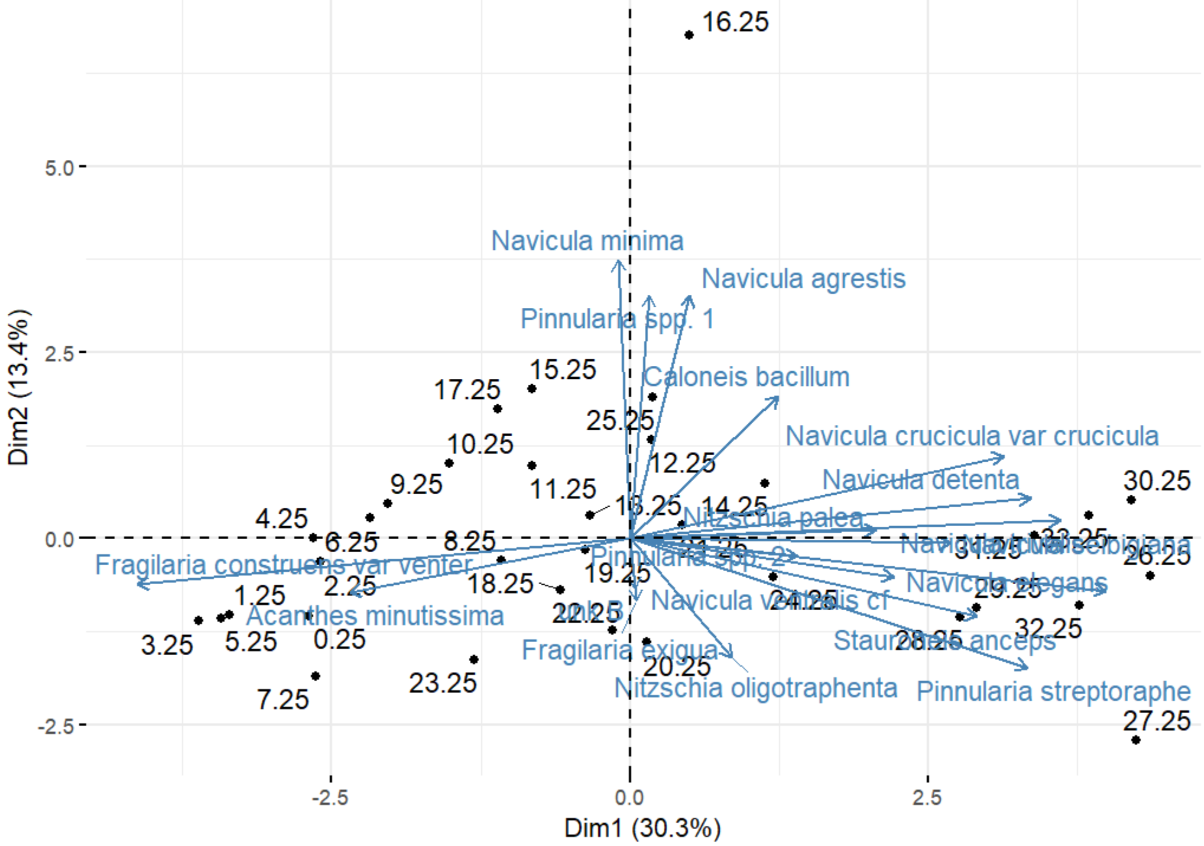


Figure 3.13. Principal component analysis biplot of axis 1 and 2, showing the diatom taxa that are characteristic throughout the puffin core depths (black points).

A total of 46 species were identified throughout the Musgrave Harbour reference core with 12 taxa with greater than 5 % relative abundance over the length of the sediment record (Fig. 3.11). *Aulacoseira perglabra* and *Stauroforma exiguiformis* were the most abundant taxa and their percent relative abundances fluctuated over the core, but in no apparent direction (Fig. 3.11). CONISS of all diatoms in the Musgrave Harbour reference core and broken stick analysis showed no significant shifts (Fig. 3.12). Visually no groupings are evident and ecologically would be challenging to infer.

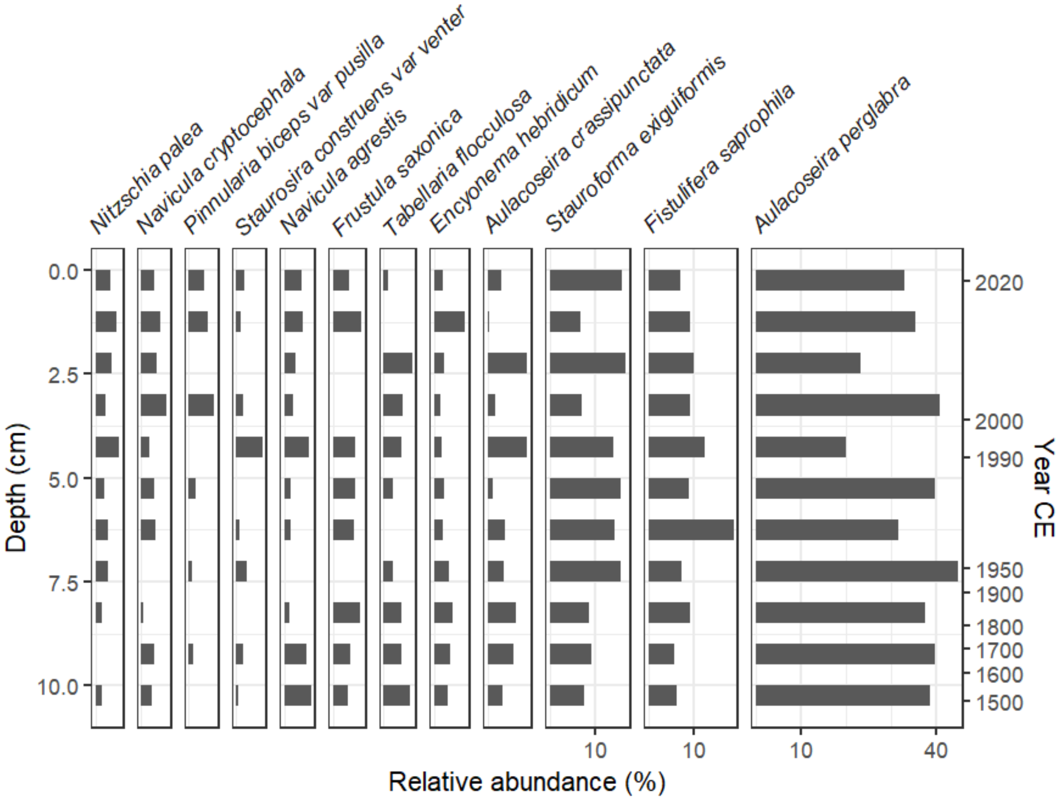


Figure 3.14. Percent relative abundance of diatoms in the Musgrave Harbour reference core. Only taxa with >5 % relative abundance are shown.

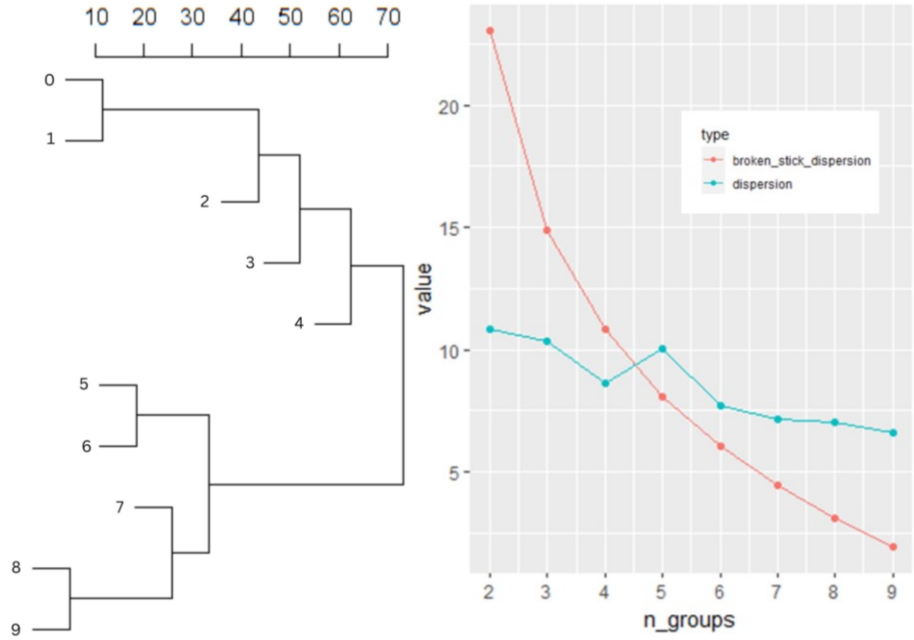


Figure 3.15. Constrained hierarchical cluster analysis (CONISS) of all diatoms in the Musgrave Harbour reference core and broken stick analysis of diatom assemblages.

3.4.7 Lipids

Cholesterol (cholest-5en-3β-ol), which is a principal component of vertebrate cell walls, was detected throughout both the impact and the reference core (Fig 3.16). There was also a high concentration of cholesterol in guano samples taken from puffin fledglings (Fig 3.16). The microbially-reduced product of cholesterol, cholestanol (5α-cholestan-3β-ol), was observed throughout the impact core, but only in two samples in the reference core (approximately dated to 1407 CE and 1631 CE). Both cholesterol and cholestanol increased in the impact core starting in the 1990s. Cholestanol and cholesterol were both 2-5 times more concentrated in the samples after 1992 than prior. The mean cholesterol from 1449 to 1992 CE was 8.25 µg/g dry wt. (*n* = 8), the mean including 1992 to 2021 CE was 100.48 µg/g dry wt. (*n* = 5).

Plants were tracked with sitosterol (β-sitosterol) and its microbially reduced forms stigmastanol (5α-stigmastan-3β-ol) and campesterol (24-methylcholesta-5-en-3β-ol). Sitosterol was observed throughout both the impact and the reference core. Stigmastanol was observed throughout the impact core, but only in one sample in the reference core (approximately dated to 2008 CE). Campesterol was detected throughout the impact core, but only in a few sections of the reference core (dated to 1807, 1925, 2001, 2008, 2013, 2021 CE).

Coprostanol (5β-cholestan-3β-ol) and epicoprostanol (5β-Cholestan-3α-ol) were only detected in the impact core, not the reference core, and only in samples from 1964, 1992, 2017, 2020, and 2021 CE. Coprostanol and epicoprostanol are associated with human fecal inputs, but coprostanol is also present in phytoplankton in low concentrations (Cheng et al., 2016). One of the guano samples from puffin fledglings in Witless Bay also contained a small amount of coprostanol (Fig 3.16). The ratio of coprostanol/cholesterol can be used to indicate human fecal contamination, and a human index value >0.2 indicates the presence of humans. There are two years in the puffin impact core which have a human index >0.2, 1992 CE (depth 10.25 cm) and 1964 CE (depth 14.25 cm).

Desmosterol (cholesta-5,24-dien-3β-ol) is present in phytoplankton and was detected in the impact core only in 1747, 1964, 1992, 2007, 2017, 2020, and 2021 CE, and continuously in all samples measured post ~1992 CE. Desmosterol was not detected in the reference core.

The percent organic carbon was also measured, as this can influence the attenuation of lipids in sediments. Both cores showed minimal changes in percent organic carbon through time (Fig. 3.16).

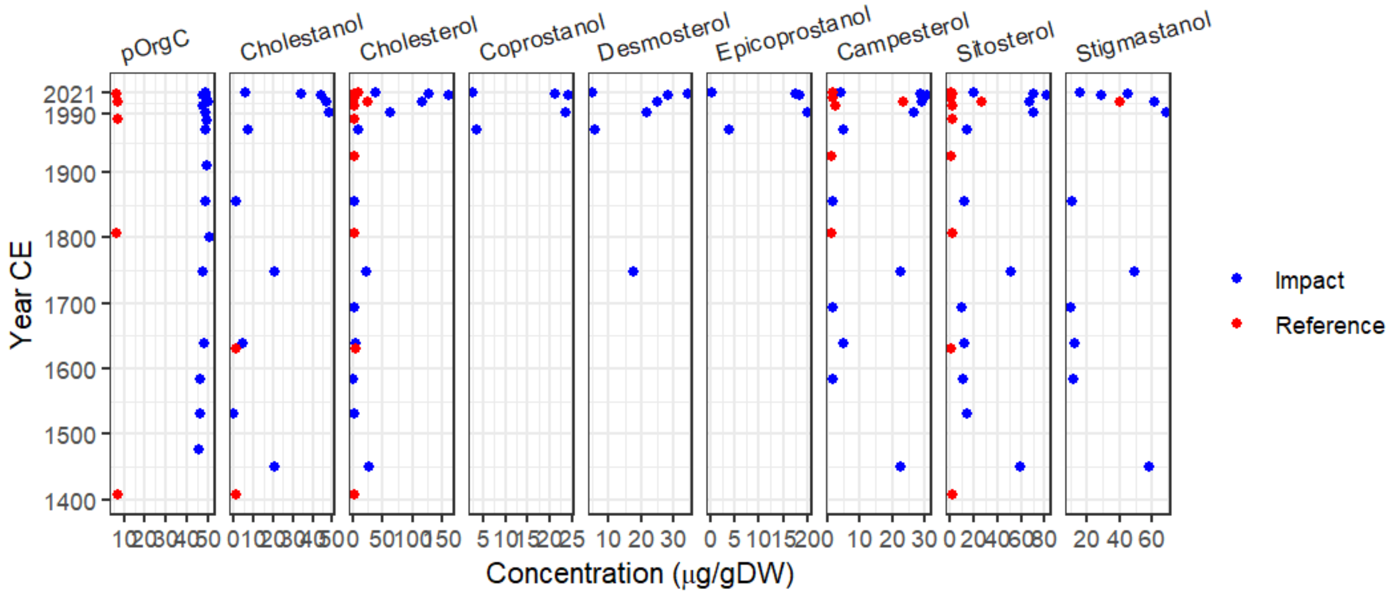


Figure 3.16. Measured sterols and stanols (µg/g d.w.) for the puffin impact and reference cores plotted with percent organic carbon on the left.

The seabird ratio of cholesterol/(cholesterol + sitosterol) has been used to track fulmars in the Arctic (Cheng et al., 2016) and seaducks in the sub-Arctic (Hargan et al., 2019). Ratios correct for differences in detection and preservation throughout the core. Because sitosterol and cholesterol are present in both the impact and reference core, and because cholesterol is the dominant lipid present in the puffin guano sampled, the seabird ratio was used as a proxy for seabird inputs. A GAM of the seabird index shows a period of significant decrease from approximately 1450 to 1525 CE, and a period of significant increase from approximately 1900 to 2021 CE (Fig 3.17).

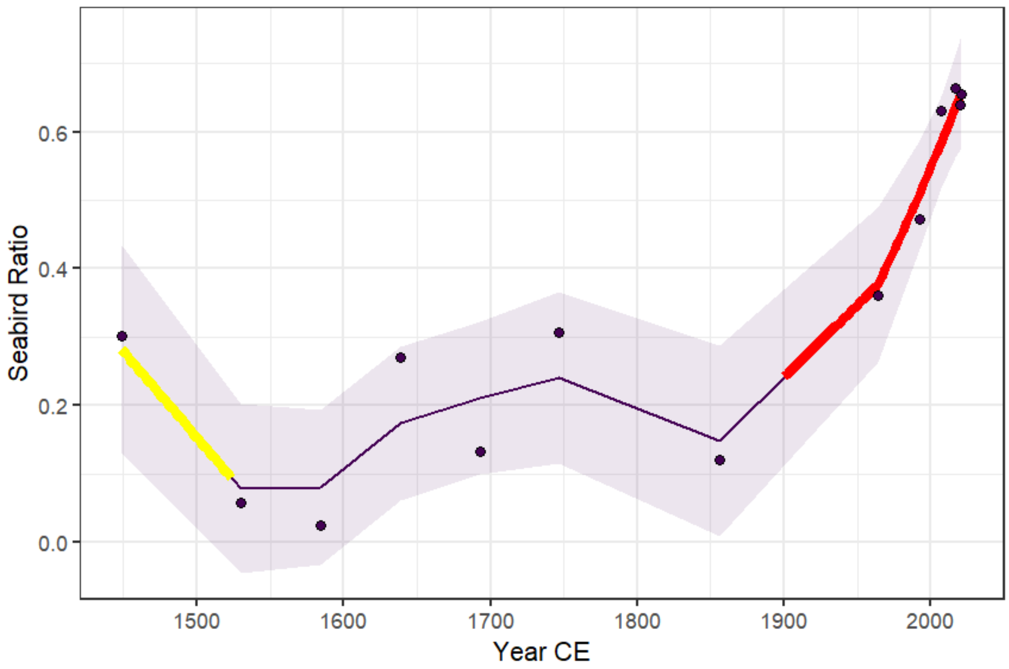


Figure 3.17. The seabird ratio ([cholesterol]/[cholesterol] + [sitosterol]; *n* = 13) for the puffin impact core fitted with a generalized additive model showing a period of significant decrease (yellow) and increase (red).

The predominant lipid in the guano collected from Witless Bay puffin fledglings was cholesterol with a mean amount of 833.5 µg/g DW (SD = 138.6 µg/g DW, *n* = 3) (Fig. 3.18). Cholestanol (13.9 µg/g DW, SD = 0.46, *n* = 1), coprostanol (3.4 µg/g DW, SD = 3.06, *n* = 1) and desmosterol (5.04 µg/g DW, SD = 1.0, *n* = 1) were only found in one of the guano samples analyzed, and relative to cholesterol concentrations are low (Fig. 3.18). Guano was aggregated from 12 different birds, as shown in Table 3.3 to obtain enough material for three analyses.

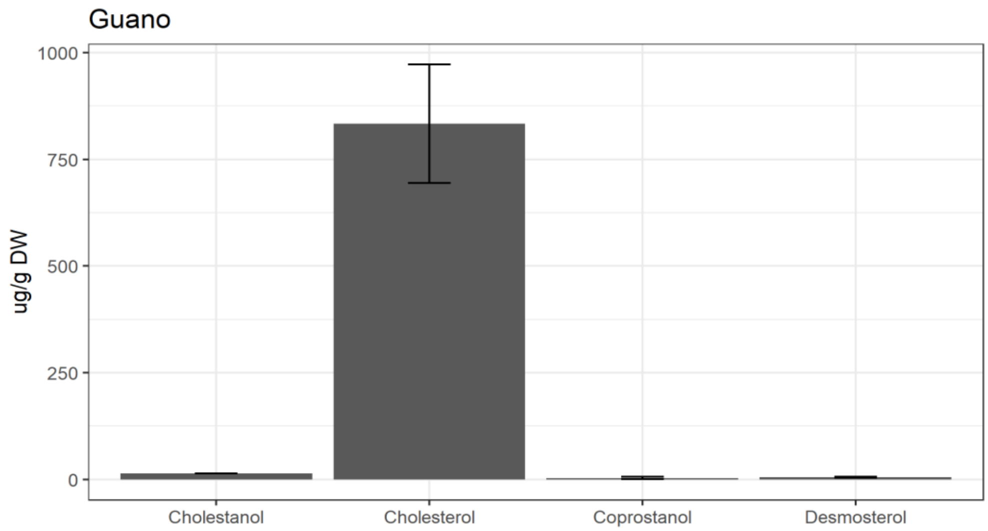


Figure 3.18. Mean sterol and stanol concentrations in puffin guano collected from fledglings in Witless Bay, NL (*n* = 3 for cholesterol, *n* = 1 for the other lipids, from 12 different birds, see Table 3.3). Error bar shows standard deviation.

Chapter 4: Discussion

4.1 Data summary and multi-proxy population reconstruction

Seabird-associated metals, Cd and Zn, increased throughout the puffin impact core, with a rapid increase in the 20th century (Figure 3.19). GAMs of these two elements shows a period of significant increase from 1816-2021 CE for Cd, and 1854-2021 CE for Zn. Metal(loid)s were corrected to titanium to account for different rates of weathering between the reference and impact core and over time. However, the concentration of titanium in the most recent sample from 2021 was very low compared with the concentration in previous sections of the core. This created a relatively high corrected concentration of the seabird associated metal(loid). This is likely because sampling was conducted in July, and the top section of the core represented less than one year of weathering, whereas sections further down are compacted and so represent more than one year. However, the puffins had already contributed almost a season's worth of Cd and Zn to the pond. These outlier values may have contributed to the low K-values of the GAMs for these metals (Table 3.5; Fig 3.8) and to the high Z-scores of Cd and Zn in the 2021 sample (Fig 3.19).

$\delta^{15}N$ in the impact core decreased from 1864-1929 CE, before rising from 1951-2020 CE, according to a GAM. Concentrations of chlorophyll *a* increased in the puffin impact pond throughout the 20th century, with a rapid increase beginning in the 1960s and continuing to the surface of the core, ~2021 (Fig. 3.7). A GAM was not performed on the reference core because the $\delta^{15}N$ remained below ~5 ‰ through the entire core and did not show an indication of seabird or marine-derived inputs.

$\delta^{13}C$ (‰) was not included in the Z-score because it does not track seabirds as reliably as the other proxies. There was a slight trend of increasing $\delta^{13}C$ values post-1900 in both the reference and impact core. However, there was no increase in organic $\delta^{13}C$ values in either core. Organisms such as puffins, that feed within the marine food web, have more positive $\delta^{13}C$ values, whereas aquatic primary producers have more negative values (Lamb et al., 2006). Since the chlorophyll *a* concentration increased throughout the impact pond sediment core, primary production by algae was likely increasing through time in tandem with increased inputs by puffins. These contradictory signals might obscure any trend in $\delta^{13}C$ values due to puffin influence (Bosch et al., 2024).

A GAM of the seabird index of lipids shows a period of significant decrease from approximately 1450 to 1525 CE, and a period of significant increase from approximately 1900 to 2021 CE (Fig 3.19). However, only 13 samples were measured for sterols and stanols for the puffin impact core, and 4 of these were clustered near the top of the core. Therefore, pin-pointing exact dates of increase and decrease for seabird-associated lipids is difficult.

The dominant diatom in the puffin impact core, *S. construens* var. *venter*, was also included in the mean Z-score. Its abundance peaked in the 1700s, before decreasing and then increasing again in the late 20th century. After ~2000 CE, *S. construens* var. *venter* became the dominant taxon with 40-70 % relative abundance.

To summarize all the seabird-associated proxies in the puffin impact core, a GAM was fitted to the mean Z-score (Fig 3.20). This shows a period of significant increase beginning in ~1966 and continuing to the surface of the core in 2021 (k-index = 0.65; p-value = 0.045) (Fig 3.20).

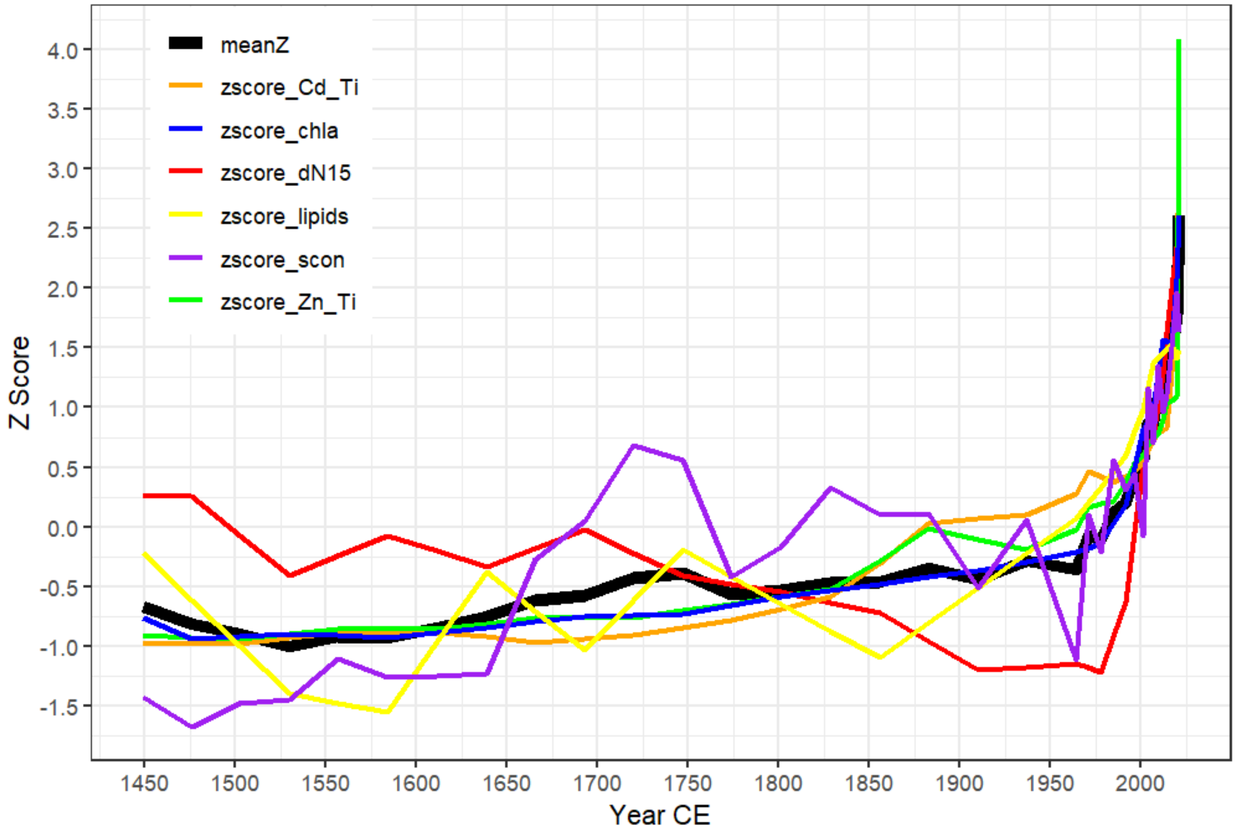


Figure 3.19 Summary of chlorophyll *a*, δ^{15}N (‰), seabird ratio (cholesterol/cholesterol + sitosterol), and seabird-associated metal(loid)s (Cd and Zn). Metal(loid)s are corrected to titanium. Mean Z-score shows the average of δ^{15}N (‰), seabird metal(loid)s (Cd, and Zn), the seabird ratio of lipids, *S. construens*, and chl *a*.

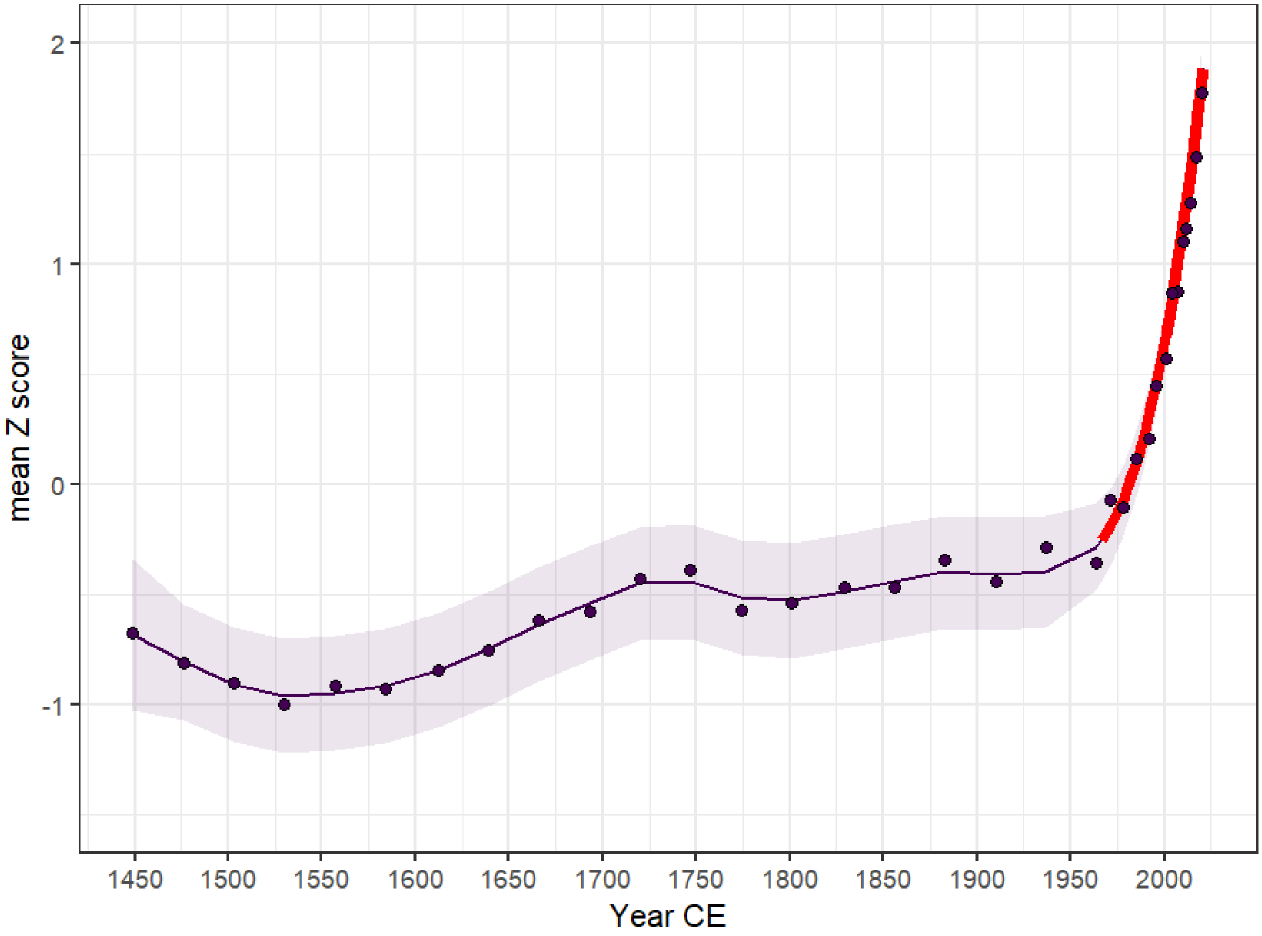


Figure 3.20 Generalized additive model of the mean Z score (k-index = 0.65; p-value = 0.045). Red line shows a period of significant increase.

4.2 Summary of the proxy changes through the cores

All proxies point to puffins nesting and breeding on Puffin Island for the length of the sediment core, from ~1450 to 2021 CE. Chlorophyll *a*, δ^{15}N values, and seabird-associated sterols and stanols, and metal(loid) were all elevated in the impact pond sediments, compared with the reference pond sediments, throughout the history of the core. The reference pond sediments showed little change in these proxies throughout the core, whereas the impact pond sediments showed increased concentrations of these proxies throughout the 20th century. There were no apparent trends in δ^{13}C in either the reference or impact core, though any trend in the impact core may have been obscured by the contradictory signals from marine derived nutrients deposited by seabirds and freshwater algae growth fueled by seabird presence (Bosch et al., 2024). Furthermore, differences in water quality between ponds was a strong indicator of heavy modern nutrient inputs from puffins on Puffin Island.

$\delta^{15}N$ values are a widely used and well-established proxy for tracking seabirds (Duda et al., 2021). A higher $\delta^{15}N$ value in sediments typically relates to greater bird numbers, up until the value equals that of the guano (Duda et al., 2020). For our puffin impact core, the GAM model showed that $\delta^{15}N$ values in the impact core decreased from ~1864-1929 CE, before rising from ~1951-2020 CE. However, it is notable that the three years with the lowest $\delta^{15}N$ values in the core all occur concurrently, in approximately 1910, 1964, and 1978 CE. Also of interest is the magnitude and speed of increase between 1992 and 2020 CE, where $\delta^{15}N$ values peaked to the highest values over the ~500-year core history. The timing of these changes roughly tracks the advent of gillnet fishing in this area, and the subsequent removal of gillnets from inshore waters in 1992 following the cod moratorium (Regular et al., 2013). It also roughly corresponds to the overfishing of capelin in the mid-20th century, followed by the collapse of the stock in the early 1990s (Rose, 2003).

Sterols and stanols have also been demonstrated to be a reliable direct proxy for seabird abundance at nesting colonies (e.g., Hargan et al., 2019; Cheng at al., 2016). Seabird guano commonly has a high concentration of cholesterol, and sterols and stanols are well-preserved in sediments (Duda et al., 2021). In the puffin impact core, a GAM of the seabird ratio of [cholesterol]/([cholesterol]+[sitosterol]) shows a period of significant decrease from approximately 1450 to 1525 CE, and a period of significant increase from approximately 1900 to 2021 CE. There is a clear increase in the seabird ratio between samples from ~1962 and 1992

CE, and the three samples taken after ~1992 (in ~2007, 2017, 2020) all show the highest concentrations of cholesterol measured in this core. This generally tracks with the trend seen for $\delta^{15}N$ values, although the gap in sampling sterols and stanols between ~1856 and ~1964 CE means I cannot pinpoint when cholesterol began to increase in the sediments in the 20th century.

Seabird-associated metal(loid)s increased throughout the puffin impact core, with a rapid increase from the mid- 20th century to present. Metal(loid)s have been used extensively to track seabird populations in sediment cores; however, some elements are subject to post-depositional effects and might become mobile under certain conditions (Duda et al., 2021). For example, although P is highly concentrated in seabird guano, in anoxic conditions P can become released from iron and aluminum rich sediments (Koski-Vähälä et al., 2001). This can give an inaccurate estimate of the amount of P deposited by seabirds (Duda et al., 2021). As and Zn may also become mobile in sediments due to changes in pH, salinity, temperature, organic matter, or redox conditions (Couture et al., 2010; Kouassi et al., 2019; Wang et al., 2015). Despite potential differences in post-depositional processes, the elements in the puffin impact core which had a bioenrichment factor greater than 1 (P, As, Cd, Se, K, Mg, and Zn) all roughly tracked an increase over the 20th century, with rapid increases from the early 1990s onwards. CONISS and broken stick analysis of all metal(loid)s in the puffin impact core indicated a significant change in metals between ~1985 and 1996 and between ~1612 and 1666 CE. A GAM of Cd and Zn show a significant increase from 1816-2021 CE and 1854-2021 CE, respectively. The correction to titanium may have resulted in low K-index values for the GAMs for these metals, due to the high Z-scores of Cd and Zn in the 2021 sample, which may have skewed these models. However, all seabird-associated metals show a steady increase in concentration over the 20th century, and the significant change in the composition of metal(loid)s between ~1985 and 1996 CE accords with the other proxies.

Chlorophyll *a*, an indirect proxy for seabirds, is indicative of primary production in the pond. Concentrations of chlorophyll *a* were relatively steady throughout the core, with a significant increase beginning in ~1964 CE, and accelerating rapidly post ~1992 CE. Chl *a* does not show a decrease anywhere in the core unlike δ^{15}N values. The timing of this increase in the mid-to late 20th century corresponds to the increase seen in the other proxies around this time period.

Diatom species assemblages in the puffin impact core were dominated by *Navicula cincta* and *Staurosira construens* var. *venter*. *N. cincta* was the most abundant taxon at the bottom of the core, with 45-50 % relative abundance between ~1450 and ~1625 CE. *N. cincta* is a widespread benthic diatom, which tends to live in waters with moderate to high levels of conductivity and elevated concentrations of chloride, sodium, and sulfate, preferring brackish and nutrient-rich inland waters (Spaulding et al., 2021; Bahls, 2012). The CONISS of the diatom assemblage revealed a shift at ~ 1625 CE, possibly driven by a decrease in *N. cincta* and increase in *S. exiguiformis* and *S. construens* var *venter*. *S. exiguiformis* is a benthic taxon that is commonly associated with lower pH. By ~1950, *S. exiguiformis* had decreased and by ~2000 CE *S. construens* var. *venter* became the dominant taxon with 40-70% relative abundance. *S. construens* v. *venter* is often, but not exclusively, found in higher pH lakes. Bosch et al. (2024) indicated that *S. construens* var. *venter* became the dominant diatom taxon in a core collected from a pond at Cape St. Mary's, NL. Here, *S. construens* var. *venter* increases and *S. exiguiformis* decreases closely tracked aquatic changes from the establishment and rapid growth of a Northern Gannet (*Morus bassanus*) colony. *S. construens* var. *venter* may favour mesoeutrophic conditions, whereas *S. exiguiformis* is oligo-mesotrophic (van Dam et al., 1994). The impact pond is small and shallow and like the modern chemistry shows, may have been high in nutrients and brackish throughout the core record. Based on the other proxies, including $\delta^{15}N$ values, seabirds have always been present at this location, and increased rapidly in the mid- to late-20th century. This could have potentially driven a shift in diatom assemblage to one dominated by *S. construens* var. *venter*, which may be more suited to high pH, eutrophic conditions.

The reference pond had a notably different assemblage of diatoms than the impact pond. *Aulacoseira perglabra* was the most abundant taxa in the Musgrave Harbour Reference core. Its percent relative abundance fluctuated over the core, but following no discernible trend. *Aulacoseira perglabra* is typically considered a tychoplanktonic taxon, occurring in deeper ponds and preferring wind mixing (Black et al., 2012). CONISS of all diatoms in the Musgrave Harbour reference core and broken stick analysis identified a shift at ~1990. This appears to be potentially driven by a small increase in *Nitzschia palea* and *Tabellaria flocculosa*, and a temporary decrease in the abundance of *A. perglabra. N. palea* is a common and widespread taxon in lakes and rivers (Trobajo et al., 2009). *T. flocculosa* is also a common taxon which is found in a wide variety of habitats, though in usually slightly acidic waters (DeColibus, 2013). Despite a shift in assemblage being identified by the CONISS, there is no clear trend in diatom assemblages throughout the core and interpretation of an environmental driver for this shift is challenging especially given that there are not concurrent changes in chlorophyll a and stable isotopes.

Most notable change occurs in the puffin impact core from ~1950 to 2021 CE, where rapid significant increases in all proxies support an expansion in the population of puffins nesting on Puffin Island in the Little Fogo Islands. Historical environmental and societal changes in Newfoundland may explain these population trends, and well as the nesting and diet ecology of puffins.

4.3 History of the region

The 20th century was a period of significant change for Newfoundland. The Northwest Atlantic underwent a significant cooling period beginning in the 1970s and lasting through the early 1990s (Colbourne, 2004). Increasing industrialization of the cod fishery beginning in the 1950s, followed by the sudden closure of the fishery in 1991, which caused major societal shifts, with many people giving up fishing and moving away from coastal villages. As well, the Atlantic Puffin's preferred food source during the breeding season, capelin, suffered a stock collapse in the early 1990s (Buren et al., 2014). Other changes, such as a decrease in hunting and egg collection for food may also have played a part in the puffin population's apparent increase at this colony in recent history.

4.4 Sea surface temperature (SST)

Sea surface temperature (SST) has been found in many studies to be correlated to puffin breeding success and survival of fledglings (e.g., Hansen et al., 2021; Kress et al., 2016). The effect of SST seems to depend on local conditions, prey availability, and the timing of SST changes. Recent breeding failures at colonies in the Gulf of Maine are likely due to declines in food availability due to fish migration as a result of ocean warming, causing breeding puffin adults to travel longer distances to provision chicks (Kress et al., 2016). Hansen et al. (2021) demonstrated a relationship between increasing SST and decreasing chick-production over 128 years at a colony in Iceland, based on historical harvest data. However, Durant et al. (2003) found that puffin breeding success at a colony in northern Norway could be best predicted by higher spring SSTs. They attributed this to earlier hatch and faster growth of prey fish species, which provided more food for breeding puffins. Barrett et al. (2012) found that the mean volume of Atlantic Puffin eggs at two colonies in Norway decreased significantly between 1980 and 2011 and attributed this to both increasing SST and declining prey availability. Interestingly, this trend is not seen in the western Atlantic, where egg volumes have been stable despite similar changes in the marine food web (Lefort et al., 2021).

The NW Atlantic underwent a warming trend in the 1950s and 1960s, before a significant cooling period beginning in the 1970s and lasting through the early 1990s (Colbourne, 2004). The 1960s were the warmest decade in the later half of the 20th century (Colbourne, 2004). The North Atlantic Oscillation (NAO) refers to the sea-level-pressure difference between the Azores and Iceland. A high NAO index tends to predict strong northwest winds, cold air and sea temperatures and heavy ice conditions off Newfoundland. The NAO index in the winters of 1983, 1989, and 1990 were the highest since 1864 (Hurrell, 1995). And water temperatures off the Newfoundland shelf reached a record low in 1991 (Colbourne, 2004). This major trend

4.5 Puffin diet and prey availability in Newfoundland

The food web of coastal Newfoundland experienced a regime shift in the 1990s. Along with the collapse in cod stocks, demersal fish species such as capelin (*Mallotus villosus*), collapsed in the early 1990s likely due to a combination of overfishing and cold ocean temperatures (Buren et al., 2019). Capelin was heavily overfished by Russian fleets beginning in the 1960s and peaking in the 1970s (Rose, 2003). The reduction in predation by groundfish and the cold temperatures favoured a build-up of crustaceans, such as northern shrimp and snow crab (DFO, 2022). Diel vertical migration patterns of capelin shifted after 1991 to deeper waters (Mowbray, 2002) and capelin spawning times were delayed by several weeks throughout the 1990s (Carscadden et al., 1997). Despite warming waters, capelin are still spawning consistently later than they were pre-1991 (Murphy et al., 2018). Overall, capelin body sizes have also decreased since the collapse (Carscadden et al., 1997).

According to Nettleship (1972) Atlantic Puffins at both southeastern Newfoundland and the south Labrador colonies typically fed chicks 60-80% (by mass) capelin. Following the collapse in Newfoundland's puffins' main prey, it could be expected that colonies would experience breeding failures and subsequent population declines. However, a study in Labrador found that following a decline in capelin abundance, puffins did not experience breeding failure and successfully fed chicks other small fish and invertebrates (Baillie and Jones, 2004). Puffins have also been shown to switch between provisioning chicks with capelin and sandlance depending on availability at Funk Island, NL (Burke and Montevecchi, 2008). Morrissey (2023) measured $\delta^{15}N$ in feathers from museum specimens and found that the mean $\delta^{15}N$ for Newfoundland Atlantic Puffin was higher between ~1960-1980 than in samples taken between 2000 and 2021, and analysis of compound specific stable isotopes showed a non-significant decrease in puffin relative trophic position from 1940 through 2021. This potentially suggests puffins have shifted to lower-trophic position prey in response to declining capelin stocks.

Despite the collapse in capelin stocks 30 years ago, Newfoundland's puffins seem to have successfully incorporated lower trophic level prey into their diets. Puffin colonies in Newfoundland have not seen declines following the collapse of their main prey, as has been the case for colonies elsewhere in the Atlantic.

4.6 Bycatch

An important cause of mortality for many diving seabirds is drowning as bycatch in fishing nets (Žydelis et al., 2009; Montevecchi, 2023). Piatt and Nettleship (1987) estimated that between 1981 and 1984, an average of 1180 puffins per year were drowned in insular Newfoundland waters from Funk Island to Cape St. Mary's, with roughly half drowning in cod gillnets and half in salmon gillnets. Regular et al. (2013) used Environment Canada monitoring data to show that populations of diving seabirds (including puffins) at the five main seabird colonies in Newfoundland increased following the groundfish moratorium and the consequent removal of gillnets and movement of remaining fishing effort to offshore waters. Benjamins et al. (2008) estimated that 649 puffins were caught in the nearshore cod fishery in Newfoundland in 2001. Bycatch in seabird winter ranges is virtually unstudied, but also has the potential to impact populations. Until the groundfish moratorium, significant offshore gillnet fisheries occurred on the Grand Banks, in the same areas used by over-wintering alcids. Piatt et al. (1984) reported that, anecdotally, significant seabird bycatch also occurred in these offshore fisheries.

4.7 Hunting

Historically, seabirds were commonly hunted for subsistence in coastal Newfoundland and their eggs were gathered from colonies (Pope, 2009). This extraction included puffins in the spring, though their harvest did not have the same cultural and food security importance as murres in Newfoundland (Montevecchi, 2006). Virtually no estimates of the scale of the historical harvest exist for species other than murres and eiders, so its impact on other seabird species is difficult to estimate (Chardine et al., 2008). Following Newfoundland joining Canada in 1949 and consequently being subject to the federal Migratory Bird Treaty Convention Act (MBTCA), hunting non-game migratory birds by non-Indigenous people for consumption or commercial uses was banned (except for the winter hunting of Common and Thick-billed Murres, which continues today). Illegal harvest of seabirds, including puffins, continued, but the scale of this is unknown (Chardine et al., 2008). Until the mid-1980s, when stricter enforcement of the MBTCA began, the deliberate setting of gillnets to catch birds for human consumption was a known practice in parts of coastal Newfoundland (Chardine, 1998). Outreach efforts designed to curb illegal harvest were also implemented in the 1980s and 1990s (Chardine et al., 2008). Currently, incidental take of puffins during the winter murre hunt is sometimes reported, but seems to be rare, as puffins generally overwinter far from the coast.

4.8 Conditions for puffins in the 20th century

In the Little Fogo Islands, boat traffic and fishing pressure all but ceased after the cod fishery moratorium in 1991. The islands were mostly abandoned and the overall human activity in the archipelago decreased drastically. The increase in puffin indicators, especially $\delta^{15}N$ values and chlorophyll *a*, observed in the impact pond in the 1990s could be due to colonization of the islands by birds once human disturbance was removed. The fishing industry in these islands has never returned to pre-moratorium levels and human activity remains low compared with pre-1991. Puffins can also be sensitive to disturbance on their colonies, especially during incubation. For example, disturbance by researchers can cause parents to abandon eggs (Rodway et al., 1996).

There is evidence that conditions since the mid-20th century may have been favourable for puffins throughout Newfoundland. For example, the puffin colony at Small Island (Wadham Islands) was established in the 1970s and had grown to an estimated 25,000 pairs by 1984 (Robertson and Elliot, 2002). Zabala (2023) observed that in 2021, one of the previously human-inhabited islands in the Little Fogo archipelago, St. Anne's Island, had active puffin burrows for the first time on record. The large puffin colony in Witless Bay, NL has also been increasing since the 1960s (Wilhelm et al., 2015).

A release of pressure from bycatch mortality, hunting, and other disturbances by humans as the 20th century progressed, coupled with resilience to the collapse of the capelin stock and to low sea surface temperatures in the latter part of the century likely explains the increase in seabird-associated proxies and inferred increase in puffin nesting numbers observed in the sediment core from Puffin Island.

4.9 Study limitations

A drawback of the approach in this study is that it is difficult to determine whether the inferred increase in puffin numbers on Puffin Island in the Little Fogo Islands is due to an overall increase in puffin numbers in the region, or due to birds abandoning other breeding sites elsewhere. For example, the colony on Small Island (Wadham Islands), northeast NL decreased from 25,000 to 6,000 pairs between 1984 and 2001, likely due to the arrival of a breeding colony of Great Black-backed Gulls (*Larus marinus*), which predate puffins (Russell and Montevecchi, 1996; Robertson and Elliot, 2002). The decrease in colony size was attributed mostly to young birds choosing to not recruit to a colony with high predation pressure rather than direct predation on adults. These birds presumably then settled elsewhere to breed. Thus, our paleolimnological record specifically supports an increase in breeding puffins on Puffin Island in the Little Fogos but cannot access whether the breeding population in northeast Newfoundland increased. To determine this through paleoecology, more sediment cores from other breeding islands in Newfoundland are necessary. However, monitoring records for Witless Bay support that overall, the NL breeding population of Atlantic Puffins was increasing through the late 20th into 21st century.

4.10 Future research

In future studies, cores should be taken from other puffin-nesting islands in the region, for example, Bakeapple Island in the Little Fogo Islands, James Island in the Wadham Islands, Baccalieu Island and Gull Island in Witless Bay. This would help to determine if the increase observed on Puffin Island as due to a regional population trend due to improving conditions, or whether the increase seen on Puffin Island was from birds fleeing poor conditions elsewhere. Unfortunately, there are not always ponds located next to seabird colonies that allow paleolimnological reconstructions of nesting seabird populations from accumulated pond sediments. In this case, peat cores taken from within the colony could potentially be used. Peat accumulates through time, similarly to pond sediments, and peat records have recently been used to reconstruct past seabird populations. For example, Wetterich et al. (2019) used stable isotopes in peat permafrost to track the establishment of a colony of little auk (*Alle alle*) and a colony of thick-billed murre in Greenland. Gąsiorowski & Sienkiewicz (2019) used elemental and stable isotope analysis on peat cores to estimate the arrival of a little auk colony in Spitsbergen. And Groff et al. (2020) used a peat record to identify seabird arrival coinciding with regional cooling in the Falkland Islands. In the absence of ponds to sample, the ability to use peat cores potentially expands our ability to track Atlantic Puffin colony establishment and trends in Northwestern Newfoundland. The work presented in this thesis nevertheless provides, to my knowledge, the first sedimentary record for an Atlantic Puffin colony and contributes to our understanding of how puffin populations have responded to the significant trends in this region over the past five centuries.

References

Appleby, P.G., & Oldfield, F. (1978). The calculation of lead-210 dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. *Catena*, *5*(1), 1-8.

Bahls, L. (2012). *Navicula cincta*. In Diatoms of North America. Available at: https://diatoms.org/species/navicula_cincta (accessed November 11, 2024).

Baillie, S.M., & Jones, I.L. (2004). Response of Atlantic Puffins to a decline in capelin abundance at the Gannet Islands, Labrador. *Waterbirds, 27*(1), 102–111.

Barrett, R.T., Nilsen, E.B., & Anker-Nilssen, T. (2012). Long-term decline in egg size of Atlantic puffins *Fratercula arctica* is related to changes in forage fish stocks and climate conditions. *Marine Ecology Progress Series*, *457*, 1-10.

Battarbee R.W., Jones V.J., Flower R.J., Cameron N.G., Bennion H., Carvalho L., & Juggins S. (2001) Diatoms. In: Smol J.P., Birks H.J.B., Last W.M. (eds). *Tracking environmental change using lake sediments. Vol. 3: terrestrial, algal, and siliceous indicators* (pp. 155–202), *Kluwer Academic Publishers,* Dordrecht, Netherlands.

Benjamins, S., Kulka, D., & Lawson, J. (2008). Incidental catch of seabirds in Newfoundland and Labrador gillnet fisheries, 2001-2003. *Endangered Species Research*, *5*, 149–160. https://doi.org/10.3354/esr00094

BirdLife International. (2018). *Fratercula arctica*. The IUCN Red List of Threatened Species 2018. Available from: https://www.iucnredlist.org. (accessed September 1, 2021).

Black, J.L., Edlund, M.B., Hausmann, S., & Pienitz, R. (2012). Small freshwater thalassiosiroid diatoms from Pleistocene sediments of Pingualuit Crater Lake, northern Québec (Canada), including description of *Cyclotella pingualuitii* sp*. nov*. *Diatom Research*, *27*(1), 53-63.

Blaauw, M., 2010. Methods and code for ‘classical’ age-modelling of radiocarbon sequences. Quaternary Geochronology *5*(5), 512-518. doi:10.1016/j.quageo.2010.01.002

Bokhorst, S., Convey, P., & Aerts, R., 2019. Nitrogen inputs by marine vertebrates drive abundance and richness in Antarctic terrestrial ecosystems. *Current Biology*, *29*(10), 1721-1727.

Bonebrake, T.C., Christensen, J., Boggs, C.L., & Ehrlich, P.R. (2010). Population decline assessment, historical baselines, and conservation. *Conservation Letters*, *3*(6), 371-378.

Bosch, J.L., Álvarez-Manzaneda, I., Smol, J.P., Michelutti, N., Robertson, G.J., Wilhelm, S.I., Montevecchi, W.A., Lang, A.S., & Hargan, K.E. (2024). Blending census and paleolimnological data allows for tracking the establishment and growth of a major gannet colony over several centuries. *Scientific Reports*, *14*(1), 20462.

Brimble, S.K., Foster, K.L., Mallory, M.L., MacDonald, R.W., Smol, J.P., & Blais, J.M. (2009). High arctic ponds receiving bio-transported nutrients from a nearby seabird colony are also subject to potentially toxic loadings of arsenic, cadmium, and zinc. *Environmental Toxicology and Chemistry*, *28*(11), 2426–2433. doi:10.1897/09-235.1

Buren, A. D., Koen-Alonso, M., Pepin, P., Mowbray, F., Nakashima, B., Stenson, G., ... & Montevecchi, W. A. (2014). Bottom-up regulation of capelin, a keystone forage species. *PLoS One*, *9*(2), e87589.

Buren, A. D., Murphy, H., Adamack, A., Davoren, G., Koen-Alonso, M., Montevecchi, W., Mowbray, F., Pepin, P., Regular, P., Robert, D., Rose, G., Stenson, G., & Varkey, D. (2019). The collapse and continued low productivity of a keystone forage fish species. *Marine Ecology Progress Series*, *616*, 155-170.

Burger, A. E., & Simpson, M. (1986). Diving depths of Atlantic puffins and common murres. *The Auk*, *103*(4), 828-830.

Burke, C. M., & Montevecchi, W. A. (2008). Fish and chicks: Forage fish and chick success in co-existing auks. *Waterbirds*, *31*(3), 372–384.

Danchin, E., & Wagner, R.H. (1997). The evolution of coloniality: the emergence of new perspectives. *Trends in Ecology & Evolution*, *12(*9), 342-347.

Camburn, K.E., & Charles, D.F. (2000). Diatoms of Low-Alkalinity Lakes in the Northeastern United States Academy of Natural Sciences of Philadelphia, Special Publication *18*, 152.

Canadian Wildlife Service. 2014. Environment and Climate Change Canada. Unpublished data.

Carscadden, J., Montevecchi, W.A., Davoren, G.K., & Nakashima. B.S. (2002). Trophic relationships among capelin (*Mallotus villosus*) and seabirds in a changing ecosystem. *ICES Journal of Marine Science*, 59(5), 1027–1033. doi.org/10.1006/jmsc.2002.1235

Chardine, J.W. (1998). Review of the seabird bycatch problem in Arctic Canada. In: Bakken, V. and Falk, K. (eds). *Incidental take of seabirds in commercial fisheries in the Arctic Countries*. Conservation of Arctic Flora and Fauna Working Group Technical Report. Circumpolar Seabird Research Group Technical Report no. (1), 9-14.

Chardine, J.W., Robertson, G.J., & Gilchrist, H.G. (2008). Seabird harvest in Canada. In Merkel, F. and Barry, T. (eds.) *Seabird harvest in the Arctic.* Conservation of Arctic Flora and Fauna Working Group. Circumpolar Seabird Research Group Technical Report no. 16, 20-29.

Cheng, W., Sun, L., Kimpe, L.E., Mallory, M.L., Smol, J.P., Gallant, L.R., Li, J. & Blais, J.

M. (2016). Sterols and stanols preserved in pond sediments track seabird biovectors in a High Arctic environment. *Environmental Science & Technology*, 50(17), 9351–9360. doi.org/10.1021/acs.est.6b02767

Cheng, W., Kimpe, L. E., Mallory, M. L., Smol, J. P., and Blais, J. M. (2021). An ~1100 yr record of human and seabird occupation in the High Arctic inferred from pond sediments. *Geology*, 49, 510–514. doi: 10.1130/G48215.1

Colman-Sadd, S.P., Hayes, J.P., & Knight, I. (1990). Geology of the Island of Newfoundland. Newfoundland Department of Mines and Energy, Geological Survey Branch, Map 90-01.

Conroy, J. L., Collins, A. F., Overpeck, J. T., Bush, M. B., Cole, J. E., and Anderson, D. J. (2015). A 400-year isotopic record of seabird response to eastern tropical Pacific productivity. *Geo: Geography and Environment,* 2, 137–147. doi: 10.1002/geo2.11

Couture, R. M., Shafei, B., Van Cappellen, P., Tessier, A., & Gobeil, C. (2010). Non-steady state modeling of arsenic diagenesis in lake sediments. *Environmental Science & Technology*, *44*(1), 197-203.

Crann, C.A., Murseli, S., St-Jean, G., Zhao, X., Clark, I.D., & Kieser, W.E. (2017). First status report on radiocarbon sample preparation techniques at the A.E. Lalonde AMS Laboratory (Ottawa, Canada). *Radiocarbon*, 59(3), 695–704. https://doi.org/10.1017/RDC.2016.55

Danchin, E., & Wagner, R.H. (1997). The evolution of coloniality: The emergence of new perspectives. *Trends in Ecology & Evolution*, *12*(9), pp.342-347.

DeColibus, D. (2013). *Tabellaria flocculosa*. In Diatoms of North America. Retrieved November 18, 2024, from https://diatoms.org/species/tabellaria_flocculosa

De La Peña-Lastra, S. (2021). Seabird droppings: Effects on a global and local level. *Science of* *the Total Environment*, 754, 142148. doi.org/10.1016/j.scitotenv.2020.142148

De La Peña-Lastra, S., Pérez-Alberti, A., Ferreira, T.O., Huerta-Díaz, M.Á., & Otero, X.L. (2022). Global deposition of potentially toxic metals via faecal material in seabird colonies. *Scientific Reports*, *12*(1), p.22392.

Dias, M.P., Martin, R., Pearmain, E.J., Burfield, I.J., Small, C., Phillips, R.A., Yates, O., Lascelles, B., Borboroglu, P.G., & Croxall, J.P. (2019). Threats to seabirds: A global assessment. *Biological Conservation*, *237*, 525-537.

Doughty, C.E., Roman, J., Faurby, S., Wolf, A., Haque, A., Bakker, E.S., Malhi, Y., Dunning, J.B., & Svenning, J.-C. (2016). Global nutrient transport in a world of giants. *Proceedings of the National Academy of Sciences*, *113*(4), 868–873. doi: 10.1073/pnas.1502549112

Duda, M.P., Hargan, K. E., Michelutti, N., & Smol, J.P. (2019). Freshwater diatom assemblages from seabird-inhabited ponds in Hudson Strait, sub-Arctic Canada. *Polar Biology*, *42*(8), 1549–1560. doi:10.1007/s00300-019-02541-0

Duda, M.P., Robertson, G.J., Lim, J.E., Kissinger, J.A., Eickmeyer, D.C., Grooms, C., Kimpe, L.E., Montevecchi, W.A., Michelutti, N., Blais, J.M., & Smol, J.P. (2020a). Striking centennial-scale changes in the population size of a threatened seabird. *Proceedings of the Royal Society B: Biological Sciences*, *287*(1919), 20192234. doi: 10.1098/rspb.2019.2234

Duda, M.P., Allen-Mahé, S., Barbraud, C., Blais, J.M., Boudreau, A., Bryant, R., Delord, K., Grooms, C., Kimpe, L.E., Letournel, B., & Lim, J.E. (2020b). Linking 19th century European settlement to the disruption of a seabird's natural population dynamics. *Proceedings of the National Academy of Sciences*, *117*(51), pp.32484-32492.

Duda, M.P., Hargan, K.E., Michelutti, N., Blais, J.M., Grooms, C., Gilchrist, H.G., Mallory, M.L., Robertson, G.J., & Smol, J.P. (2021). Reconstructing long-term changes in avian populations using lake sediments: Opening a window onto the past. *Frontiers in Ecology and Evolution*, *9*, 698175.

Dunnington D.W., Libera N., Kurek J., Spooner I.S., & Gagnon G.A. (2022). "tidypaleo: Visualizing Paleoenvironmental Archives Using ggplot2." *Journal of Statistical Software*, *101*(7), 1–20. doi: 10.18637/jss.v101.i07.

Durant, J.M., Anker-Nilssen, T., & Stenseth, N.C. (2003). Trophic interactions under climate fluctuations: The Atlantic puffin as an example. *Proceedings of the Royal Society of London. Series B: Biological Sciences*, *270*(1523), pp.1461-1466.

Fauchald, P., Anker-Nilssen, T., Barrett, R., Bustnes, J.O., Bårdsen, B.J., Christensen-Dalsgaard, S., Descamps, S., Engen, S., Erikstad, K.E., Hanssen, S.A., & Lorentsen, S.H. (2015). The status and trends of seabirds breeding in Norway and Svalbard. Norwegian Institute for Nature Research Report 1151, 84.

Fayet, A.L., Clucas, G.V., Anker-Nilssen, T., Syposz, M., & Hansen, E.S. (2021). Local prey shortages drive foraging costs and breeding success in a declining seabird, the Atlantic puffin. *Journal of Animal Ecology, 90*, 1152–1164. https://doi.org/10.1111/1365-2656.13442

Gąsiorowski, M., & Sienkiewicz, E. (2019). Bird population changes reconstructed from isotopic signals of peat developed in a nutrient enriched tundra. *Science of the Total Environment*, *646*, 1359-1366.

Gallant, L.R., Grooms, C., Kimpe, L.E., Smol, J.P., Bogdanowicz, W., Stewart, R.S., Clare, E.L., Fenton, M.B., & Blais, J.M. (2020). A bat guano deposit in Jamaica recorded agricultural changes and metal exposure over the last> 4300 years. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *538*, 109470.

Gallant, L.R., Hargan, K.E., Kimpe, L.E., Michelutti, N., Grooms, C., Savelle, J.M., Smol, J.P. Blais, J.M. (2024). Sedimentary biomarkers and bone specimens reveal a history of prehistoric occupation on Somerset Island (Arctic Canada). *Proceedings of the Royal Society B*, *291*(2026), 20232915.

Geology of the Island of Newfoundland. Geological Survey Branch, Department of Mines and Energy, Government of Newfoundland and Labrador, 1990. www.gov.nl.ca/iet/files/mines-investments-geology-map-nl.pdf

Glew, J.R. (1988). A portable extruding device for close interval sectioning of unconsolidated core samples. *Journal of Paleolimnology*, *1*(3). doi:10.1007/BF00177769

Glew, J. R., & Smol, J. P. (2016). A push corer developed for retrieving high-resolution sediment cores from shallow waters. *Journal of Paleolimnology*, *56*(1), 67–71. doi:10.1007/s10933-015-9873-z

Government of Canada. (2022). Groundfish Newfoundland and Labrador Region NAFO Subarea 2 + Divisions 3KLMNO. https://www.dfo-mpo.gc.ca/fisheries-peches/ifmp-gmp/groundfish-poisson-fond/2020/groundfish-poisson-fond-2_3klmno-eng.htm#toc1

Grant, M.L., Bond, A.L., & Lavers, J.L., 2022. The influence of seabirds on their breeding, roosting and nesting grounds: A systematic review and meta-analysis. *Journal of Animal Ecology*, *91*(6), 1266-1289.

Graven, H., Allison, C. E., Etheridge, D. M., Hammer, S., Keeling, R. F., Levin, I., Meijer, H.A.J., Rubino, M., Tans, P.P., Trudinger, C.M., Vaughn, B.H., & White, J.W. (2017). Compiled records of carbon isotopes in atmospheric CO_2 for historical simulations in CMIP6. *Geoscientific Model Development*, *10*(12), 4405-4417.

Groff, D.V., Hamley, K.M., Lessard, T.J., Greenawalt, K.E., Yasuhara, M., Brickle, P., & Gill, J.L. (2020). Seabird establishment during regional cooling drove a terrestrial ecosystem shift 5000 years ago. *Science advances*, *6*(43), p.eabb2788.

Hansen, E.S., Sandvik, H., Erikstad, K.E., Yoccoz, N.G., Anker-Nilssen, T., Bader, J., Descamps, S., Hodges, K., Mesquita, M.D.S., Reiertsen, T.K., & Varpe, Ø. (2021). Centennial relationships between ocean temperature and Atlantic puffin production reveal shifting decennial trends. *Global Change Biology*, *27*(16), pp.3753-3764.

Hargan, K.E., Michelutti, N., Coleman, K., Grooms, C., Blais, J.M., Kimpe, L.E., Gilchrist, G., Mallory, M., & Smol, J.P. (2017). Cliff-nesting seabirds influence production and sediment chemistry of lakes situated above their colony. *Science of the Total Environment*, *576*, 85-98.

Hargan, K.E., Gilchrist, H.G., Clyde, N.M., Iverson, S.A., Forbes, M.R., Kimpe, L.E., Mallory, M.L., Michelutti, N., Smol, J.P., & Blais, J.M. (2019). Multicentury perspective assessing the sustainability of the historical harvest of seaducks. *Proceedings of the National Academy of Sciences*, *116*(17), 8425-8430.

Harris, M.P. (1983). Biology and survival of the immature Puffin, *Fratercula arctica*. *Ibis 125,* 56-73.

Harris, M. P., & Wanless, S. (2011). The Puffin. T & AD Poyser, Bloomsbury Publishing Plc. London, UK.

Hedd, A., Fifield, D. A., Burke, C. M., Montevecchi, W. A., Tranquilla, L. M., Regular, P. M., Buren, A.D, & Robertson, G. J. (2010). Seasonal shift in the foraging niche of Atlantic puffins Fratercula arctica revealed by stable isotope (δ15N and δ13C) analyses. *Aquatic Biology*, *9*(1), 13-22.

Hobson, K.A., Piatt, J.F. & Pitocchelli, J. (1994). Using stable isotopes to determine seabird trophic relationships. *Journal of Animal Ecology*, 786-798.

Hornung RW, Reed LD. 1990 Estimation of average concentration in the presence of nondetectable values. *Applied Occupational and Environmental Hygiene*, *5*, 46–41.

Hurrell, J.W. (1995). Decadal trends in the North Atlantic Oscillation: Regional temperatures and precipitation. *Science*, *269*(5224), 676-679.

Jenkins, E., Gulka, J., Yurkowski, D.J., Le François, N.R., Wong, E., & Davoren, G.K. (2020). Isotopic discrimination (δ^{15}N, δ^{13}C) in captive and wild Common Murres (*Uria aalge*) and Atlantic Puffins (*Fratercula arctica*). *Physiological and Biochemical Zoology*, *93*(4), 296–309. https://doi.org/10.1086/709460

Kassambara, A., Mundt, F. (2020). factoextra: Extract and Visualize the Results of Multivariate Data Analyses. R package version 1.0.7, https://CRAN.R-project.org/package=factoextra

Kersten, O., Star, B., Leigh, D.M., Anker-Nilssen, T., Strøm, H., Danielsen, J., Descamps, S., Erikstad, K.E., Fitzsimmons, M.G., Fort, J. & Hansen, E.S. (2021). Complex population structure of the Atlantic puffin revealed by whole genome analyses. *Communications Biology*, *4*(1), p.922.

Komada, T., Anderson, M. R. & Dorfmeier, C.L. (2008). Carbonate removal from coastal sediments for the determination of organic carbon and its isotopic signatures, δ^{13}C and δ^{14}C: comparison of fumigation and direct acidification by hydrochloric acid. *Limnology and Oceanography: Methods*, *6*(6), 254-262.

Koski-Vähälä, J., Hartikainen, H., & Tallberg, P. (2001). Phosphorus mobilization from various sediment pools in response to increased pH and silicate concentration. *Journal of Environmental Quality*, *30*(2), 546-552.

Kouassi, N. G. L. B., Yao, K. M., Sangare, N., Trokourey, A., & Metongo, B. S. (2019). The mobility of the trace metals copper, zinc, lead, cobalt, and nickel in tropical estuarine sediments, Ebrie Lagoon, Côte d'Ivoire. *Journal of soils and sediments*, *19*, 929-944.

Kouwenberg, A.-L., Mark Hipfner, J., McKay, D.W. & Storey, A.E. (2013). Corticosterone and stable isotopes in feathers predict egg size in Atlantic Puffins *Fratercula arctica*. *Ibis*, *155*(2), 413–418. doi.org/10.1111/ibi.12030

Krammer, K.,& Lange-Bertalot, H. (1991) Bacillariophyceae. In: Ettl, H., Gerloff, J., Heynig, H. & Mollenhauer, D. (Eds.). *Süsswasserflora von Mitteleuropa*. 1-3, 1-576. Gustav Fisher Verlag, Stuttgart, Germany.

Kress, S.W., Shannon, P. & O'Neal, C. (2016). Recent changes in the diet and survival of Atlantic puffin chicks in the face of climate change and commercial fishing in midcoast Maine, USA. *Facets*, *1*(1), 27-43.

Kristensen, T.J. (2011). Seasonal bird exploitation by Recent Indian and Beothuk Hunter-Gatherers of Newfoundland. *Canadian Journal of Archaeology* 35: 292–322.

Lamb, A. L., Wilson, G. P., & Leng, M. J. (2006). A review of coastal palaeoclimate and relative sea-level reconstructions using $\delta^{13}C$ and C/N ratios in organic material. *Earth-Science Reviews*, *75*(1-4), 29-57.

Lefort, K.J., Major, H.L., Bond, A.L., Diamond, A.W., Jones, I.L., Montevecchi, W.A., Provencher, J.F., Robertson, & G.J. (2021). Long-term stability in the volume of Atlantic Puffin (Fratercula arctica) eggs in the western North Atlantic. *Canadian Journal of Zoology*, *99*(8), 653-657. doi.org/10.1139/cjz-2020-0254

Liu, X., Sun, L., Xie, Z., Yin, X. & Wang, Y. (2005). A 1300-year record of penguin populations at Ardley Island in the Antarctic, as deduced from the geochemical data in the ornithogenic lake sediments. *Arctic, Antarctic, and Alpine Research*, 37(4), 490–498. doi: 10.1657/1523-0430(2005)037[0490:AYROPP]2.0.CO;2

Liu, X., Nie, Y., Sun, L., and Emslie, S. D. (2013). Eco-environmental implications of elemental and carbon isotope distributions in ornithogenic sediments from the Ross Sea region, Antarctica. *Geochimica et Cosmochimica Acta,* 117, 99–114. doi: 10.1016/j.gca.2013.04.013

Lowther, P. E., A. W. Diamond, S. W. Kress, G. J. Robertson, K. Russell, D. N. Nettleship, G. M. Kirwan, D. A. Christie, C. J. Sharpe, E. F. J. Garcia, & P. F. D. Boesman (2020). Atlantic Puffin (*Fratercula arctica*), version 1.0. In Birds of the World (S. M. Billerman, Editor). Cornell Lab of Ornithology, Ithaca, NY, USA.

McCay, B.J. 1979. "Fish is Scarce": Fisheries Modernization on Fogo Island, Newfoundland. In Andersen, R. (ed). *North Atlantic Maritime Cultures: Anthropological Essays on Changing Adaptations.* 9th International Congress of Anthropological and Ethnological Sciences, Chicago, Ill, USA.

Mallory, M. L., Mahon, L., Tomlik, M. D., White, C., Milton, G. R., & Spooner, I. (2015). Colonial marine birds influence island soil chemistry through biotransport of trace elements. *Water, Air, & Soil Pollution*, *226*, 1-8.

Michelutti, N., & Smol, J.P. (2016). Visible spectroscopy reliably tracks trends in paleo-production. *Journal of Paleolimnology*, *56*(4), 253-265.

Michelutti, N., Wolfe, A. P., Vinebrooke, R.D., Rivard, B. & Briner, J.P. (2005). Recent primary production increases in arctic lakes. *Geophysical Research Letters*, *32*(19). doi.org/10.1029/2005GL023693

Michelutti, N., Blais, J.M., Cumming, B.F., Paterson, A.M., Rühland, K., Wolfe, A.P. & Smol, J.P. (2010). Do spectrally inferred determinations of chlorophyll a reflect trends in lake trophic status? *Journal of Paleolimnology*, 43(2), 205–217. doi.org/10.1007/s10933-009-9325-8

Miles, W.T.S., Mavor, R., Riddiford, N.J., Harvey, P.V., Riddington, R., Shaw, D.N., Parnaby, D. & Reid, J.M. (2015). Decline in an Atlantic Puffin population: Evaluation of magnitude and mechanisms. *PLOS One*. *10*(7): e0131527.

Minagawa, M. and Wada, E. (1984). Stepwise enrichment of 15N along food chains: further evidence and the relation between δ15N and animal age. *Geochimica et cosmochimica acta*, *48*(5), 1135-1140.

Montevecchi, W.A., Chaffey, H., Burke, C., 2006. Hunting for security: Changes in the exploitation of marine birds in Newfoundland and Labrador. In Parrish, C.C., Turner, N.J. & Solberg, S.M. (eds). *Resetting the Kitchen Table: Food security, culture, health and resilience in coastal communities* (pp. 99-113). Nova Science Publishers Inc., New York, NY, USA.

Montevecchi, W.A. (2023) Interactions between fisheries and seabirds: Prey modification, discarding and bycatch. In Young, L. and Vander Werf, E. (Eds). *Conservation of Marine Birds* (pp. 57-95). Academic Press, London U.K.

Moritz, S. and Bartz-Beielstein, T. (2017). “imputeTS: Time Series Missing Value Imputation in

R." *The R Journal*, *9*(1), 207-218. doi: 10.32614/RJ-2017-009

Morrissey, M. (2023). Seabirds of Newfoundland and Labrador: Using stable isotope techniques to investigate changing trophic position over ~120 years, and examining their influence on terrestrial coastal ecosystems. Master's Thesis. Memorial University of Newfoundland.

Nettleship, D.N. (1972). Breeding success of the Common Puffin (*Fratercula arctica L.)* on different habitats at Great Island, Newfoundland. *Ecological Monographs*, *42*(2), 239-268.

Orwin, K.H., Wardle, D.A., Towns, D.R., St. John, M.G., Bellingham, P.J., Jones, C., Fitzgerald, B.M., Parrish, R.G. & Lyver, P.O. (2016). Burrowing seabird effects on invertebrate communities in soil and litter are dominated by ecosystem engineering rather than nutrient addition. *Oecologia 180*, 217–230. doi.org/10.1007/s00442-015-3437-9

Otero, X. L., De La Peña-Lastra, S., Pérez-Alberti, A., Ferreira, T. O. & Huerta-Diaz, M. A. (2018). Seabird colonies as important global drivers in the nitrogen and phosphorus cycles. *Nature Communications*, *9*(1), 246. doi:10.1038/s41467-017-02446-8.

Piatt JF, Nettleship, D.N. & Threlfall, W. (1984). Net-mortality of common murres and Atlantic puffins in Newfoundland, 1951–81. In: Nettleship, D.N., Sanger, G.A. & Springer, P.F. (eds) Marine birds: their feeding ecology and commercial fisheries relationships (pp. 196–206). Supply and Services Canada, Ottawa, ON.

Piatt, J. F., & Nettleship, D. N. (1987). Incidental catch of marine birds and mammals in fishing nets off Newfoundland, Canada. *Marine Pollution Bulletin*, *18*(6), 344-349.

Pope, P.E. (2009). Early migratory fishermen and Newfoundland's seabird Colonies. *Journal of the North Atlantic 2*(1), 57. doi.org/10.3721/037.002.s107

Pratte, I., Robertson, G., & Mallory, M. (2017). Four sympatrically nesting auks show clear resource segregation in their foraging environment. *Marine Ecology Progress Series*, 572, 243- 254. doi.org/10.3354/meps12144

Protected Areas Association of Newfoundland and Labrador. (2008). North Shore Forest. URL https://www.gov.nl.ca/ecc/files/publications-parks-ecoregions-island-3-north-shore-forest.pdf (accessed November 12, 2021).

R Core Team (2020). _R: A Language and Environment for Statistical Computing_. R Foundation for Statistical Computing, Vienna, Austria. <https://www.R-project.org/>

Reavie, E., & Smol, J. (2001). Diatom-environmental relationships in 64 alkaline southeastern Ontario (Canada) lakes: a diatom-based model for water quality reconstructions. *Journal of Paleolimnology*, *25*, 25-42.

Regular, P., Montevecchi, W., Hedd, A., Robertson, G., & Wilhelm, S. (2013). Canadian fishery closures provide a large-scale test of the impact of gillnet bycatch on seabird populations. *Biology letters*, *9*(4), 20130088. doi.org/10.1098/rsbl.2013.0088

Reimer, P., Austin, W., Bard, E., Bayliss, A., Blackwell, P., Bronk Ramsey, C., Butzin, M., Cheng, H., Edwards, R., Friedrich, M., Grootes, P., Guilderson, T., Hajdas, I., Heaton, T., Hogg, A., Hughen, K., Kromer, B., Manning, S., Muscheler, R., Palmer, J., Pearson, C., van der Plicht, J., Reimer, R., Richards, D., Scott, E., Southon, J., Turney, C., Wacker, L., Adolphi, F., Büntgen, U., Capano, M., Fahrni, S., Fogtmann-Schulz, A., Friedrich, R., Köhler, P., Kudsk, S., Miyake, F., Olsen, J., Reinig, F., Sakamoto, M., Sookdeo, A. & Talamo, S. (2020). The IntCal20 Northern Hemisphere radiocarbon age calibration curve (0–55 cal kBP). *Radiocarbon*, *62*(4), 725-757.

Robertson, G.J. & R.D. Elliot. (2002). Changes in seabird populations breeding on Small

Island, Wadham Islands, Newfoundland. In Technical Report Series no. 381. Canadian Wildlife Service, Atlantic Region. Ottawa, ON.

Rodway, M.S., Montevecchi, W.A. & Chardine, J.W., 1996. Effects of investigator disturbance on breeding success of Atlantic puffins *Fratercula arctica*. *Biological Conservation*, *76*(3), 311-319.

Rose, G.A. (2003). Fisheries resources and science in Newfoundland and Labrador: an independent assessment. *Royal Commission on Renewing and Strengthening Our Place in Canada*.

Rühland, K., Karst, T., Paterson, A., Gregory-Eaves, R., Smol, J.P. & Cumming, B.F. 1999. Standard Sediment Sample Preparation Methods for Siliceous Microfossils (Diatoms and Chrysophyte Scales and Cysts). PEARL: Paleoecological Environmental Assessment and Research Laboratory. Department of Biology Queen's University. Available at: https://www.queensu.ca/pearl/methods/diatoms.php. (accessed May 1, 2022).

Rühland, K., Paterson, A, & Smol, J.P. (2015). Lake diatom responses to warming: reviewing the evidence. *Journal of paleolimnology*, *54*, 1-35.

Russell, J. & Montevecchi, W.A. (1996). Predation on adult puffins *Fratercula arctica* by Great Black-backed Gulls *Larus marinus* at a Newfoundland colony. *Ibis*, *138*, 791-794. dx.doi.org/10.1111/j.1474-919X.1996.tb08839.x

Schelske, C.L. & Hodell, D.A. (1995). Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. *Limnology and Oceanography*, *40*(5), 918–929. doi.org/10.4319/lo.1995.40.5.0918

SGS Canada Inc. (2014) Rocks to results: a practical guide to laboratory operations, 5th edition. SGS Canada Inc., Ontario.

Sherwood, G.D. & Rose, G.A. (2005). Stable isotope analysis of some representative fish and invertebrates of the Newfoundland and Labrador continental shelf food web. *Estuarine, Coastal and Shelf Science*, *63*(4), 537–549. doi.org/10.1016/j.ecss.2004.12.010

Shoji, A., Elliott, K.H., Aris-Brosou, S., Mizukawa, H., Nakayama, S.M.M., Ikenaka, Y., Ishizuka, M., Kuwae, T., Watanabe, K., Escoruela Gonzalez, J. & Watanuki, Y. (2019). Biotransport of metallic trace elements from marine to terrestrial ecosystems by seabirds. *Environmental Toxicology and Chemistry*, *38*(1), 106-114.

Shorefast Website. (2022). Available at: www.shorefast.org/about-us/fogo-island/ (accessed September 16, 2022).

Smol, J.P. and Stoermer, E.F. (eds.) (2010). *The diatoms: applications for the environmental and earth sciences*. Cambridge University Press.

Spaulding, S.A., Bishop, I.W., Edlund, M.B., Lee, S., Furey, P., Jovanovska, E. & Potapova, M. Diatoms of North America. https://diatoms.org (accessed November 12, 2021).

Standard Methods. (2018). American Public Health Association, American Water Works Association, and Water Environment Federation. Available from: www.standardmethods.org/ (accessed September 25, 2022).

Stewart, E.M., Vu, M., Michelutti, N., Hargan, K., Grooms, C., Kimpe, L.E., Blais, J.M.& Smol, J.P. (2019). Pond sediments on nesting islands in eastern Lake Ontario provide insights into the population dynamics and impacts of waterbird colonies. *Journal of Great Lakes Research*, *45*(2), 350-359.

Strunk, A., Olsen, J., Sanei, H., Rudra, A. & Larsen, N.K. (2020). Improving the reliability of bulk sediment radiocarbon dating. *Quaternary Science Reviews*, *242*, 106442.

Thompson, D.R., Lilliendahl, K., Solmundsson, J., Furness, R.W., Waldron, S. & Phillips, R.A. (1999). Trophic relationships among six species of Icelandic seabirds as determined through stable isotope analysis. *Condor, 101*(4), 898–903. doi-org.qe2a-proxy.mun.ca/10.2307/1370085

Trobajo, R., Clavero, E., Chepurnov, V.A., Sabbe, K., Mann, D.G., Ishihara, S. & Cox, E.J. (2009). Morphological, genetic and mating diversity within the widespread bioindicator *Nitzschia palea* (Bacillariophyceae). *Phycologia*, *48*(6), 443–459. doi.org/10.2216/08-69.1

Van Dam, H., Mertens, A. & Sinkeldam, J. (1994). A coded checklist and ecological indicator values of freshwater diatoms from the Netherlands. *Netherland Journal of Aquatic Ecology*, *28*, 117-133.

Velarde, E., Anderson, D.W. & Ezcurra, E. (2019). Seabird clues to ecosystem health. *Science*, *365*(6449), 116-117.

Wang, Z., Wang, Y., Zhao, P., Chen, L., Yan, C., Yan, Y., & Chi, Q. (2015). Metal release from contaminated coastal sediments under changing pH conditions: Implications for metal mobilization in acidified oceans. *Marine Pollution Bulletin*, *101*(2), 707-715. doi: 10.1016/j.marpolbul.2015.10.026

Wetterich, S., Davidson, T.A., Bobrov, A., Opel, T., Windirsch, T., Johansen, K.L. & González-Bergonzoni, I., Mosbech, A. & Jeppesen, E. (2019). Stable isotope signatures of Holocene syngenetic permafrost trace seabird presence in the Thule District (NW Greenland). *Biogeosciences*, *16*(21), 4261-4275.

Wilhelm, S.I., Mailhiot, J., Arany, J., Chardine, J.W., Robertson, G.J. & Ryan, P.C. (2015). Update and trends of three important seabird populations in the western North Atlantic using a geographic information system approach. *Marine Ornithology*, *43*, 211-222.

Wilhelm, S.I. (2023). Environment and Climate Change Canada. Unpublished data.

Wood, J.R. & De Pietri, V.L. (2015). Next generation paleornithology: Technological and methodological advances allow new insights into the evolutionary and ecological histories of living birds. Auk, *132*, 486–506. doi:10.1642/AUK-14-257.1

Wood, S.N. (2011). Fast stable restricted maximum likelihood and marginal likelihood estimation of semiparametric generalized linear models. *Journal of the Royal Statistical Society (B), 73*(1), 3-36.

Zabala Belenguer, R. (2023). Estimating breeding status in Atlantic puffin colonies across Newfoundland: A methodological comparison. Master's Thesis. Memorial University of Newfoundland.

Żydelis, R., Bellebaum, J., Österblom, H., Vetemaa, M., Schirmeister, B., Stipniece, A., Dagys, M., van Eerden, M. & Garthe, S. (2009). Bycatch in gillnet fisheries–an overlooked threat to waterbird populations. *Biological Conservation*, *142*(7), 1269-128.

Appendix 1

Table 1. Site characteristics for the puffin impact pond, mainland reference, and Fogo Island reference ponds. No information was available on surficial geology.

Pond	Puffin Impact	Mainland Reference	Fogo Reference
Latitude	5521571.11 m N	5511269.00 m N	5476647.00 m N
Longitude (21U)	707830.81 m E	707709.00 m E	715521.00 m E
Size (length x width) (m)	25x11m	1000x1000	100x90m
Maximum Depth (m)	0.36	1.5	Unknown
Age*	Silurian	Silurian to Devonian	Silurian to Devonian
Lithography*	subaerial mafic and felsic volcanics	granitoid suites	granitoid suites
Tectonic*	overlap	late intrusions	late intrusions
Ecoregion**	North Shore Forest	North Shore Forest	North Shore Forest
Dominant vegetation	grasses	trees	trees

* NL gov interactive map. Colman-Sadd et al. (1990)

** Protected Areas Association of Newfoundland and Labrador (2008)

Appendix 2

Table 1. Water chemistry for the puffin impact pond and the Fogo Island reference pond.

type	Analysis	Units	Reporting detection limit (RDL)	Fogo Reference	Puffin Impact	Uncertainty
total metals	Aluminum	µg/L	30	< 30	68.1	± 0.025
total metals	Antimony	µg/L	30	< 30	< 30	± 0.012
total metals	Arsenic	µg/L	5	< 5	8.1	± 0.012
total metals	Barium	µg/L	60	< 60	< 60	± 0.014
total metals	Beryllium	µg/L	4	< 4	< 4	± 0.014
total metals	Bismuth	µg/L	1	< 1	< 1	± 0.196
total metals	Boron	µg/L	40	< 40	828	± 0.022
total metals	Cadmium	µg/L	2	< 2	< 2	± 0.016
total metals	Calcium	mg/L	4	< 4	139	± 0.780
total metals	Chromium	µg/L	3	< 3	< 3	± 0.015
total metals	Cobalt	µg/L	2	< 2	< 2	± 0.012
total metals	Copper	µg/L	5	< 5	< 5	± 0.012
inorganic	DOC (as C)	mg/L	1	7.1	29.7	± 0.42
total metals	Iron	µg/L	300	< 300	< 300	± 0.019
total metals	Lead	µg/L	3	< 3	< 3	± 0.012
total metals	Magnesium	mg/L	0.2	1.5	326	± 0.552
total metals	Manganese	µg/L	3	19.6	69.9	± 0.012
total metals	Mercury	µg/L	2	< 2	< 2	± 0.04
total metals	Molybdenum	µg/L	20	< 20	< 20	± 0.012
total metals	Nickel	µg/L	4	< 4	< 4	± 0.013
total metals	Phosphorus	mg/L	0.2	< 0.2	3.6	± 0.567
total metals	Potassium	mg/L	0.8	< 0.8	116	± 0.992
total metals	Selenium	µg/L	8	< 8	< 8	± 0.013
total metals	Silver	µg/L	6	< 6	< 6	± 0.003
total metals	Sodium	mg/L	1	20.6	2850	± 1.026
total metals	Strontium	µg/L	5	8.6	3260	± 0.039
total metals	Thallium	µg/L	2	< 2	< 2	± 0.012
inorganic	TIC (as C)	mg/L	0.6	0.7	3.2	± 0.66
total metals	Tin	µg/L	4	< 4	< 4	± 0.083
total metals	Titanium	µg/L	1.5	2.2	147	± 0.006
inorganic	TKN	mg/L	0.6	1.05	4.12	± 0.478
total metals	Uranium	µg/L	1	< 1	< 1	± 0.006
total metals	Vanadium	µg/L	2	< 2	4	± 0.012
total metals	Zinc	µg/L	100	< 100	< 100	± 0.013

Appendix 3

Table 1. Reporting detection limits (RDL) for metal(loid)s in sediments and puffin guano.

Element	µg/g
Al	1
As	0.5
Ba	0.01
Be	0.02
Bi	0.09
Ca	1
Cd	0.02
Co	0.01
Cr	0.5
Cu	0.1
Fe	0.3
K	0.3
Li	2
Mg	0.1
Mn	0.1
Mo	0.1
Na	1
Ni	0.1
P	3
Pb	0.05
Sb	0.8
Se	0.7
Sn	0.5
Sr	0.02
Ti	0.1
Tl	0.02
U	0.002
V	1
Y	0.004
Zn	0.7

Appendix 4

Table 1. Metal(loid) concentrations in the Little Fogo Island puffin impact core (μg/L).

midpoint	0.25	1.25	3.25	5.25	7.25	9.25	11.25	13.25	15.25	17.25	19.25	21.25	23.25	25.25	27.25	29.25	31.25	33.25
year	2021	2020	2014	2010	2004	1996	1985	1971	1937	1883	1829	1774	1720	1666	1612	1557	1503	1449
Ag	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71
Al	3500	3900	3800	3800	3900	4000	4300	4400	4300	4200	4000	4000	4000	4000	4400	4500	4500	4600
As	12	17	18	18	18	19	17	15	14	13	12	11	10	9.6	9.6	9.6	9.5	10
Ba	5	4.6	2.6	2	1.6	1.8	2	2.1	2	2	2.2	2.6	2.5	2.8	3.2	3.4	3.4	3.8
Be	0.18	0.18	0.17	0.17	0.16	0.17	0.18	0.19	0.18	0.18	0.17	0.17	0.16	0.15	0.17	0.18	0.18	0.19
Bi	0.06364	0.06364	0.096	0.06364	0.06364	0.095	0.12	0.11	0.1	0.1	0.099	0.06364	0.06364	0.06364	0.06364	0.06364	0.06364	0.06364
Ca	10000	12000	12000	12000	13000	13000	13000	14000	13000	13000	14000	14000	15000	14000	14000	15000	15000	15000
Cd	4	3.9	3.2	3.2	3.2	3.2	3.3	3.4	3.3	3.2	2.9	2.8	2.8	2.7	3.4	3.4	3.4	3.4
Co	1.3	1.8	1.7	1.7	1.5	1.7	1.8	1.7	1.7	1.8	1.6	1.7	1.8	1.9	1.7	1.7	1.7	1.7
Cr	1	67	2.7	2.8	1.8	2.2	3.8	2.4	2.8	2.2	1.7	1.8	1.9	3.1	2.3	2.4	2.4	2.5
Cu	8.8	9.8	9.9	10	10	11	11	12	12	12	11	12	12	12	13	13	12	12
Fe	1400	2300	1700	1800	1900	2000	2400	2400	2300	2400	2800	3200	3600	4600	5100	4800	4800	4900
Hg	0.25	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
K	2700	2900	2500	2200	2000	1900	1600	1500	1500	1400	1300	1300	1300	1200	1100	1100	1100	1000
Li	1.414214	1.414214	1.414214	1.414214	1.414214	1.414214	1.414214	1.414214	1.414214	1.414214	1.414214	1.414214	1.414214	1.414214	1.414214	1.414214	1.414214	1.414214
Mg	11000	13000	13000	13000	13000	13000	13000	13000	13000	13000	13000	14000	14000	14000	13000	13000	13000	13000
Mn	20	34	25	23	22	20	19	18	18	19	19	19	19	19	21	20	20	22
Mo	2	3.2	3.6	3.4	3.5	3.9	4.4	4.6	4.8	5	4.9	4.7	4.4	4.6	5.4	4.7	4.8	5.1
Na	41000	45000	42000	39000	38000	37000	33000	33000	32000	30000	30000	30000	31000	29000	25000	26000	25000	23000
Ni	4.7	31	5.8	5.9	5.5	6	6.8	6.1	6.2	5.6	5.4	5.5	5.7	6.2	5.6	5.7	5.6	5.8
P	4200	3800	3200	2800	2600	2400	2000	1800	1700	1400	1200	1100	1100	1100	1100	1100	1100	1200
Pb	40	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

Sb	4.242641	4.242641	4.242641	4.242641	4.242641	4.242641	4.242641	4.242641	4.242641	4.242641	4.242641	4.242641	4.242641	4.242641	4.242641	4.242641	4.242641	4.242641
Se	2.1	2.3	2.3	2.5	2.5	2.7	2.7	2.9	2.8	2.8	3	3.1	3.2	3.1	3.4	3.3	3.3	3.5
Sn	0.353553	0.353553	0.353553	0.353553	0.353553	0.353553	0.353553	0.353553	0.353553	0.52	0.87	0.51	0.353553	0.353553	0.353553	0.353553	0.353553	0.353553
Sr	260	250	200	190	200	190	200	210	210	210	210	220	220	220	220	220	220	220
Ti	59	80	84	85	89	94	100	100	110	110	130	140	150	150	180	180	190	190
Tl	0.014142	0.022	0.031	0.031	0.024	0.031	0.033	0.033	0.028	0.036	0.035	0.031	0.031	0.024	0.014142	0.014142	0.014142	0.014142
U	2.7	2.8	3	3.1	3.3	3.4	3.6	3.7	3.7	3.9	4.4	4.6	4.7	4.7	4.9	4.9	4.9	4.9
V	4	4.3	4.5	4.6	4.7	5.1	5.3	5.5	5.6	5.7	5.5	5.3	5.4	5.5	5.6	5.7	5.8	6
Y	3.9	3.7	3.7	3.9	4.1	4.2	4.7	4.8	4.7	4.5	4.5	4.8	5.1	5.1	5.8	6.1	6	6.1
Zn	79	57	59	55	56	56	53	52	49	53	49	49	49	49	55	55	55	56

Table 2. Metal(loid) concentrations in the Musgrave Harbour reference core (µg/L).

midpoint	0.25	2.25	4.25	5.25	6.25	6.75	7.25	7.75	8.25	10.25
year	2021	2013	2001	1982	1925	NA	1807	NA	1631	1145
Ag	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71
Al	7700	9400	11000	8900	9500	7800	8800	8500	10000	10000
As	3.5	3.4	4.2	3.3	3.2	2.3	2.4	2.2	2.9	2.9
Ba	17	18	21	21	18	17	18	17	19	19
Be	0.57	0.66	0.76	0.72	0.68	0.67	0.75	0.73	0.79	0.81
Bi	0.52	0.86	1.1	0.74	0.89	0.64	0.75	0.75	1.1	1
Ca	720	1400	1600	1100	1500	890	1200	1200	1600	1600
Cd	0.23	0.3	0.34	0.26	0.26	0.27	0.36	0.29	0.25	0.19
Co	6.6	6.5	6.8	6.9	6.2	5.7	6.2	5.9	6.3	6.5
Cr	25	26	28	27	25	24	26	26	29	29
Cu	5.7	5.6	140	5.8	5.2	4.9	5.7	5.9	5.8	5.7
Fe	14000	14000	13000	12000	13000	10000	11000	11000	12000	13000
Hg	0.98	NA	NA	1.78	NA	1.13	0.9	0.51	NA	NA
K	400	570	590	420	540	340	400	380	550	590
Li	13	13	13	14	13	12	13	12	13	15
Mg	2900	3800	3700	2900	3600	2600	2800	2700	3800	4000
Mn	440	340	370	370	330	310	340	320	330	320
Mo	0.8	1	1.3	1	1.1	1	1.1	1.1	1.5	1.3
Na	72	100	120	59	100	42	72	69	110	100
Ni	22	23	24	24	22	21	23	22	23	25
P	580	660	770	700	690	670	730	710	780	720
Pb	13	NA	NA	13	NA	9.2	9.4	9.2	NA	NA
Sb	4.24	4.24	4.24	4.24	4.24	4.24	4.24	4.24	4.24	4.24
Se	0.49	0.71	0.83	0.49	0.49	0.49	0.49	0.49	0.74	0.49
Sn	0.9	0.83	1.1	1.1	0.68	0.7	0.8	0.8	0.68	0.64
Sr	5.2	7.2	9.4	7.7	7.8	6.1	8.2	8.2	8.4	8.2
Ti	290	380	390	320	370	270	300	280	390	400
Tl	0.05	0.06	0.071	0.07	0.064	0.06	0.07	0.07	0.079	0.085

U	7	8.6	10	9	8.7	8	9.2	9.4	11	11
V	16	16	17	17	16	15	16	16	17	17
Y	4.3	4.3	4.5	4.7	4.1	4.3	4.7	4.6	4.5	4.5
Zn	41	49	120	48	44	39	43	44	51	51