Role of Seasonal Melt Streams in Heavy Metal and Nutrient Transport from an Antarctic Penguin Colony

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Abstract

Despite the perception that Antarctica is pristine, concentrations of heavy metals and persistent organic pollutants have been recorded at increasing levels. Heavy metals may be present within the Antarctic terrestrial environment through natural geologic processes, long-range atmospheric transport, anthropogenic point sources, and biological transport. While the biological transport of contaminants remains frequently overlooked, in the Arctic, it has been shown to rival atmospheric fluxes of contaminants. Adélie penguins are known vectors for transporting heavy metals and nutrients from within the marine environment and depositing them on the land through guano, feathers, eggshells, and whole carcasses. The incorporation of this material in deep ornithogenic soils has resulted in Adélie penguin colonies being identified as sites of heavy metal and nutrient accumulation. Despite seasonal glacial melt streams that erode these colony soils, their role in heavy metal and nutrient transport is largely under-researched. Therefore, this study evaluated the redistribution of heavy metals and nutrients via melt streams. Stream discharge and load, in addition to soil heavy metal and nutrient content, were also assessed.

Five sites along two streams, one flowing through an Adélie penguin colony (P1 to P5) and a control stream with no penguin influence (C1 to C5), were compared throughout this research. Melt water within the Adélie penguin colony had elevated arsenic, cadmium, and lead (p<0.05), with total heavy metal concentrations exceeding New Zealand freshwater guidelines for ecological health up to 37, eight, and two times, respectively. Cadmium and lead were found mostly in particulate form (dissolved cadmium <22 % and dissolved lead <11 %), however, there was a relatively higher portion of arsenic (up to 72 %) that was dissolved (<45 μm). This indicates increased bioavailability and concern for toxicity of arsenic.

Nutrient anions (ammonium, nitrate, and phosphate) were also elevated in penguin-influenced water compared to the control stream (p<0.05), surpassing water quality guidelines up to

1038, 1017, and 551 times. When accounting for differences in discharge, stream loads of heavy metals and nutrients were significantly higher within the Adélie penguin colony (p<0.05), with nitrate and phosphate exhibiting the most prominent differences (p<0.01). In both streams, discharge exhibited large fluctuations on both diurnal and daily time scales (P3 16.7 L s^{-1} to 53.3 L s^{-1}; C3 10.8 L s^{-1} to 14.7 L s^{-1}) and was correlated strongly with air temperature (P3 R=0.88, C3 R=0.81). The pH of all stream sites was circumneutral to basic (6.86 to 8.07). This research suggests that seasonal melt streams play a critical role in redistributing potentially toxic levels of heavy metals and nutrients from penguin colonies into the Southern Ocean.

Ornithogenic soil samples from the penguin colony had up to 27, 71, and six times higher arsenic, cadmium, and lead compared to two sampled control soils (p<0.05). Ammonium, total nitrogen, and total carbon were also significantly more enriched with up to 5727, 2454, and 484 times higher concentrations than the control soils (p<0.05). These enrichments were particularly significant with the upper 44 cm. Concentrations of arsenic in the topsoil (0 - 2 cm) and cadmium at soil depths 0 – 44 cm were present in concentrations that exceeded the Canadian ecological quality guidelines for soil. The pH of all soils was neutral to basic (7.78 to 9.86) reflecting the basic basalt parent material. These findings support previous research that ornithogenic soils are sites of heavy metal and nutrient accumulation.

Given the fluctuating nature of melt streams, both daily and seasonally, results are likely to be variable over longer time scales and therefore, more research is suggested to quantify this. Moreover, climate change disproportionately affects polar regions with expected temperature rises. Thus, understanding how melt streams intensify in flow, duration, and transport capacity is an essential area of investigation, to which this research provides important baseline data.

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1 Introduction

1.1 Background

Antarctica is generally considered 'pristine' due to its geographic isolation and short history of human occupation. Despite this, it has been dramatically affected by anthropogenic perturbations and is not exempt from the presence of human contaminants (Chu et al., 2019). Recent research has reported the presence of various contaminants, including organochlorines, polychlorinated biphenyls, pesticides (Wu et al., 2020), flame retardants (Lewis et al., 2020), microplastics (Aves et al., 2022), and increasing concentrations of heavy metals (HMs) (Webb et al., 2020).

Globally, HM production and emissions have increased since the 1940s due to human activities such as mining and fossil fuel combustion (Jaishankar et al., 2014; Nriagu, 1996). Consequently, these HMs have inevitably been deposited within the Antarctic marine and terrestrial environments (Tuohy et al., 2015), a problem exacerbated by the fact that polar regions are known repositories of anthropogenic contamination (Corsolini, 2009; Xie et al., 2022). This issue is of extreme cause for concern, given that many HMs serve no beneficial purpose within organisms, are highly toxic even in trace concentrations, and persist in the environment due to their resistance to degradation (Briffa et al., 2020; Tchounwou et al., 2012).

Anthropogenically derived HMs may be deposited onto terrestrial Antarctica through direct point sources, atmospheric deposition, and biological transportation (Webb et al., 2020). The role of biological transport is often overlooked, however, research in the Arctic has reported biologically transported fluxes which rival atmospheric fluxes (Blais et al., 2005). Biological transport involves the movement of HMs present within the marine food chain and their subsequent deposition onto the land (Blais et al., 2005). This is through biotic vectors, primarily seabirds such as Adélie penguins (*Pygoscelis adeliae*) (Bargagli, 2008; Blais et al., 2007; Puasa et al., 2021).

Adélie penguins forage primarily on krill in the open ocean; their high trophic position makes them susceptible to accumulating large quantities of HMs through bioaccumulation and biomagnification (Campbell et al., 2005; Chu et al., 2019; Xie & Sun, 2008). As they breed on land, metals are deposited within colonies as seabird-related substrates such as guano, feathers, eggshells and whole carcasses (Brasso et al., 2012; De La Peña-Lastra et al., 2022). This effect is amplified within Adélie penguin colonies, where birds return to the same nest sites for millennia, facilitating the accumulation of extensive ornithogenic, or 'bird-formed', soils (Emslie et al., 2007; Emslie et al., 2014). Therefore, ornithogenic soils within Adélie penguin colonies are known as sites of HM and nutrient accumulation (Liu et al., 2013; Nie et al., 2012; Sun & Xie, 2001). This is especially significant within Antarctica, where background nutrient levels are low, and environments are typically considered oligotrophic. Adélie penguin colonies play a crucial role in supporting a large portion of Antarctica's terrestrial ecological diversity, providing nutrients to support abundances of mosses, lichens, and invertebrates (springtails, mites, and roundworms) (Bokhorst et al., 2019; Polis et al., 1997). Therefore, Adélie penguin colonies can both nourish nutrient-poor regions and can potentially be sources of contaminants.

Adélie penguin colonies are situated on relatively scarce, ice-free areas along the Antarctic coast, often situated between large ice caps or glaciers and the sea (Emslie et al., 2007). In the austral summer, 24-hour radiation leads to the formation of glacial melt streams that persist for 6 to 12 weeks, with stream peak flow coinciding with the peak thawing of soil in mid-January (Howard-Williams et al., 1986). These streams flow through penguin colonies and erode ornithogenic soils before emptying into the sea. This is particularly important when we consider that many areas of Antarctica have been losing mass with higher rates of melting, which is accelerated by climate change (Oh et al., 2022; Rignot et al., 2019). These changes have significant repercussions for the surrounding ecosystems (Oh et al., 2022). Despite this, the movement of HMs and nutrients from penguin colonies into the wider environment has received limited attention.

1.2 Aims and objectives

The overarching aim of this thesis was to determine if seasonal melt streams within the Cape Bird northern Adélie penguin colony play a role in the transport of HMs and nutrients from penguin colonies and into the marine environment. To determine this, four objectives were developed:

1. Determine HM and nutrient concentrations within a penguin-influenced and a control stream, looking at how concentrations change over the length of the streams.
2. Characterise the physiochemical nature of the streams through pH, electrical conductivity (EC), and turbidity measurements.
3. Investigate the differences in stream discharge and how this affects HM and nutrient transport between the penguin-influenced and control streams.
4. Analyse soil HM and nutrient content of penguin-influenced and control soils in addition to their physiochemical nature.

This research will add to the growing knowledge of penguins' influence on their immediate environment and how colonies concentrate nutrients and HMs. This research is the first, to our knowledge, to investigate the role of ephemeral glacial melt streams in the movement of potentially toxic elements from the terrestrial to the marine environment, in an Antarctic penguin colony.

1.3 Thesis outline

Chapter 2 reviews the current literature surrounding the Antarctic environment, Adélie penguin colonies, and their interactions with HM and nutrients.

Chapter 3 provides a complete description of the field site used in this study and detailed methodology involved in field sampling, data collection, laboratory assays, and statistical analyses.

Chapter 4 presents the findings regarding the influence of melt water streams in HM and nutrient transfer from the Cape Bird northern colony. This is written in the form of a journal article, which may be adapted for publication. Because of this format, there will be some repetition between chapters 1-

5. Not all analyses conducted as part of this research are included within this paper. These subsidiary analyses are discussed briefly in the methods chapter and then included as supplementary information in the appendices.

Chapter 5 concludes the thesis, summarising the main findings of this research as well as discussing limitations and making recommendations for future research.

2 Literature review

2.1 Introduction

To understand the role melt water streams play in transferring HMs and nutrients, it is essential to investigate literature and relevant background material on their sources and movement within the environment, both presently and through the lens of future climate change within Antarctica. This review will first cover a broad view of the Antarctic environment, with particular reference to the threats of environmental climate change. It then focusses on the environment at Cape Bird, then information on Adélie penguin colonies and the formation of ornithogenic soils is provided. This is followed by a section on HM and nutrient cycles and presence within Antarctica, leading to a section on Adélie penguin colonies as secondary sources of enrichment. Lastly, environmental contaminant measurement and current research gaps within this field will be covered.

2.2 The Antarctic environment

Antarctica is isolated from other continents and has maintained its current geographical position for approximately 45 million years (Bargagli, 2008). The formation of the Drake Passage between the Antarctic Peninsula and South America about 30 million years ago allowed a connection between the Pacific and Atlantic oceans, leading to the establishment of the Antarctic Circumpolar Current (Bargagli, 2008). This current encircles Antarctica, separating it from warmer southward flowing currents, which enhances its isolation and cooling (Bargagli, 2008).

Today, most of the Antarctic continent is covered by a permanent ice sheet with an average thickness of two kilometres (Bargagli, 2008). Other ice-covered regions include ice shelves (extensions of the continental ice sheet on the ocean surface) and fast ice (sea ice attached to land or ice shelves) (Scientific Committee on Antarctic Research, 2009). Ice-free terrain comprises a mere 0.18 % of the continent and is often found in insular and discontinuous patches (Burton-Johnson et al., 2016; Convey et al., 2014). This ice-free terrain can take the form of exposed mountain peaks, glacial moraine slopes,

coastal beaches, and ice-free valleys (Lee et al., 2017). Permanently ice-free areas are essential breeding grounds for seals and seabirds, supporting most of Antarctica's ecological biodiversity (Lee et al., 2017).

Antarctica's climate stands out as one of its most distinguishing features, characterised by being both the coldest and the driest place on Earth (Convey et al., 2014; Zarinah, 1993). Average annual temperatures range from -10 °C on the coast, to -50 °C inland. The lowest recorded temperature on Earth, -89.2 °C, was measured at Russia's Vostok Station on the Polar Plateau in East Antarctica (Scientific Committee on Antarctic Research, 2009). These extremes are significantly influenced by Antarctica's high-latitude location, where the continent experiences 24-hour darkness in the austral winter and 24-hour daylight during the austral summer. Despite high summer sunlight hours, average temperatures remain low, primarily due to the substantial ice cover creating a high albedo effect, reflecting a significant portion of radiation into the atmosphere (Wendler & Kelley, 1988). The absence of clouds, especially in the continent's interior, further contributes to heat loss (Wendler & Kelley, 1988). Consequently, Antarctica sustains a negative radiation balance for most of the year, resulting in lower surface temperatures than the surrounding atmosphere (Wendler & Kelley, 1988).

Antarctica's aridity is primarily due to the intense cold, which keeps water in a frozen state (Convey et al., 2014). As air temperatures consistently remain below freezing, humidity levels are extremely low, and precipitation, primarily in the form of snow, is scarce (Zarinah, 1993). When snow occurs, it often sublimates directly to a gaseous phase, making it unavailable to biota (Convey et al., 2014). Antarctica is also characterised by strong katabatic winds, where gravity moves dense air from high elevations in the central continent down towards the coast, reaching speeds of up to 200 kph (Wendler & Kelley, 1988). Despite the cold and arid conditions, some coastal areas experience sufficiently warm enough temperatures to trigger ice caps and glacial melt during peak summer (Campbell & Claridge, 1987; Oh et al., 2022). This is particularly pronounced in the lower latitudes and coastal regions (Howard-Williams et al., 1986). The melting of ice caps at the edges of ice-free coastal areas results in glacial melt water

streams during the austral summer, creating localised areas with more favourable conditions for mosses and other forms of life to flourish (Yin et al., 2023). Melt streams within Antarctica tend to be intermittent and extremely variable (Howard-Williams et al., 1986).

The extreme isolation and harsh environmental conditions in Antarctica have shaped the evolution of a distinctive biota (Barnes et al., 2006). Although ice-free areas constitute a relatively small portion of the continent, they host diverse life forms, including algae, fungi, mosses, liverworts, and lichens (Lee et al., 2017; Rogers, 2007). The majority of fauna species in Antarctica are microscopic nematodes, tardigrades, rotifers, and microarthropods such as springtails (Convey, 2001; Hughes et al., 2015). The marine environment in Antarctica, in contrast to the terrestrial environment, is notably diverse, with the Antarctic benthos home to over 17,000 macrozoobenthic species and classified as having an intermediate species richness (Gutt et al., 2004). However, higher taxa like fishes and molluscs are underrepresented within the Southern Ocean (Clarke & Johnston, 2003). Antarctica is home to five species of penguin: the Adélie, Chinstrap *(Pygoscelis antarcticus),* Emperor *(Aptenodytes forsteri),* Gentoo *(Pygoscelis papua),* and Macaroni *(Eudyptes chrysolophus)* (Emslie et al., 2014). Chinstrap, Gentoo, and Macaroni penguins are only found on the Antarctic Peninsula and sub-Antarctic islands (Oceanites, 2021). Adélie penguins are the most abundant of the penguin species, found on both continental Antarctica, and the sub-Antarctic islands (Emslie et al., 2014).

The sub-Antarctic islands are found within a region of 45 ° to 60 ° and includes islands such as the Campbell islands, Macquarie island, and the South Shetland islands (Jelinski et al., 2023). Sub-Antarctic islands experience relatively warmer and more humid conditions. These milder conditions support an increased species richness (Jelinski et al., 2023).

2.2.1 Human activities in Antarctica

Historically, Antarctica's dominant human activity has been scientific research and science-related infrastructure, with 75 operating research stations (COMNAP, 2017). Most stations are situated on ice-free ground, an important habitat for birds, seals, terrestrial flora, and fauna, creating significant

ecological pressure and competition within coastal margins (Tin et al., 2008). The focus of activities on Antarctica has been shifting from science to tourism, the now fastest-growing activity (Tin et al., 2008). The number of tourist visitors per annum has been increasing, with 106,006 visitors in 2022 to 2023 (IAATO, 2022). Tours are usually via cruise vessels to accessible, ice-free, biologically rich locations, or those of historical value, with over 70 % cruise vessels landing (IAATO, 2022; Tin et al., 2008).

2.2.2 Antarctica and climate change

Climate change has disproportionately affected polar regions, with the Antarctic experiencing significant changes due to its complex interactions between the sea, land, ice, and atmosphere (Hancock et al., 2020; Smith Jr. et al., 2014). These effects are diverse and dynamic, with the most prominent current changes summarised below.

Rising temperatures have reduced ice sheet mass (Figure 1) (Smith et al., 2020) as well as sea ice extent and duration since 1976 (Figure 2) (Parmesan, 2006). Global ocean temperatures reached a new record high in 2021, contributing to the lowest recorded Antarctic sea ice extent in the following summer in February 2022 (Raphael & Handcock, 2022). There 1.2 million km^2 less sea ice than the previous minimum (Raphael & Handcock, 2022). Further reductions were seen in February 2023, with an additional 136,000 km^2 loss from the 2022 low (NSIDC, 2023).

Significant reductions in sea ice have been predicted to trigger a trophic cascade within Antarctic ecosystems (Parmesan, 2006). Reduced winter sea ice has been linked with lower krill (*Euphausia superba*) densities during the following summer (Atkinson et al., 2004). Krill is a vital food source for various fish, seabirds, and marine mammals, with changes to their populations causing ripple effects throughout the ecosystem (Parmesan, 2006). Furthermore, a reduction of sea ice extent directly affects penguins, including the Adélie and Emperor penguins (Parmesan, 2006). Both species are ice obligates, with Emperor penguins rearing their chicks on landlocked sea ice, while Adélie penguins rely on sea ice for the krill populations that breed and feed beneath it (Parmesan, 2006). Warming and the subsequent summer ice reduction have been correlated with declines in Emperor penguin populations,

resulting in a 50 % reduction in surviving adults from the Terre Adélie colony in the past 50 years (Barbraud & Weimerskirch, 2001).

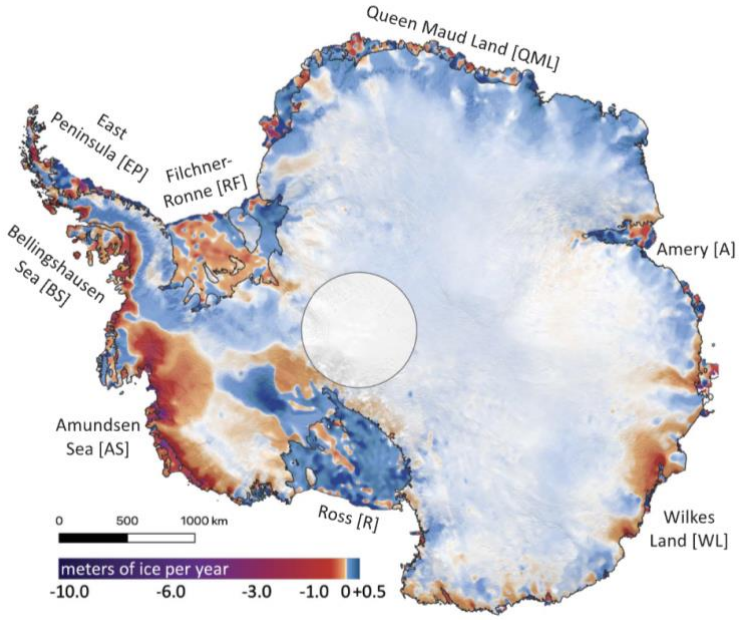

Figure 1: Ice mass loss of Antarctica from 2003 to 2019. Sourced from Smith et al. (2020).

In contrast, penguins like the Chinstrap and Gentoo species, who forage in the open ocean, have expanded their range southward due to diminishing ice (Clucas et al., 2014; Emslie et al., 1998). Interestingly, these species have been encroaching upon the Antarctic Peninsula for the last 50 years, despite palaeoecological evidence suggesting Gentoo penguins have been absent from this region for 800 years prior (Emslie et al., 1998). Rising temperatures have also led to an increase of invasive plant species, such as vascular grasses (*Deschampsia antarctica*) and cushion plants (*Colobanthus quitensis*), expanding abundance into novel ice-free areas during the last 27 years (Smith Jr. et al., 2014).

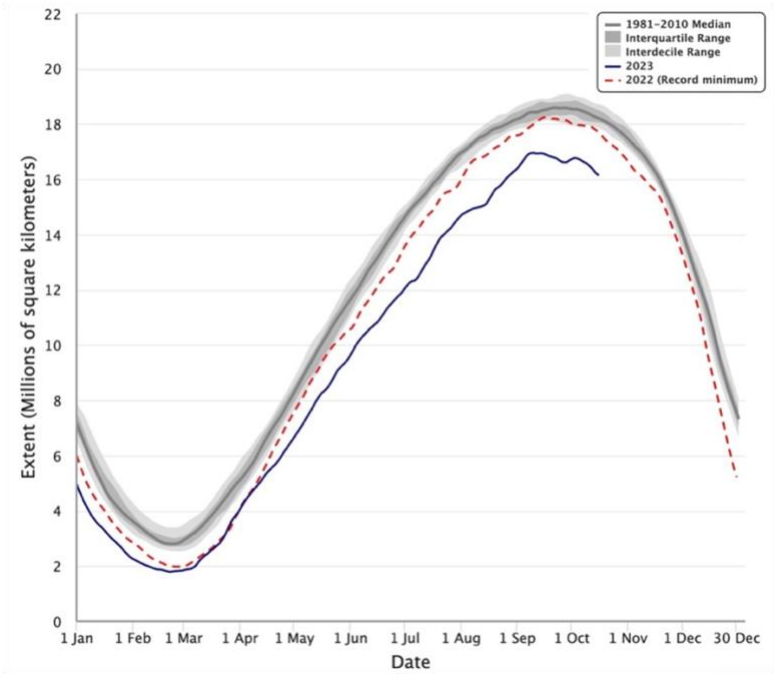

Figure 2: Antarctic sea ice extent (Ocean area with at least 15 % sea ice). Sourced from NSIDC (2023).

2.2.3 Antarctica and climate change future projections

Convey and Peck (2019) have identified three environmental factors expected to significantly affect Southern Ocean species: rising temperatures, altered sea ice patterns, and ocean acidification. There is a predicted 3.4 ± 1 °C increase of Antarctic interior temperatures (Mayewski et al., 2009). These rising temperatures can be attributed to increased absolute positive temperatures and cumulative positive degree days (Siegert et al., 2019). Elevated temperatures may lead to 17,267 km^2 of ice-free area in Antarctica being exposed by 2100 (Lee et al. (2017). This warming will also contribute to increased glacial melt, which not only releases a higher volume of water but may also increase the longevity of the melting season (Lee et al., 2017). Warming has also been predicted to influence sea ice extent, with models forecasting a further 30 % decrease within the next 70 years (Mayewski et al., 2009).

Southern Ocean ecosystems have some of the highest vulnerability to ocean acidification globally, with expected reductions in pH (Hancock et al., 2020). Ocean acidification results from

increased anthropogenic carbon dioxide (CO_2) emissions, which are subsequently absorbed by the world's oceans (Hancock et al., 2020). Polar regions are disproportionately affected by this acidification because of naturally low buffering and increased CO_2 solubility at lower temperatures (Hancock et al., 2020; Monteiro et al., 2020; Orr et al., 2005). Increasing levels of Southern Ocean CO_2 and the subsequent acidification have been shown to negatively impact phytoplankton, microalgae, invertebrates, and fish (Monteiro et al., 2020). Current and future changes within the Southern Ocean will have detrimental impacts at the organism and ecosystem levels, affecting species survival, abundance, and distribution (Mayewski et al., 2009; Monteiro et al., 2020; Smith Jr. et al., 2014). As a result of climate change, Cimino et al. (2016) have estimated that Adélie penguin populations will reduce by approximately 20 % by 2060.

2.2.4 Global importance of the Antarctic environment

Antarctica and the Southern Ocean provide crucial ecosystem services, one of the most important being climate regulation (Pertierra et al., 2021). Antarctica and the Southern Ocean act as repositories for heat, which has the effect of mitigating atmospheric warming and influences not only global temperatures but cyclone and storm cycles (Armour et al., 2016; Frölicher et al., 2015; Mayewski et al., 2009). Antarctica also plays a role in regulating global geochemical cycles, most notably those of the water and carbon cycle (Pertierra et al., 2021). Antarctica contains 70 % of the world's freshwater in frozen form, which maintains both ocean salinity and sea levels (Pertierra et al., 2021). Antarctica and the Southern Ocean also represent an important global carbon sink (Pertierra et al., 2021). The Ross Sea region in particular, is principal in CO_2 draw-down, comprising 25 % of Southern Ocean CO_2 draw-down during the austral summer (Arrigo et al., 2008). The importance of protecting the Southern Ocean is also emphasised from an ecological point of view, as it is a habitat of unique assemblages of flora and fauna species not found anywhere else (Pertierra et al., 2021).

Antarctica's uniqueness also extends to its political and international management, an exclusive feature that serves as a powerful symbol to the rest of the world (Tin et al., 2008). Antarctica

is governed internationally by the Antarctic Treaty System, which designates Antarctica and its surrounding islands south of 60°S latitude as a "natural reserve, devoted to peace and science" (Antarctic Treaty System, 2013; Tin et al., 2008). The Antarctic Treaty was signed by twelve countries in Washington DC on 1 December 1959 (Antarctic Treaty System, 2013). Since then, the Antarctic Treaty has expanded into the Antarctic Treaty System, which includes complementary management initiatives to accomplish the primary objectives of the treaty (Antarctic Treaty System, 2013). The legal text devoted to environmental issues is the Protocol on Environmental Protection to the Antarctic Treaty, also known as the Madrid Protocol, which was signed in 1991 and entered into force in 1998. The Madrid Protocol applies to all human activities in Antarctica, including tourism, science and non-governmental activities developed within the limits of the Antarctic Treaty. Following this text, all visitors must avoid the taking or harmful interference with flora and fauna, prevent the introduction of non-native species and diseases, follow all waste management provisions, comply with the regulations concerning Antarctic Specially Protected Areas (ASPAs) and Antarctic Specially Managed Areas (ASMAs), conduct all operations in a safe and environmentally responsible manner, and plan all activities to have no more than a minor or transitory impact on the Antarctic environment. Despite these stringent environmental regulations for all visitors travelling to Antarctica, anthropogenic contaminants (HM, organic pollutants, and microplastics) have still been recorded in Antarctic ice cores, marine sediments, tissues of Antarctic fauna, snow, and water samples (Aves et al., 2022; Bargagli, 2008; Chu et al., 2019; Corsolini, 2009)

2.3 The Cape Bird environment

Ross Island is situated within the Ross Sea region, which covers 960,000 km^2 of relatively shallow, yet ecologically rich marine environment (Arrigo et al., 2008) (Figure 3). The island itself is formed from four volcanoes; Mount Erebus (3, 704 m), Mount Terror (3, 262 m), Mount Terra Nova (2, 130 m), and Mount Bird (1, 800 m) (Dochat et al., 2000). Of these, Mount Bird is a shield volcano,

forming the northernmost part of Ross Island (Dochat et al., 2000). The Bird Ice Cap is centred atop Mount Bird, which drains into several outlet glaciers, the largest being Shell Glacier (Dochat et al., 2000).

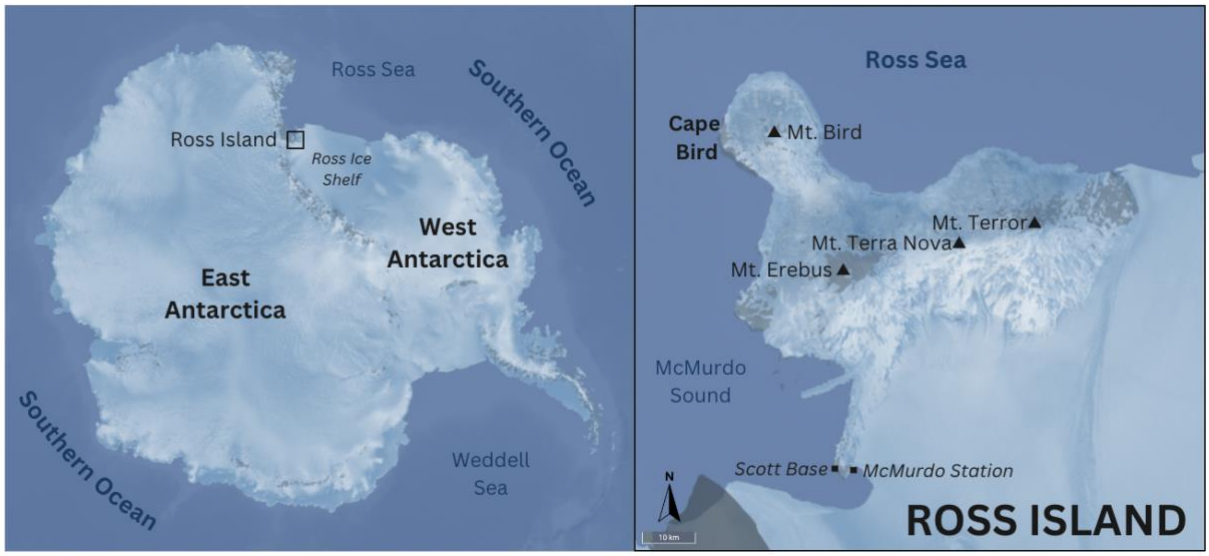

Figure 3: Key features of Antarctica and Ross Island. Imagery obtained Manaaki Whenua - Landcare Research (2023).

On Ross Island, soils exist where ice and snow cover are not permanent (Hewitt et al., 2021). Most soils within the Ross Sea region comprise a 'desert pavement' atop relatively unconsolidated and gravelly soil, whose active layer changes depth with seasonal thaw. This active layer may be over one meter deep during the austral summer or in warmer coastal areas. During the winter and in more southerly locations this active layer may be totally absent (soil is frozen to the surface). When present, this active layer sits atop ice-cemented permafrost, which is classified as having a temperature <0 °C for a minimum of two years (Hewitt et al., 2021).

The ice-free areas of Cape Bird run along the western base of Mount Bird, bordering the McMurdo Sound (Dochat et al., 2000). The ice-free terrain extends some 15 kilometres along the coast and is formed from poorly sorted diamicton, known as the Cape Bird Drift (Dochat et al., 2000). In locations north of the Shell Glacier, the Cape Bird Drift has been measured at over 30 m thick (Dochat et al., 2000). Cape Bird Drift mantles a bedrock of lava flows, breccias, agglomerates, pillows of trachyte,

and basalt (Dochat et al., 2000). Low-lying beaches at Cape Bird have five wave-washed sediment "beach ridges," formed from sharp crested gravel ridges that run parallel to the coastline (Dochat et al., 2000). These permanently ice-free zones along coastal beaches are home to multiple penguin colonies and provide habitat for South polar skua (*Stercorarius maccormicki*).

The climate of Ross Island experiences fluctuating and severe weather due to its position at the conjunction of three dissimilar air masses (Monaghan et al., 2005). However, Cape Bird's more northerly location subjects it to a higher degree of relatively warm and moist air from the Ross Sea, in contrast to more southerly Ross Island locations such as at Scott Base, Pram Point (Monaghan et al., 2005). The University of Wisconsin Space, Science, and Engineering Centre has established and maintained an automated weather station (AWS) at Cape Bird since 28 January 1991 (University of Wisconsin, 2017). Since its inception, this station has recorded a maximum air temperature of 7.6 °C, a minimum air temperature of -45 °C, and a peak wind speed of 44.8 m s^{-1} (University of Wisconsin, 2017).

2.3.1 Melt water streams

The 24-hour solar radiation during the austral summer contributes to increased temperatures and subsequent glacial melt (Campbell & Claridge 1987). Melting occurs on both the glacier surface and the terminal face (Campbell & Claridge 1987). This forms streams which flow for 6 to 12 weeks, with peak flow coinciding with peak soil thaw in mid-January (Cullis et al., 2014; de Mora et al., 1994; Peter et al., 1998). In the McMurdo Sound coastal area, streams formed by glacial melting are abundant and highly dynamic (Howard-Williams et al., 1986). The discharge of glacial melt water streams is highly variable on both an inter-annual and a daily basis The variation in McMurdo Dry Valleys stream flow is also substantial, with Peter et al. (1998) reporting a 5 to 10-fold difference in diurnal fluctuation. The primary controls on diurnal stream variation are sun position in relation to the glacial face and air temperature (Howard-Williams et al., 1986; Peter et al., 1998). Geomorphic factors such as channel width and steepness also strongly affect flow (Peter et al., 1998). Research on the physiochemical

properties of these melt streams also shows considerable variation within reported results. Melt waters within the McMurdo Sound and McMurdo Dry Valleys exhibit a wide pH range of six to 10 and have temperatures ranging from zero to 11 °C (de Mora et al., 1994; Howard-Williams et al., 1986). Glacial melt streams are also known to be relatively rich in inorganic nutrients, which reflects the chemistry of the source glacier and surrounding geology (Downes et al., 1986; Howard-Williams et al., 1986)

As liquid-water in Antarctica is a limiting factor of biota growth, glacial melt streams are crucial for providing fresh water to organisms (Yin et al., 2023). Consequently, they support some of the most abundant stands of mosses and algae, with McMurdo Dry Valley streams having extensive epilithic microbial mats and abundant benthic algae (Cullis et al., 2014; Yin et al., 2023). These microbial mats can survive many years in a freeze-dried state in the absence of water, becoming photosynthetically active when water returns (Cullis et al., 2014). Vegetated stream beds are also key habitats being associated with micro-herbivores such as protozoa, rotifers, nematodes, and tardigrades (Howard-Williams et al., 1986).

Melt streams within the Cape Bird region are characterised as short and steep, typically flowing for approximately one kilometre from the Bird Ice Cap and through unstable moraine before emptying into the Ross Sea (Downes et al., 1986; Howard-Williams et al., 1986). Due to the unconsolidated nature of Cape Bird parent material and bedrock, melt streams typically have high levels of suspended particles, which gives the Cape Bird streams a “grey appearance” (Howard-Williams et al., 1986). Downes et al. (1986) reported 606 ± 142 g m^{-3} of suspended sediment, measured one hour before the period of maximum flow; this contrasts to the “clear” waters of Fryxell Stream within the McMurdo Dry Valleys, with 1.7 ± 0.8 g m^{-3} suspended sediment when measured at peak flow. Like other Antarctic melt streams, those at Cape Bird typically flow between December and January, coinciding with maximum ice thaw (Howard-Williams et al., 1986). There are multiple melt streams observed to flow ephemerally through the Cape Bird northern penguin colony, which have been characterised as shallow, braided, and highly variable (Howard-Williams et al., 1986).

Stream discharge from a Cape Bird northern penguin colony melt water stream was measured by Howard-Williams et al. (1986). Early in the season, when flow was low, it was difficult to discern diel changes in discharge. However, as the melting season progressed and flow increased, strong diel patterns became evident. A minimum stream discharge of 2 L s^{-1} was recorded shortly after the minimum air temperature at 2 am, while maximum stream flow 162 L s^{-1} was recorded shortly after peak air temperature between 4 and 6 pm (Table 1). Howard-Williams et al. (1986) also investigated other melt streams within the McMurdo Sound, reporting differing timings of their diel discharge when compared to the Cape Bird stream; however, all discharges were correlated with air temperatures and the glacial aspect in relation to the sun. This research by Howard-Williams et al. (1986) highlights the importance of considering the timing of grab sampling with respect to capturing representative water samples.

Table 1: Previously recorded stream discharges of a melt stream at Cape Bird northern penguin colony. Measurements were recorded over the 18/19 January 1984 by Howard-Williams et al. (1986).

Date	Time of day	Discharge L s^{-1}
18 January 1984	0900	2
	1500	102
	2100	110
19 January 1984	0900	3
	1300	8
	1500	162

2.4 Adélie penguin colonies

2.4.1 Adélie penguin overview

Adélie penguins the most abundant penguin in Antarctica, with an estimated 3.79 million breeding pairs (Emslie et al., 2014; Lynch & LaRue, 2014). Found on the fringe of continental Antarctica and in the sub-Antarctic islands, Adélie penguins require ice-free terrain for breeding (Ainley & deLeiris, 2002; Emslie et al., 2014). Habitats for the nest sites also require yearly pack ice surrounding them in

winter and early spring, walking access to the sea, and slopes less than 45° with abundant gravel or stones for nest-building (Ainley & deLeiris, 2002). These sites are usually in proximity to glaciers, relying on glacial moraine for nest-building material (Ainley & deLeiris, 2002). Adélie penguins form colonies, which are an assemblage of demographically related penguins, breeding within an eight-kilometre radius (Ainley & deLeiris, 2002). There are an estimated 251 Adélie penguin colonies in Antarctica, with about a million breeding pairs across 20 active colonies in the Ross Sea region (Lynch &LaRue, 2014). Within these colonies, penguins occupy nest territories in smaller groups called 'sub-colonies' (Ainley & deLeiris, 2002). Their territory within the sub-colonies is contiguous and contentious, abutting from one to six other territories (Ainley & deLeiris, 2002). During peak breeding season, Adélie penguin colonies can have a density of up to 1.4 nests per m^2 (Beaulieu et al., 2009). These nests are built with stones, typically 3 to 5 cm in size, rebuilt atop previous years' remnant nests (Emslie et al., 2014). Most Adélie penguins return to the same nest each breeding season, and as a result, layers of ornithogenic soils form, representing 100 to 1000's of years of penguin activity (Emslie et al., 2014). The cold and dry environment facilitates mummification and the preservation of tissues such as eggshells, bones, feathers, and sometimes whole carcasses within these penguin soils (Emslie et al., 2007; Sun et al., 2013). Radiocarbon dating of organic remains from occupied and abandoned Adélie penguin colony nests within the Ross Sea region provides evidence of occupation beyond 45,000 cal. years BP (Emslie et al. 2007). Thus, Adélie colonies contain a natural archive of penguin tissue, their prey, and any contaminants consumed and can provide thousands of years of biological and biochemical information (Sun et al., 2013).

2.4.2 Adélie penguin breeding, foraging and diet

The high latitude location and short summer in Antarctica places many ecological constraints on breeding, and as a result, it is usually synchronised (Ancel et al., 2013). Adélie penguins reach sexual maturity at three to four years of age, where they select a mate and build a pebble nest within a few days of arrival onto land after winter migration. Nest sites are usually in a high, dry place, such as a

beach ridge (Ancel et al., 2013). Adélie penguins breed annually, having up to two eggs between each mated pair, with the young raised over three months (Ainley & DeMaster, 1980). After producing the egg/s, parents alternate incubation duties for approximately a month (Ainley & deLeiris, 2002). Then post-hatching, parents alternate foraging trips to feed their chicks for the first three to four weeks of its life. When the chicks have reached an age of four to seven weeks, they are left unguarded, often forming creches to minimise heat loss and predation by skua. At this stage, the parents are able to forage simultaneously as the chick grows rapidly. Once chicks are about nine weeks old, their down is replaced by waterproof plumage, allowing them to go out to sea in the winter. After chick fledging, parents undertake their annual moult, replacing their feathers over a period of 15 to 25 days. Throughout the breeding season, chick mortality is high at ~30 to 50 %, fluctuating with skua predation, food availability, and parental experience (Ainley & deLeiris, 2002).

Adélie penguins are a migratory species, however, the extent of migration depends on their colony location (Ainley & deLeiris, 2002). Penguins within lower latitudes may not migrate as winter temperatures are sufficiently warm enough (Ainley & deLeiris, 2002). Ross Island colonies and colonies within higher latitudes, however, have an annual migration, spending winter and early spring on pack ice (Ainley & deLeiris, 2002; Ballard et al., 2010). During the approximate time of the spring equinox, this initiates hyperphagia, persistent feeding and subsequent fattening prior to migration (Ainley & deLeiris, 2002). Adélie penguins then migrate to arrive at their colony during spring, where they remain for eight months until winter migration back to the pack ice. Juvenile penguins will usually return to their colony of hatching, with over half of penguins breeding within the same sub-colony of their natal site (Ainley & deLeiris, 2002). Penguins from Ross Island colonies, such as those within the Cape Bird, are thought to migrate the furthest, travelling approximately 2,800 km, which may contribute to higher exposure to contaminants (Ballard et al., 2010; Davis et al., 2001).

Modern Adélie penguins feed primarily on krill (*Euphausia superba*) and fish, such as the Antarctic silverfish (*Pleura-gramma antarcticum*) (Emslie & Patterson, 2007). The dependence of Adélie

penguins on a fish-based diet compared to krill, increases with increasing latitude (Emslie & Patterson, 2007; Hong et al., 2021). Adélie penguins at Cape Hallett within the Ross Sea region feed on mostly krill (65.5 %), whereas the Adélie penguins at the more northerly Inexpressible Island have a diet comprised of 47 % krill (Hong et al., 2021).

The earliest radiocarbon date for the occupation of Adélie penguins at Cape Bird is approximately 390 A.D, however, records show there may have been several abandonment and reoccupation events (Nie et al., 2015). Manaaki Whenua New Zealand Landcare Research has conducted aerial surveys of penguin populations at 39 penguin colonies on Ross Island. The most recent available data from 2019 shows that the total population at Cape Bird was 72,733 breeding pairs split across three colonies: the northern (50,358 breeding pairs), middle (4,476 breeding pairs) and southern (17,899 breeding pairs) colonies (Lyver, 2020) (Figure 4).

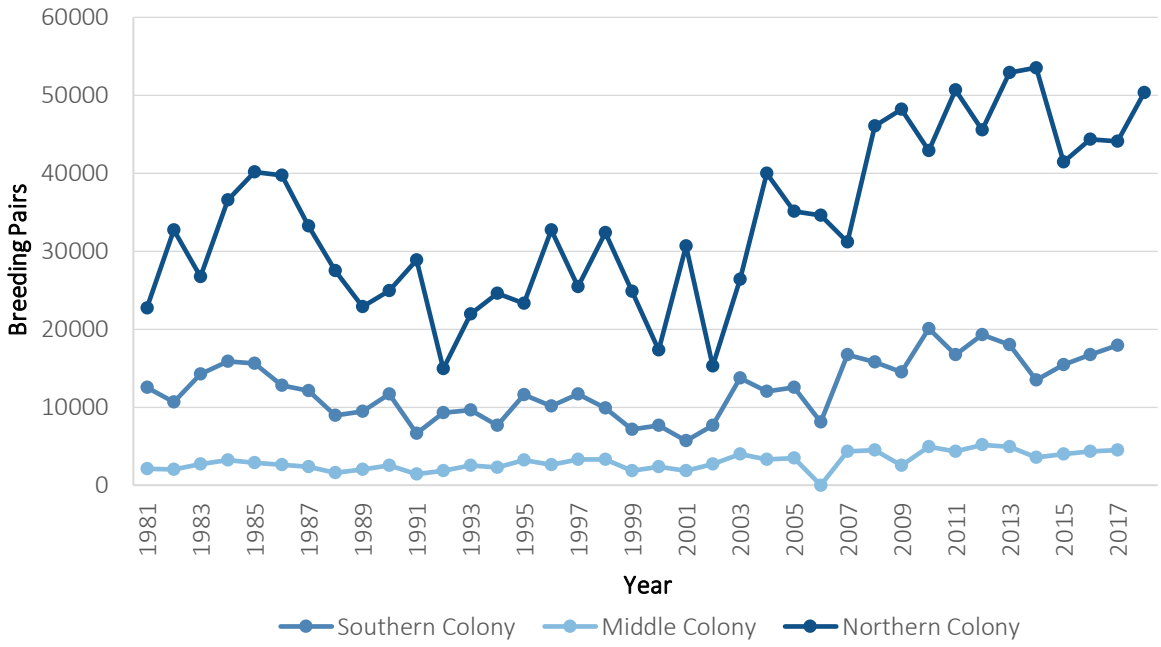

Figure 4: Aerial survey of Adélie penguin breeding pair population at Cape Bird colonies from 1981 to 2019. Data since 2019 is unavailable due to Covid-19. Sourced from Lyver (2020).

2.4.3 Ornithogenic soils

The term 'ornithogenic soils' was first used by Russian biologist E. E. Syroechkovsky (1959) to describe Adélie penguin soil at Haswell Island, Antarctica. It has since been used to categorise soils from a range of climates that are heavily influenced by bird activity and their organic material.

Ornithogenic soils are formed from bird guano accumulation where marine birds, such as penguins, congregate for nesting (Heine & Speir, 1989). While on land, they excrete guano, transferring organic matter and potential contaminants from the sea, where they feed almost exclusively, onto the terrestrial environment (Heine & Speir, 1989). The pygoscelis penguin genus (Adélie, Chinstrap, and Gentoo) has been observed to deposit 10 kg of fresh guano per m^2 (Tatur & Mayrcha, 1984). The Adélie penguin behaviour of building nests with facilitates the deposition of material, which ultimately forms the ornithogenic soil (Emslie et al., 2014; Hofstee, 2006). The resulting ornithogenic soil has a well-defined layer of guano, which sharply overlies unconsolidated mineral soil (Ugolini, 1972). Guano accounts for 85 % of organic matter left by penguins on land but the incorporation of preserved bones, eggshells, feathers, and whole carcasses into an ornithogenic soil profiles is common (Burger et al., 1978; Emslie et al., 2014). The surface layer of the ornithogenic soil may also form a hard crust due to the extreme desiccation and compression from penguin traffic (Lyver et al., 2014). Skua's also nest in areas surrounding penguin colonies, and their presence can also supplement organic matter to the soils (Lyver et al., 2014).

The penguin occupation changes both the physical and chemical properties of the soil, including altering particle size distribution, reducing soil pH, and increasing nutrients such as inorganic nitrogen, phosphorous, and organic carbon content (Orchard & Corderoy, 1983; Simas et al., 2007; Ugolini, 1972). Ornithogenic soils have some of the most abundant organic matter contents of Antarctic soils (Orchard & Corderoy, 1983; Speir & Cowling, 1984). This localised increase of nutrients within ornithogenic soils is a result of a penguin diet high in protein, differing chemically from other soils with a high organic carbon content, where organic carbon is derived mainly from plants (Orchard &

Corderoy, 1983; Speir & Cowling, 1984). Ugolini (1972) also reported high salinity content within ornithogenic soils due to the proximity to the sea, aridity, and penguin nasal salt excretions.

Within penguin colonies, the ornithogenic soils build up to form characteristic mounds (Figure 5). These mounds are areas where penguins deposit most of their guano atop previous years' nesting sites (Hofstee, 2006). Consequently, the deepest and oldest orthogenic soils are present at the bottom of the mounds. These raised areas offer protection from the seasonal melt water streams and keep the penguin chicks, whose downy feathers lack waterproofing, above deep snow (Hofstee, 2006). Abandoned penguin mounds usually have a surface of guano only as pebbles have been removed by other nesting penguins (Lyver et al., 2014). Between mounds are low-lying 'inter-mounds' which are comprised mostly of beach gravels and sand, however, may have a crust of surface guano formed from adjacent mound run-off (Hofstee, 2006).

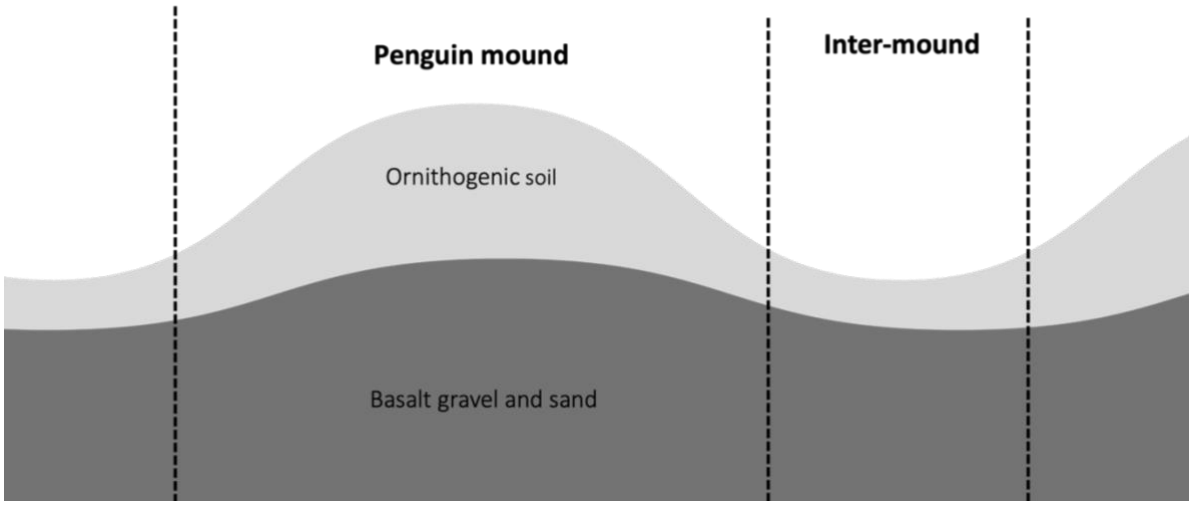

Figure 5: Diagram of the relationship between penguin mounds and inter-mounds in ornithogenic soils. Figure adapted from Hofstee (2006).

All species of pygoscelis penguins form ornithogenic soils, however, it is the ornithogenic soils from Adélie colonies that are deeper and more extensive (Emslie et al., 2014). The colder and more arid environment of Adélie penguin colonies facilitates soil preservation as microbial decomposition is slower compared to the warmer and more humid environments of the Gentoo and Chinstrap penguins

(Heine & Speir, 1989; Orchard & Corderoy, 1983). Therefore, there is a higher accumulation of guano in Adélie penguin nesting areas (Heine & Speir, 1989; Orchard & Corderoy, 1983). Chinstrap and Gentoo penguins also nest on exposed ridges and slopes, which is less conducive to soil formation than the relatively flat beach ridges of the Adélie penguin (Emslie et al., 2014). As a result, the oldest soils from Chinstrap and Gentoo pygoscelis penguins have been dated at ~1000 cal. years BP, however, Adélie penguins have soils of over 45,000 cal. years BP in age (Emslie et al., 2010; Emslie et al., 2007).

2.5 Heavy metals in Antarctica

Heavy metals (including metalloids) are those that are naturally found with a high density (>5 g cm^{-3}) (Jaishankar et al., 2014). Also known as "trace metals" due to their natural presence in low concentrations, HMs include essential elements such as copper, cobalt, iron, magnesium, manganese, nickel, and zinc (Tchounwou et al., 2012). Living organisms require essential HMs in low concentrations to maintain and operate biochemical and physiological functions. If levels of HM concentration exceed the tolerance threshold of organisms, this can lead to toxicity. Heavy metals also include non-essential elements such as arsenic (As), cadmium (Cd), mercury (Hg), lead (Pb), and uranium, which are not necessary to organisms at any concentration. These may be acutely toxic and carcinogenic even in extremely low quantities, often in the parts per million (ppm) or parts per billion (ppb) concentration range (Tchounwou et al., 2012). In the cases of both essential and non-essential HMs, toxicity depends on the element and a suite of interacting chemical and biological factors including, exposure time, concentration, and the physiology of the exposed species (Jaishankar et al., 2014).

The extreme toxicity of HMs is due to their interaction with biological systems and imposition at protein and natural binding sites, often displacing essential metals (Jaishankar et al., 2014). However, the specific mechanisms of HM interactions are not always well understood (Jaishankar et al., 2014; Tchounwou et al., 2012). In general, HM presence leads to malfunctioning and apoptosis of cells involved in key interactions, such as DNA replication and metabolism (Tchounwou et al., 2012). The resistance of HMs to degradation and, often, detoxification also increases their threat, with HMs

accumulating within vital biological organs, including the heart, brain, and kidneys, where they disrupt normal functioning (Briffa et al., 2020; Singh et al., 2011). As a result, HM toxicity is linked to various diseases and carcinogenesis, with the highest degree of toxicity for As, Cd, Cr, Pb, and Hg (Tchounwou et al., 2012). These five metals are internationally recognised as having high public health and ecological significance, with environmental HM contamination being a serious concern (Ali et al., 2019; Tchounwou et al., 2012).

Globally, HM production and emissions have increased significantly since the 1940s (Nriagu, 1996). Despite Antarctica's geographic isolation, increases in global HMs mean that it is inevitable that they are deposited into and accumulate within the Antarctic marine and terrestrial environments (Tuohy et al., 2015; Webb et al., 2020).

2.5.1 Sources of heavy metals in Antarctica

According to Webb et al. (2020), there are four possible sources of metals in terrestrial Antarctica: natural geologic processes, direct human activities, long-range atmospheric deposition (LRAT), and biological transportation.

Heavy metals may be present from naturally occurring geological processes, including erosion, weathering of the earth's crust, and volcanic eruptions (Jaishankar et al., 2014). In Antarctica, where many glaciers exist, glacial expansion and retreat may be an important geologic source of HMs (Webb et al., 2020). The movement of glaciers erodes the underlying bedrock, releasing metals that are potentially transported in melt run-off (Webb et al., 2020).

Historically, inputs from direct human activity were generally low, as the extreme environment discouraged Antarctic and Southern Ocean exploration (Chu et al., 2019). However, since the early 1900s, the first anthropogenic impacts began with hunting and exploring (Chu et al., 2019; Frenot et al., 2005). Currently, the 64 permanent research stations and tourist activity present the main source of locally derived point-source contamination (Chu et al., 2019). An enhancement of contaminant input

around research stations and popular tourist locations is related to aging station infrastructure, power generators, aircraft, ship traffic, and vehicle or vessel fuel spills (Bargagli, 2008; Chu et al., 2019; Cossa et al., 2011; Webb et al., 2020). Historic contamination sources from bases may also contribute to legacy HMs, such as from the nuclear power plant (PM-3A) at McMurdo Station, Ross Island (Bargagli, 2008). This was operational between 1964 and 1972. Former waste disposal sites associated with the day-to-day operations of national research stations also add HMs into the environment. Until the Madrid Protocol came into force in the 1990s, waste was disposed of at landfill sites close to stations, disposed of into the sea, or burnt in the open air (Bargagli, 2008).

There is increasing interest in understanding how airborne contaminants move and are deposited through LRAT. Long-range atmospheric transport is the deposition of aerosols more than 100 km in distance (Bargagli, 2008). In Antarctica, LRAT is exacerbated by katabatic winds from Antarctica's interior, which is compensated by a flow of air towards the South Pole in the high troposphere. This transports contaminants to the southern polar atmosphere where precipitation, often as snow, effectively deposits metals onto continental Antarctica and the Southern Ocean (Bargagli, 2008). The deposition of contaminants via LRAT is influenced by various factors, including geographical features, proximity to the source, temperature, and physiochemical properties (Corsolini, 2009). Polar environments are disproportionately affected by increased deposition as colder temperatures increase condensation; thus, polar environments become sinks for global contaminants (Corsolini, 2009; Tuohy et al., 2015). In this way, HMs originally from other continents within the southern hemisphere may be deposited onto terrestrial Antarctica and in the Southern Ocean (Bargagli, 2008; Corsolini, 2009; Tuohy et al., 2015). Planchon et al. (2002) have shown that chromium, copper, Pb, uranium, and zinc concentrations within Antarctic snow have increased up to 18-fold within the last few decades as a result of southern hemisphere enrichment from non-ferrous metal mining emissions (Planchon et al., 2002).

Biological transport is the movement of contaminants present within the marine food-chain, from both anthropogenic and natural sources, and their subsequent deposition onto the land in Antarctica through biotic vectors, primarily seabirds (Figure 6) (Puasa et al., 2021). Biological transport is possible through the biological persistence of HMs and long biological half-lives, which allows HMs to bioaccumulate and/or biomagnify (Campbell et al., 2005). Bioaccumulation is the build-up of a persistent contaminant within the lifetime of a single organism (Puasa et al., 2021). This occurs when metal uptake is faster than metabolization and excretion (Puasa et al., 2021). The extent of bioaccumulation depends on the metal, exposure, the elimination rate of the receiving organism, and its lifespan (Ali et al., 2019). Adélie penguins are reasonably long-lived (10 to 20 years) which provides a longer time for HM accumulation. Biomagnification also occurs in tandem with bioaccumulation, where HMs and pollutants are transferred to higher trophic levels within food chains in increasing concentrations (Ali et al., 2019). Biomagnification results in a disproportionate toxicological effect in higher and apex predators, such as penguins (Puasa et al., 2021).

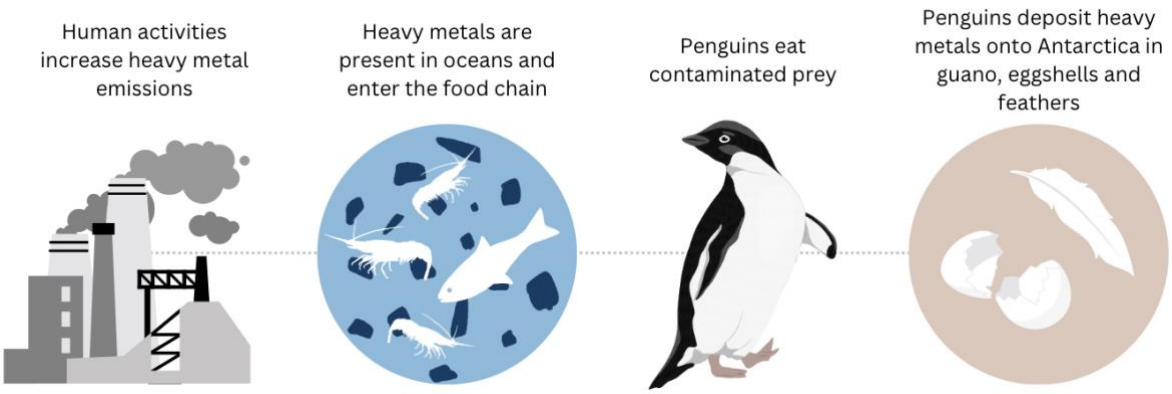

Figure 6: Biological transport of anthropogenic HMs into the Antarctic environment.

The concept of biomagnification was first recognised within insecticides after the analysis of dichlorodiphenyldichloroethane (DDT) within marine-seabird based food web (Córdoba-Tovar et al., 2022). Since then, biomagnification has been validated and extended to other chemicals and food webs, including the heavy metals Cd, Hg and Pb (Córdoba-Tovar et al., 2022; Raj & Das, 2023), and persistent

organic pollutants such as polychlorinated biphenyls and microplastics (Saley et al., 2019; Wu et al., 2022).

Determining As biomagnification within food webs has been controversial, with conflicting results between studies (Lou et al., 2016). Biomagnification is a complex process affected by a multitude of factors such as species physiology, environmental conditions, chemical characteristics, and trophic structure (Córdoba-Tovar et al., 2022; Du et al., 2021). Due to this, As may not exhibit biomagnification in all food webs and environments (Córdoba-Tovar et al., 2022). In some cases, the conclusion of the absence of biomagnification within As may be derived from the wrongful interpretation of results. Higher As concentrations in lower trophic levels may not always indicate the absence of biomagnification and may be a result of increased species-specific bioaccumulation. Further disagreement may have also arisen because the biomagnification potential of As is less when compared to other well-known biomagnifying metals such as Hg. Therefore, Córdoba-Tovar et al. (2022) suggest that the biomagnification mechanism differs between As and Hg, causing dissimilar results when comparing the two. Several studies have resolved controversy and demonstrated the presence of As biomagnification within Southern Ocean and penguin food webs (Espejo et al., 2017; Furtado et al., 2019; Jerez, Motas, Benzal, Diaz, Vidal, et al., 2013). Arsenic biomagnification within penguins is thought to be enhanced due to its high affinity within krill, which have been demonstrated to concentrate As and Cd several times higher than in surrounding waters (Metcheva et al., 2011; Mirzoeva et al., 2022).

The biological transport of contaminants through the mechanisms of bioaccumulation and biomagnification is often ignored; however, in the Arctic it has been shown to outweigh the atmospheric flux of contaminants, making it an important yet often overlooked route of HM contamination (Blais et al., 2005). Despite the perception of the Antarctic as pristine, due to these mechanisms of contaminant transport and deposition, the presence of HMs from anthropogenic origins is rising (Chu et al., 2019).

2.5.2 Key heavy metals in Antarctica

Arsenic, Cd, and Pb have been chosen as key heavy metals. This is because they have been recorded in increasing concentrations in Antarctica, are biogenically enriched within colonies, and are highly toxic in low quantities (Brimble et al., 2009; Chu et al., 2019; Metcheva et al., 2011; Szefer et al., 1993; Xie & Sun, 2008). These key HMs, their likely sources, environmental behaviour, toxicity, and presence within penguins are summarised below, followed by their occurrence within ornithogenic soils.

Arsenic is the 20th most abundant element on earth (Jaishankar et al., 2014). It is classed as a metalloid, as it has metal and non-metal characteristics (Kumar et al., 2022). Volcanic emissions are the most important source of natural As; however, human activities such as the use of pesticides, mining, and fossil fuel combustion vastly outweigh natural emissions (Schwanck et al., 2016). Anthropogenic sources contribute 24,000 tonnes of As to the global atmosphere per year (IARC, 2012; Schwanck et al., 2016). In highly industrialised areas, more than 98 % of atmospheric As inputs are from anthropogenic sources (Schwanck et al., 2016).

In natural environments, the chemistry of As is determined by its two redox forms, arsenite (As III) and arsenate (As V) (Nriagu et al., 2007). Arsenic V is the most commonly found form of As within soil and water; however, As III is the most mobile and toxic (Nriagu et al., 2007). Arsenic is easily converted between forms based on environmental conditions (Kumar et al., 2022). At low pH and high redox potentials, adsorption of both forms of As to Fe and Al oxides immobilise As (Nriagu et al., 2007). Conversely, high pH and redox potential favour dissolved species (Nriagu et al., 2007). When environmental redox potential is stable, even small changes in pH have a large effect on the solubility of free-hydrated and absorbed As ions (Elder, 1988). This is particularly important as Antarctic melt streams are characterised by their low buffering capacity (Nędzarek et al., 2014). Many common As compounds have a high water solubility, therefore, As contamination of water bodies such as lakes, rivers, groundwater, and precipitation is a serious health concern (Chung et al., 2014).

Arsenic limits many fundamental biochemical and metabolic processes (Abbas et al., 2018). In plants, one of the most dangerous effects is the production of reactive oxygen species, which cause irreparable damage to essential macromolecules and plant metabolism (Abbas et al., 2018). With phytoplankton amongst some of the most sensitive species to As (Abbas et al., 2018; Neff, 1997). In humans, As has been linked to several major diseases, such as cancer, diabetes, and neurodegeneration (Fatoki & Badmus, 2022). Studies have shown that As levels within penguins were highest in soft tissues and in guano (Jerez, Motas, Benzal, Diaz, & Barbosa, 2013; Metcheva et al., 2011). It is supposed that diet is the key route of exposure with correlations between As concentrations in stomach contents and guano (Jerez, Motas, Benzal, Diaz, & Barbosa, 2013). Several studies have recorded high levels (>5 μg g^{-1} dry weight) of As in guano (Ancora et al., 2002; Metcheva et al., 2006; Yin et al., 2008), with Sparaventi et al. (2021) notably recording up to 7.4 μg g^{-1} dry weight in Chinstrap penguin guano.

Cadmium is non-biodegradable and widely distributed within the environment, occurring naturally from rock weathering, forest fires, and volcanoes (Khan et al., 2022; Kumar et al., 2022). Globally, primary sources of Cd are from Cd-nickel battery manufacturing, mining, and plastic stabilisers (Khan et al., 2022). According to Bi et al. (2006) 90 % of Cd emissions in the environment are from human sources. Cd is most commonly found in divalent form or in compounds with oxygen and sulphur. Cd compounds are generally hydrophilic, and therefore enter the food chain easily (Khan et al., 2022).

Within soils, Cd may be held as free hydrated ions within solution, in complexes with organic matter, absorbed to clays and metal oxides or oxyhydroxides and is often found in association with Pb or zinc (Kubier et al., 2019). The bioavailability of Cd is directly related to soil organic matter content, with Cd availability decreasing with increasing organic matter (Khan et al., 2017; Kumar et al., 2022). This is due to an increase of ion exchange capacity (Khan et al., 2017; Kumar et al., 2022). Cadmium binding to oxide and oxyhydroxide surfaces is also directly linked to soil pH and salinity which affects the surface charge and thus binding ability (Appelo & Postma, 2004; Greger et al., 1995). Therefore, high clay content, high organic matter, high pH, and low salinity favour Cd adsorption and

immobilisation (Greger et al., 1995; Kubier et al., 2019). In fresh water Cd^{2+} is the dominant species and preferentially remains in solution at a pH of <6.5 (Kubier et al., 2019). Cd also forms water-soluble complexes with anions such as chlorine and sulphate, as well as with dissolved organic matter (Kubier et al., 2019).

Cadmium is easily taken up by plants, affecting their growth and morphology (Sanità di Toppi & Gabbrielli, 1999). In animals, Cd is a known carcinogen, provoking DNA damage and altering the expression of genes (Khan et al., 2022). At a cellular level, it causes disruption through competition with calcium (Ca^{2+}) at enzymatic locations (Campbell et al., 2005). Once consumed, Cd is stored in the liver and kidneys, and within penguins, it has been seen to accumulate within feather vanes (Campbell et al., 2005; Sun et al., 2020). Jerez, Motas, Benzal, Diaz and Barbosa (2013) have also noted high Cd accumulation in penguin chick soft tissues (hepatic and renal) and feathers despite their relatively short life spans. They concluded that Cd exposure began during egg development, where it was passed on from the mother. Within adult Gentoo penguins, feathers and excreta were the most common forms of Cd elimination, with an average Cd concentration in guano almost twice as high as in feathers (Metcheva et al., 2011). Some of the highest accounts of Cd within penguin guano have been from Adélie penguins at Terra Nova Bay, Ross Sea region, with 5.8 μg Cd g^{-1} dry weight (Ancora et al., 2002; Sparaventi et al., 2021). Espejo et al. (2014) investigated Cd concentrations in penguin guano over a six-year time frame and found a three-times increase in guano Cd over that period.

Lead is naturally occurring and abundant within the earth's crust, released through rock weathering and volcanic processes (Nriagu, 1996). Anthropogenic sources account for 60 % of the Pb present globally, with a history of Pb pollution that spans over four millennia (Renberg et al., 2000; Van de Velde et al., 2005). Currently, some of the largest sources of Pb pollutants are fuel, paint production, mining, manufacturing of batteries, cosmetics, and ammunition (Jaishankar et al., 2014). Prior to the prohibition of leaded petrol in 2021, 100,000 to 200,000 tonnes of Pb was emitted annually from vehicle exhausts in the United States alone (Jaishankar et al., 2014). The widespread use of Pb globally

has seen Pb deposited over Antarctica as revealed by increasing concentrations within Antarctic snow and ice cores (McConnell et al., 2014; Van de Velde et al., 2005).

In soils, Pb may occur as free metal ions, complexes with inorganic anions, as inorganic ligands, or absorbed onto particle or clay surfaces (Pourrut et al., 2011) When Pb is incorporated into soils, it has low mobility due to strong binding with humic and fulvic acids within organic matter, causing Pb accumulation in organic matter rich soils (Cecchi et al., 2008; Harrison & Laxen, 1984; Pourrut et al., 2011). Lead often reacts with available anions such as phosphate, sulphate, and carbonate, forming Pb salts (Harrison & Laxen, 1984). One of the most stable and insoluble Pb salts is pyromorphite ($Pb_5(PO_4)_3Cl$), which is formed when phosphorous is present (Cotter-Howells, 1996). Therefore, Pb solubility and bioavailability in soil increase with low cation exchange capacity, low organic matter, low phosphorous content, and low pH (Harrison & Laxen, 1984). In water, Pb mobility and distribution is closely controlled by its chemical speciation, which depends on the nature of the waterbody (Harrison & Laxen, 1984). In circumneutral conditions, Pb solubility and toxicity is also strongly affected by hardness (high calcium and magnesium content) as Pb^{2+} strongly complexed by carbonate in water (Harrison & Laxen, 1984).

Within biota, Pb^{2+} replaces key divalent cations such as magnesium (Mg^{2+}), calcium (Ca^{2+}), and iron (Fe^{2+}) which disrupts normal metabolism and cell function (Jaishankar et al., 2014). Lead can accumulate in plants, leading to adverse effects, including reduced germination, growth, nutritional uptake, photosynthesis, and respiration inhibition (Pourrut et al., 2011). Within humans, Pb toxicity affects almost all bodily functions, is a carcinogen, and a neurotoxin (Jaishankar et al., 2014; Wani et al., 2015). Its strong affinity to calcium leads Pb to readily accumulate within the bones, feathers, and eggshells of penguins (Jerez, Motas, Benzal, Diaz, & Barbosa, 2013; Metcheva et al., 2006). A study by Metcheva et al. (2011) revealed feathers and eggshells of Gentoo penguins had an average of 1.52 μg Pb g^{-1} dry weight and 0.68 μg Pb g^{-1} dry weight, respectively (Metcheva et al., 2011). Espejo et al. (2014)

reported concentrations of up to 2.9 μg Pb g^{-1} dry weight in guano and, over a six-year time frame, found an almost 9-fold increase within the guano of Gentoo penguins.

Due to how heavy metals accumulate within penguin tissues, they have been used as bioindicators (Brasso et al., 2012; Liu et al., 2013). Bioindicators are living organisms that measure the health of the ecosystems they inhabit, gauging environmental contamination and the effect of various perturbations (Carravieri et al., 2013; Puasa et al., 2021; Rajpar et al., 2018). Several studies, including Brasso et al. (2012), Carravieri et al. (2013), and Metcheva et al. (2006), have demonstrated the successful use of penguins for monitoring heavy metals and potentially toxic substances within their environment.

2.5.3 Ornithogenic soils and key heavy metals

Heavy metals are biologically transported onto the land by Adélie penguins and deposited within guano, feathers, eggshells, and carcasses (Liu et al., 2013). Due to the extreme cold and aridity in Antarctica, which facilitates the preservation of biological material, HMs are incorporated within the ornithogenic soils (Liu et al., 2013). Combined with the high trophic position of Adélie penguins, exacerbating bioaccumulation and biomagnification, Adélie penguin colonies become sites of heavy metal accumulation (Liu et al., 2013; Otero et al., 2018). In the Antarctic, where many ecosystems are considered oligotrophic, inputs from seabirds create stark contrasts to the background HM and nutrient levels of the surrounding environments (Liu et al., 2013).

Several studies have investigated the HM enrichment of ornithogenic soils, with concentrations of As, Cd, and Pb summarised in Table 2. Castro et al. (2021) investigated HM content in Antarctic ornithogenic soils associated with Adélie penguins, Southern giant petrel (*Macronectes giganteus*), Gentoo, and Chinstrap penguins, compared to control soils. An enrichment of Pb up to 23 times was found in ornithogenic soils compared to non-ornithogenic soils because of penguin activity (Castro et al., 2021). Studies have also shown a high degree of variation in HM concentration in ornithogenic soils. It has been noted that samples near point sources of contamination, such as areas of high research

station density and high ship traffic, had higher concentrations of HMs, implying their increased biological transport (Jerez et al., 2011; Santamans et al., 2017). Santamans et al. (2017) detected extremely high Pb concentrations in Antarctic Peninsula soil (87.55 μg Pb g^{-1} dry weight) located near the Hannah Channel, a commonly used tourist passage (Lynch et al., 2010). The species of penguin present may also have an impact on transfer and thus concentrations because of differences in diet; however, results have been inconclusive. Comparisons between Gentoo and Chinstrap species have not shown differences between transport efficiency and HM soil enrichment (Espejo et al., 2014; Santamans et al., 2017). However, Jerez et al. (2011) noticed interspecies differences in HM accumulation within feathers, but it is not known if these differences in penguins are correlated with differences in soil concentrations.

Table 2: Previously recorded heavy metal concentrations in Antarctic penguin-influenced ornithogenic soils. Concentrations reported in μg g^{-1} dry weight unless otherwise specified.

Reference	Location	Sample	As	Cd	Pb
			μg g^{-1}	μg g^{-1}	μg g^{-1}
a	Antarctic Peninsula	Soil	-	-	11.25
b	South Shetland Islands	Soil	8.09	4.92	1.45
c	Cape Hallett	Soil	13.00 ppm	16.00 ppm	6.00 ppm
d	South Shetland Islands	Soil	6.49	1.84	5.69
d	Deception Island	Soil	3.11	1.66	1.99
d	Antarctic Peninsula	Soil	3.56	2.38	87.55

a: Castro et al. (2021), b: Cipro et al. (2018), c: Hofstee (2006), d: Santamans et al. (2017)

2.6 Nutrients in Antarctica

Nitrogen (N) and phosphorous (P) are essential elements for all life forms. Their corresponding biogeochemical cycles are some of the most important in the biosphere as they influence primary production within the marine and terrestrial environment (Otero et al., 2018). However, despite their importance, a thorough understanding of their cycles is lacking, particularly concerning nutrient dynamics in polar environments (Otero et al., 2018). The current state of knowledge on the cycles and pathways for N and P is summarised below with specific reference to the Antarctic environment and nutrient sources. This is followed by the occurrence of N and P within ornithogenic soils.

2.6.1 Nitrogen cycle

Nitrogen is required for various essential molecules and biochemical reactions and is a critical constituent of proteins, biological macromolecules, and chlorophyll (Zhang et al., 2020). The N cycle is a biogeochemical process where N is exchanged between soil, organisms, the atmosphere, and the ocean. The cycle begins with fixation, which converts atmospheric N into biologically available form. Despite N being the fourth most abundant element by biomass, it is often found as gaseous atmospheric N in the form of dinitrogen (N_2) (Figure 7), Atmospheric N is inert and unavailable to most organisms because of the chemical's strong triple covalent bond (Zhang et al., 2020). In natural systems, most organisms obtain biologically available forms of N, such as ammonia (NH_3) and ammonium (NH_4^+), from lightning or biological fixation of N by microbial organisms (Otero et al., 2018). In Antarctic soils, the Cyanobacteria, *Nostoc commune*, is one of the predominant N fixers (Ortiz et al., 2020). Nitrification is the sequential conversion of NH_3 or NH_4^+ to nitrite (NO_2^-) then nitrate (NO_3^-) (Pascoal et al., 2022). This is an aerobic process usually undertaken by prokaryotes. Nitrite and NO_3^- can be subsequently denitrified under anaerobic conditions (Pascoal et al., 2022). This is the stepwise reduction of NO_2^- into N_2 gas, returning N to the atmosphere and removing bioavailable N from the system (Hayashi, 2022). Nitric and nitrous oxides are intermediate products in the denitrifying process (Hayashi, 2022). An alternative N pathway is anammox, the anaerobic oxidation of NH_3, first discovered by Mulder et al. (1995) in the 1990s. During anammox, microbes oxidize ammonia back into N_2 using NO_2^- as the electron acceptor (Pascoal et al., 2022). This occurs in low-oxygen or anoxic environments. Another process in the N cycle is NH_3 volatilization, which is the enzymatic hydrolysis of urea, often originating from animal manure, into NH_3 gas (Pascoal et al., 2022).

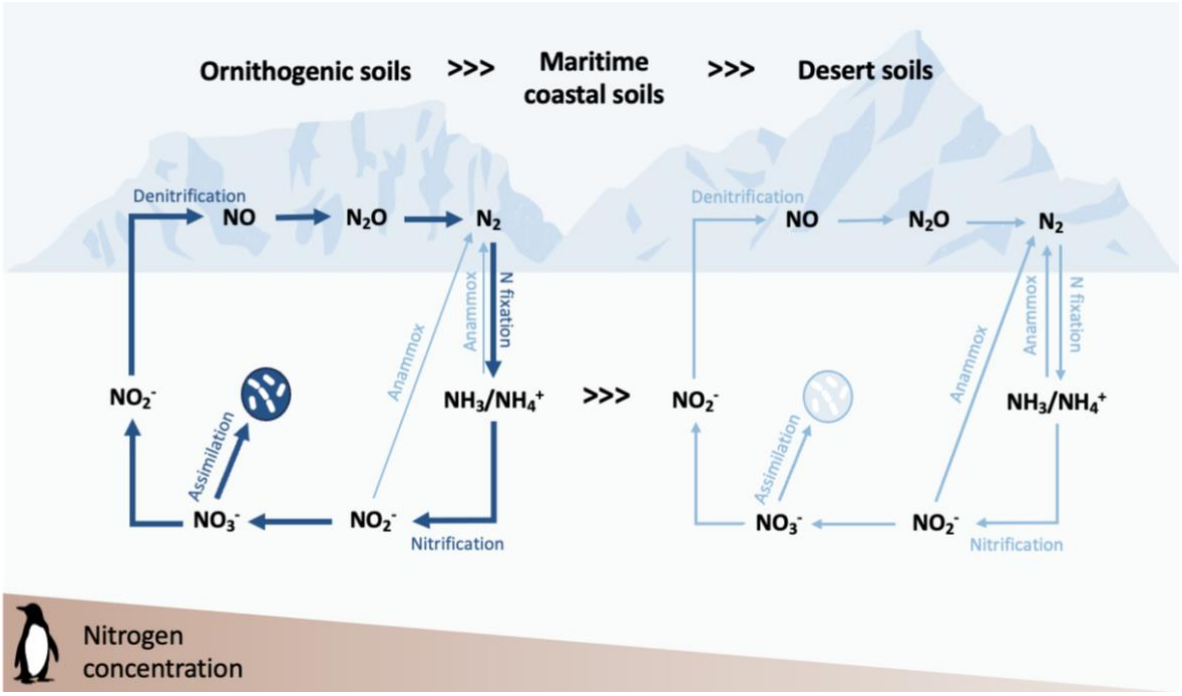

Figure 7: Nitrogen cycling processes in Antarctic soils across the hetero-oligotrophic spectrum. The line thickness represents the importance of individual cycle steps for the different soil types. Figure adapted from Ortiz et al. (2020).

Before human intervention, bioavailable forms of N, such as NH_3, NH_4^+, NO_2^-, NO_3^-, and nitrogen oxides (NO_x), did not typically accumulate within natural systems (Galloway et al., 2003). However, due to the widespread cultivation of legume species associated with biological N fixation, the combustion of fossil fuels, and the creation of the Haber-Bosch process, global rates of bioavailable N species have increased (Galloway et al., 2003). This has increased air pollution and environmental eutrophication (Galloway et al., 2003; Sinha et al., 2017; Wu et al., 2021).

In Antarctica, the N cycle is strongly influenced by the extreme environmental conditions (Ortiz et al., 2020). The combination of low water availability, low temperatures, and low nutrient availability results in slower N cycling in Antarctica compared to other regions worldwide (Ortiz et al., 2020; Smith, 1985). Continental Antarctica is largely devoid of higher eukaryotes, such as animals, plants, and fungi, leading prokaryotes to play a central role in N turnover (Ortiz et al., 2020). Consequently, most Antarctic soils are oligotrophic and naturally low in N (Galloway et al., 2003; Lee et al., 2012; Ortiz et al., 2020).

The only exception to this being nutrients transferred by seabirds. Globally penguins deposit the highest amount of total nitrogen (TN) to the terrestrial environment, transferring 307 Gg annually (Otero et al., 2018). Research by Lindeboom (1979) on King and Macaroni penguin guano showed that N comprised 20-21 % of guano with 170-160 mg uric acid, 18-26 mg organic N, 13-15 mg NH_4^+, 1.1-1.6 mg nitric acid per gram of dry weight. This results in N dynamics within penguin colonies differing significantly from the rest of Antarctica (Wu et al., 2023; Zhu, Liu, Ma, Sun, Xu, & Liguang, 2009). The N cycling within penguin colonies occurs at a comparatively, very high rate, with fresh guano being mineralized almost completely after three days (Hadas & Rosenberg, 1992). In penguin colonies, NH_3 volatilisation is also an important part of the N cycle, compared to other areas of Antarctica. Urea and uric acids are the dominant form of N deposited in guano, which is often rapidly volatilised (Hadas & Rosenberg, 1992; Lindeboom, 1979, 1984). Some of this volatilised ammonia gets redeposited in the surrounding area, therefore N inputs from bird colonies can affect a terrestrial area far larger than the colony itself (Bokhorst et al., 2019; Lindeboom, 1979). Additionally, studies have shown high levels of N_2O emissions from penguin-influenced soils (Zhu, Liu, Ma, Sun, Xu, & Liguang, 2009), high NO_3^- (Speir & Cowling, 1984), high NH_4^+ (Hofstee, 2006; Speir & Cowling, 1984), and low to no NO_2^- (Lindeboom, 1979, 1984; Speir & Cowling, 1984).

Further information on N concentrations within ornithogenic soils may be found in section 2.6.3. Overall, studies of N cycling within Antarctica are relatively limited, encompassing very few geographic locations and ecosystem types, despite N cycling being a core component of ecosystem servicing in Antarctica (Ortiz et al., 2020).

2.6.2 Phosphorous cycle

Phosphorus (P) is an essential nutrient for biological productivity, serving as a fundamental component of DNA, RNA, and energy production (Fink et al., 2016). These functions influence organisms' cell growth and energy transfer (Fink et al., 2016). The P cycle is an important global biogeochemical process that involves the transformation of P between various forms as it circulates

through the environment. Unlike the N cycle, the P cycle is relatively less complex, primarily due to reduced mobility of P (Otero et al., 2018).

Globally, most P exists in the form of primary inorganic phosphate (PO_4^{3-}) minerals, with apatite being the most abundant ((Fink et al., 2016; Otero et al., 2018). These are found in most igneous, metamorphic, and sedimentary rock types (Fink et al., 2016; Heindel et al., 2018; Otero et al., 2018). Inorganic phosphorous may be weathered from the original parent material rock through physical, chemical and microbial processes, eventually becoming incorporated into soils and sediments (Fink et al., 2016). The availability, behaviour, and mobility of this weathered P in soils and sediments is significantly influenced by factors such as temperature, pH, and the presence of oxygen (Fink et al., 2016). Biota and microbial organisms take up any bioavailable P and transform inorganic P to organic P (Otero et al., 2018). Phosphorous also tends to bind with any aluminium and iron hydroxides present to form secondary phosphates, often occluding bioavailable P (Fink et al., 2016). This occurs predominately in acidic and oxic environments (Otero et al., 2018). However, within changing conditions occluded P can also be liberated, this is in environments such as anoxic freshwater or estuarine sediments, or in high pH oxic marine sediments. Any sedimentary and buried P may also re-enter the cycle through tectonic uplift and geologic processes, which expose P to be weathered (Otero et al., 2018).

In Antarctica, the extreme conditions influence the weathering and release of P from parent materials (Bate et al., 2008). In the McMurdo Dry Valleys, the weathering and release of bioavailable P occurs slowly and is biologically facilitated. Consequently, the lacustrine environments within the McMurdo Dry Valleys are some of the most P-limited aquatic ecosystems on earth (Bate et al., 2008). In extremely P-limited areas, this can have a major influence on reducing the potential for primary production (Qin et al., 2014). Penguin guano therefore represents an important input of P to ecosystems, comprising between 15.2 to 38.6 μg P g^{-1} dry weight (Burger et al., 1978). In an Adélie penguin colony in the Vestfold Hills, East Antarctica, 167,036 kg of P is deposited annually during the

summer breeding season (Qin et al., 2014). Globally, penguins have been identified as a major source of environmental P, with annual guano P contribution estimated at 51 Gg P (Otero et al., 2018). Research by Pereira et al. (2013) has found that in penguin-influenced soils, PO_4^{3-} leachates may be found within the permafrost. This is a result of variation in seasonal permafrost and active layer depth changes allowing leachates to move deeper during times of higher thaw (Pereira et al., 2013). It has been noted that ornithogenic soils have a high retention capacity for P due to high organic matter contents, however, they frequently reach saturation due to continuous additions (Ziółek & Melke, 2014). When P saturation is reached, soluble P may be leached to waterbodies (Otero et al., 2015). Penguin colonies also emit phosphine into the atmosphere (Zhu, Liu, Ma, Sun, Xu, & Sun, 2009; Zhu, Wang, et al., 2014). However, phosphine redeposition into the surrounding area is low (Nedzarek, 2007). Consequently, the movement of P between land, streams, and sea is likely of greater importance in the P cycle in Antarctica (Nedzarek, 2007).

2.6.3 Ornithogenic soils and nutrients

Penguin colonies are sites of nutrient accumulation through their guano and biotic material being incorporated into ornithogenic soils (Hofstee, 2006; Speir & Cowling, 1984). Table 3 summarises concentrations of nutrients from previous studies in Antarctic penguin ornithogenic soils. Speir and Cowling (1984) conducted orthogenic soil research in the early 1980s at Cape Bird, Antarctica, and found ornithogenic soils on active mounds, or recently active mounds, had up to 16.4 % dry weight TN, with uric acid (2.3-9.1 % dry weight) and NH_4^+ (4.1-6.9 % dry weight) being the dominant N forms (Speir & Cowling, 1984). Soils within long abandoned mound sites reported very little residual N remaining, with almost no uric acid present (Speir & Cowling, 1984).

Soils within active mounds had 8 mg g^{-1} of total P, with only 6 % of this as biologically available P (Smykla et al., 2015). In abandoned nesting colonies, the same study found a total P of 15.7 mg $g^{-1,}$ with 3.5 % of this being biologically available (Smykla et al., 2015) The higher total P in relict colonies indicates an accumulation of P in these ornithogenic soils with age (Smykla et al., 2015). A similar trend

was found by Speir and Cowling (1984), where soils within active mounds in the Cape Bird Adélie penguin colony had 3.4 % inorganic P however, recently abandoned nests had 5 % inorganic P (Speir & Cowling, 1984). This is likely due to substantial quantities of organic matter and large portions of insoluble P, allowing high levels to be maintained over time (Otero et al., 2015; Simas et al., 2006; Zhu, Wang, et al., 2014; Ziółek & Melke, 2014). Simas et al. (2007) additionally found that P concentrations increased with soil depth and, therefore, age.

N and P concentrations were relatively high in ornithogenic soils, with some variation between studies (Table 3). Feeding behaviours have been cited for nutrient concentration differences between ornithogenic soil results. Regarding dietary sources, krill has a low N content (0.023 g N g^{-1} dry weight) compared to some fish species, such as the Chaplain (*Mallotus villosus*), which has 0.046 g N g^{-1} dry weight (De La Peña-Lastra, 2021). Therefore, penguins who consume higher amounts of krill are likely to have guano with a lower N content. The soil's age will also significantly impact nutrient content, varying between active and abandoned ornithogenic soils (Speir & Cowling, 1984).

Table 3: Previously recorded nutrient concentrations in ornithogenic soils within penguin colonies in Antarctica. Results are expressed in percentage of dry weight.

Reference	Location	Sample	TC	TN	Total P
			%	%	%
a	Cape Bird	Soil	24.00	16.00	5.40
b	King George Island	Soil	18.00	7.00	14.00
c	Antarctic Peninsula	Soil	17.20	9.58	-
d	Cape Hallett	Soil	-	12.07	12.30
e	South Shetland Islands	Soil	20.91	10.40	4.91
e	Deception Island	Soil	10.45	5.22	3.51
e	Antarctic Peninsula	Soil	24.12	4.98	12.78

a: Speir and Cowling (1984), b: Tatur and Mayrcha (1984), c: Cipro et al. (2018), d: Hofstee (2006), e: Santamans et al. (2017)

2.7 Penguin colonies as secondary sources of enrichment

Penguins play a vital role in biochemical cycling by transporting HMs and nutrients from the marine to the terrestrial environment, where they contribute to the formation of ornithogenic soils

(Huang et al., 2014). The accumulation of these HMs and nutrients within ornithogenic soils, however, has been shown to impact nearby ecosystems through water and air enrichment (Myrcha et al., 1985; Otero et al., 2018).

Penguin colonies have been observed to enrich melt streams with nutrients. As melt streams flow through colonies, they erode ornithogenic soils and become enriched. Howard-Williams et al. (1986) and Downes et al. (1986) investigated a melt stream in the Cape Bird northern colony and noted an increase of N and P concentrations within the penguin colony (Table 4). While the dissolved organic N reported in both studies are comparable, Downes et al. (1986) reported notably lower levels of dissolved organic P with no significant enrichment within the penguin colony. The Cape Bird stream exhibited significant differences from other melt streams in the McMurdo Sound with an absence of penguin activity, such as Fryxell stream, which was considered nutrient-poor and oligotrophic (Howard-Williams et al., 1986). Tatur and Myrcha (1983) also noted that stream morphology is important to transport capacity with high-energy melt streams that are closest to the sea, such as those within Cape Bird, exhibiting the highest nutrient return. Nedzarek (2010) researched a melt stream passing through an abandoned penguin colony and found that nutrient concentrations were considered eutrophic, with up to 1.68 mg total P L^{-1} and 4.26 mg N L^{-1}.

Table 4: Nutrients (dissolved reactive phosphorous (DRP), dissolved organic phosphorous (DOP), dissolved organic nitrogen, and dissolved organic nitrogen (DON), of upper and lower reaches of glacial Cape Bird ornithogenic impacted melt water streams and Fryxell stream in the McMurdo Dry Valleys.

Reference	Stream	Reach	DRP	DOP	NH_4^+	NO_3^-	DON
			mg m^{-3}	mg m^{-3}	mg m^{-3}	mg m^{-3}	mg m^{-3}
a	Cape Bird	Upper	32.6	35.6	12.8	21.4	56
a	Cape Bird	Lower	106	110	155.5	365	197
b	Cape Bird	Upper	-	3	-	-	56
b	Cape Bird	Lower	-	4	-	-	231
a	Fryxell	Lower	0.2	0.9	DL	2.0	37.1

a: Howard-Williams et al. (1986), b: Downes et al. (1986), DL: Below detection limit

Creek water and lacustrine environments within and/or near to penguin colonies have also been researched to become enriched in heavy metals (Table 5). Creek water and lake water studies by Nędzarek et al. (2014) on the sub-Antarctic King George Island, with catchment areas comprising ornithogenic soils, showed concentrations of 18 μg As L^{-1}, up to 0.51 μg Cd L^{-1}, and 4.22 μg Pb L^{-1}. Accumulation of ornithogenic soils, stream dynamics, and thus, heavy metal transport on the sub-Antarctic islands differs significantly when compared to the Antarctic (Jelinski et al., 2023). Therefore, this enrichment highlights the need of this research within higher latitude locations.

Sediments within penguin-influenced lacustrine environments have been found to exhibit enrichment levels twice as high as background levels (Xie & Sun, 2008). Xie & Sun (2008) reported an average As concentration of 12.41 μg As g^{-1} dry weight and a maximum of 16.9 μg As g^{-1} dry weight within a 34 cm sediment core. Significantly, concentration peaks were found to be correlated to penguin colony population (Xie & Sun, 2008). Sun and Xie (2001) investigated Pb levels within a 3000-year sediment core from a lake influenced by Adélie, Chinstrap and Gentoo penguins. Their findings revealed elevated Pb concentrations in penguin-affected sediments, which were correlated to anthropogenic lead emissions indicating their transport to Southern Ocean food webs. Concentration peaks spiked considerably with the industrial revolution, and more recently, have risen further within the past 50 years (Sun & Xie, 2001).

Table 5: Previously recorded heavy metal concentrations in Antarctic penguin-influenced ornithogenic lacustrine sediments. Concentrations are reported in μg g^{-1} dry weight for sediment and μg L^{-1} for water samples.

Reference	Location	Sample	As	Cd	Pb
a	Ardley Island	Lake sediment	-	-	29.20 ppm
b	Antarctic Peninsula	Lake sediment	16.90	-	-
c	Amanda Bay	Lake sediment	-	-	23.80
d	King George Island	Creek water	0.18	0.51	4.22
d	King George Island	Lake water	0.18	0.39	3.53

a: Sun and Xie (2001), b: Xie and Sun (2008), c: Huang et al. (2014), d: Nędzarek et al. (2014)

Surface water run-off from Adélie, Chinstrap and Gentoo formed ornithogenic soils in the South Shetland Islands, were investigated for nutrient concentrations (Tatur & Myrcha, 1983). Their study documented NH_4^+ concentrations of up to 170 mg L^{-1}, and NO_3^- of 43 mg L^{-1}. These findings led them to describe these waters as being "naturally fertilized".

Lindeboom (1984) reported high levels of NH_4^+ volatilisation resulting in air enrichment creating what they have referred to as an "ammonia shadow" with subsequent deposition. Bokhorst et al. (2019) have demonstrated that N deposition can occur well beyond a kilometre away from penguin colony boundaries, contributing valuable nutrients to the ecosystem. Regions adjacent to penguin colonies can be an oasis for vegetation, particularly mosses and lichens, correlating with higher abundances of insects, mites, and worms (Bokhorst et al., 2019; Erskine et al., 1998; Otero et al., 2018). Conversely, active penguin colonies are more adverse for plant establishment due to trampling and excessive manuring (Otero et al., 2018). Excessive nutrient levels can exert toxic effects and potentially lead to the formation of 'dead zones' within the colony (Grant et al., 2022; Otero et al., 2018; Wootton, 1991).

It is essential to consider how future climate change may impact colony environments and potentially become a source of secondary contamination. With the predicted increased glacial melting associated with climate change in Antarctica, there is likely an increase in the intensity, volume, and duration of glacial melt streams. However, the impact of these changes on melt stream transport of nutrient and heavy metal-rich ornithogenic material remains uncertain (Smith et al., 2020). Reduced ice, due to increased melting may uncover more legacy contaminants, or contaminants being newly exposed resulting from natural rock weathering (Balbus et al., 2013). Elevated temperatures can affect chemical reactions within biota, increasing metabolism (Moore et al., 1997). This can increase the potential for bioaccumulation and biomagnification within penguins and, also increase microbial activity, which also facilitates nutrient cycling (Moore et al., 1997). Furthermore, the persistence and

mobility of HMs and nutrients are sensitive to climate change and may increase in toxicity (Balbus et al., 2013).

Climate change is also set to alter the conditions of the receiving Southern Ocean environment. The vulnerability of the Southern Ocean to ocean acidification is expected to reduce pH in near-shore environments significantly (Hancock et al., 2020). This could influence the chemical state and binding of HMs and nutrients, which are being carried by melt streams, consequently affecting their bioavailability and toxicity.

Overall, research on the chemical composition of seasonal melt streams impacted by penguin activity is limited, indicating a gap in the understanding of this ecological system.

2.8 Measuring environmental contaminants

This section introduces some of the field methods used throughout this research, within the context of sampling within Antarctica, practicalities of their use, and method limitations.

2.8.1 Conventional grab sampling

Conventional grab sampling involves the collection of a sample in a specific location at one point in time. It is frequently employed within Antarctic research for water, soil, sediment, and ice testing, as well as monitoring of trends over time (Aves et al., 2022; Metcheva et al., 2011; Nedzarek, 2010). Grab sampling is favoured because of its practicality, simplicity, and cost-effectiveness, making it a valuable tool for monitoring analytes. There are limitations to this approach, particularly when sampling streams as grab sampling investigates one location at a specific point in time. As a result, it may fail to capture spatial and temporal variations or fluctuations. This effect is pronounced when sampling extremely dynamic and variable water systems such as glacial melt waters, particularly when dealing with environmental contaminants present in trace amounts (< ppm). Therefore, when using grab sampling as a method, it should be used judiciously with consideration of environmental changes incorporated into the sampling methodology.

Grab sampling has commonly been used in Antarctica and the subantarctic islands to measure HMs and nutrients in water (Downes et al., 1986; Howard-Williams et al., 1986; Nedzarek, 2010). This is mainly due to the ease of sampling, which is particularly advantageous within the cold and harsh Antarctic environments where alternative methods, such as electronic samplers, can be challenging to implement.

2.8.2 Diffusive gradients in thin-films

Diffusive gradients in thin-films (DGT) were first patented in 1993 as a method for the passive sampling of specific analytes within aquatic environments (Davison, 2016). DGT are predominantly used for the measurement of inorganic solutes within waterbodies and sediments (Davison, 2016). These devices consist of a <0.45 µm pore-size protective membrane filter situated on top of an ion-permeable gel, which is backed by a binding resin (Davison, 2016). These components are supported by a piston and cap, as illustrated in Figure 8 (Davison, 2016). Diffusive gradients in thin-films are deployed within a soil solution or natural waters, exposing the diffusive gel for a known duration. When this deployment time is combined with analyte concentration, it enables a time-weighted average concentration to be calculated through Fick's First Law of Diffusion (Davison & Zhang, 1994; Saeed et al., 2018). The longer DGT are deployed, the more targeted analytes they can accumulate, provided device saturation does not occur (Davison & Zhang, 1994). As DGT are deployed over longer time scales, results can capture temporal variations that conventional grab sampling may miss. Therefore, when used in conjunction with, or as an alternative too, DGT provides a more accurate representation of chemical dynamics in irregular waterbodies.

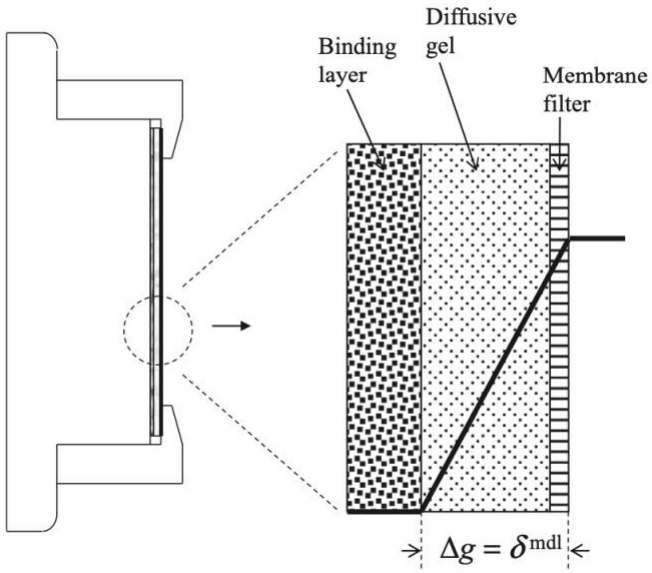

Figure 8: Cross-section diagram of a DGT showing different binding layers from Davison (2016)

First used to assess metals in Antarctic water and sediment pore-water by Larner et al. (2006), the use of DGT within Antarctica is relatively novel and, to our knowledge, only limited to three studies (Koppel et al., 2019; Koppel et al., 2021); Larner et al. (2006) Since Koppel et al. (2019) used DGT successfully for investigating HM toxicity in a marine environment and Koppel et al. (2021) used DGT to assess soil metal contaminants. The promising results from these studies showcase the potential for effective use of DGT within the Antarctic landscape.

2.8.3 Determination of stream flow rate

When considering concentrations of analytes within streams, having an understanding of stream flow and discharge is paramount. The discharge of a stream influences biological habitats, morphology, and most applicably to this research, rates of analyte transport (Moore, 2004). Two of the most commonly used methods to measure the discharge of a stream are the use of a current meter combined with stream area measurements, or through the installation of a weir (Moore, 2004). However, in shallow, steep, or cascading streams, current meters are unable to be used, and their accuracy is compromised and weirs may not always be practical to install, particularly in Antarctica,

where much of the environment is protected and stream manipulation is disapproved (Day & Day, 1977; Moore, 2004). An alternative method is to gauge stream flow by using a chemical tracer and determining its dilution following mixing within the stream (Day & Day, 1977; Moore, 2004). The most commonly used chemical tracer is table salt or sodium chloride (NaCl). This is injected, and the time taken for the EC pulse from the tracer to dilute back to background levels is measured at a downstream point (Moore, 2004). The precision of the dilution gauging technique is within 5 %, the same level of accuracy as current metering, making it a good alternative (Day & Day, 1977).

In an Antarctic setting, Howard-Williams et al. (1986) estimated discharge at a melt stream at Cape Bird using stream velocities obtained with a pygmy current meter or, in some reaches where this was not feasible, by using a neutrally buoyant float with appropriate corrections. Other streams commonly researched in Antarctica, such as those in the McMurdo Dry Valleys, have permanent weirs installed (Howard-Williams et al., 1986). To our knowledge, sea-sourced saltwater dilution gauging has not been used for discharge measurement in Antarctica; however, we believe it to be a promising and less invasive method of measurement in environmentally sensitive streams.

2.8.4 Environmental standards

To understand the ecological impact of HMs and nutrients found within melt water streams, the results from this research will be compared to fresh water and soil quality guidelines (Table 6). Within Australia and New Zealand water quality is monitored with joint standards formed by two governmental councils, the Agriculture and Resources Management Council of Australia and New Zealand (ARMCANZ) and the Australian and New Zealand Environment and Conservation Council (ANZECC). Together, they have formed research-based fresh-water quality guidelines (ANZFG) since 1992. Guidelines have had several revisions as new toxicant and ecological data becomes available. The ANZFG provide values for different levels of ecosystem protection with 80 %, and 99 %, representing the respective percentage of species that are expected to be protected. Within this research, values for

99 % ecological protection were used as per the guidelines for areas with high conservation requirements and ecological values.

Table 6: Water and soil guideline values for ecological protection for 99 % of species (ANZECC and ARMCANZ, 2000) and for agricultural land use (CCME, 1997).

Indicator	ANZFG Water	CEQG Soil
	99 %	Agricultural
Arsenic (As III)	1.00 µg L^{-1}	-
Arsenic (As V)	0.80 µg L^{-1}	-
Arsenic (Total)	-	12.00 µg g^{-1}
Cadmium	0.06 µg L^{-1}	1.40 µg g^{-1}
Lead	1.00 µg L^{-1}	70.00 µg g^{-1}
Nitrate	17.00 µg L^{-1}	-
Ammonia	320.00 µg L^{-1}	-
Ammonium	10.00 µg L^{-1}	-
Total nitrogen	295.00 µg L^{-1}	-
pH	6.50 - 7.50	6-8
Phosphate	9.00 µg L^{-1}	-
Total phosphorous	26.00 µg L^{-1}	-
Turbidity	4.10 NTU	-

Soil samples were also compared to Canadian ecological quality guidelines (CEQG) for soil ecological and human health. The CEQG was developed by the Canadian Council for Ministers of the Environment (CCME) and are research-based guidelines that provide threshold values under four different land use scenarios, including agricultural, residential, commercial, and industrial land uses. Comparisons within this research have been made to the agricultural guidelines as these represent the lowest thresholds for the highest levels of protection. The CEQG was chosen for soil comparison as Canadian soils are subject to freeze-thaw patterns as those of Antarctica.

It is acknowledged that while comparison with these frameworks provides important insights into the degree of contamination within Antarctic terrestrial ecosystems, their values may not always be entirely relevant for Antarctica as they are created for mildly disturbed systems. However, no guideline values for Antarctic ecosystems exist. The scientific research that forms the foundation of the

guideline values may also be based on specific local biota (not endemic to Antarctica) and environmental conditions different to that of the Antarctic continent. Furthermore, while there is a body of research that documents health issues related to metal toxicity in Arctic animals, to our knowledge, no research on toxicant thresholds in Adélie penguins currently exists.

2.9 Research gaps

Penguins' role as vectors for transferring HMs and nutrients from one environment to another is a rapidly expanding field of research. However, there is a notable lack of studies exploring the repercussions of penguin activity on surrounding ecosystems. A substantial knowledge gap persists concerning the impact of seasonal melt streams on the mobilisation and dissemination of accumulated HM and nutrients from Antarctic ornithogenic soils. Establishing a baseline understanding of HM and nutrient transport is vital for recognising potential hotspots of nutrient enrichment and toxicity. Such data will also serve as a foundational reference point for forecasting transport patterns under various climate change scenarios. This study, to the best of our knowledge, will be the first to investigate the role of glacial melt streams in the transport of both HMs and nutrients from an Antarctic Adélie penguin colony and into the marine environment.

3 Methodology

3.1 Introduction

This chapter provides the full methodology employed throughout this research. This begins by describing the location of the field site, including a justification of sampling sites and sampling day selection. This is followed by detailed site descriptions and then the field, laboratory, and statistical methods utilized.

3.2 Location

An over 45,000 years of Adélie penguin occupation in the Ross Sea region has resulted in the formation of extensive ornithogenic soils on Ross Island (Emslie et al., 2007). Situated on the northwest coast of Ross Island, the Cape Bird northern colony is home to approximately 50,000 breeding pairs (Lyver, 2020). Here, deep ornithogenic soils are situated on coastal beach ridges, between glacial moraine deposits and unconsolidated beach gravels (Dochat et al., 2000). During the austral summer, melt water streams emanate from the Bird Ice Cap, flowing into the McMurdo Sound and Ross Sea (Figure 9) (Dochat et al., 2000; Howard-Williams et al., 1986).

On December 28, 2022, a reconnaissance mission was conducted to select sample and control streams. Within the Cape Bird Northern Colony, three melt streams were observed, each potentially serving as penguin-influenced sample streams. These streams underwent observation, focusing on morphology and flow over a 24-hour period. The stream chosen for sampling stood out due to its consistent flow and greater water depth, along with the notable presence of ornithogenic soils on both sides. During reconnaissance, areas were observed along the course of the northern colony stream channel where water had cut directly into the penguin nesting mounds with visible erosion of nesting material. The control stream was deemed the most suitable among the accessible melt streams devoid of direct penguin influence within its stream catchment. The control stream lay at a distance of approximately one kilometre from the penguin colony sample stream, with the assumption of negligible

differences in soil parent material and atmospheric deposition of HMs. The distance between the control and penguin-influenced streams is an important consideration as local geological disparities hold the potential to complicate metal comparisons (Evenset et al., 2007). Further details regarding location selection are expanded upon in section 3.3, addressing experimental design, with additional descriptions of streams and individual sample locations available in section 3.4.

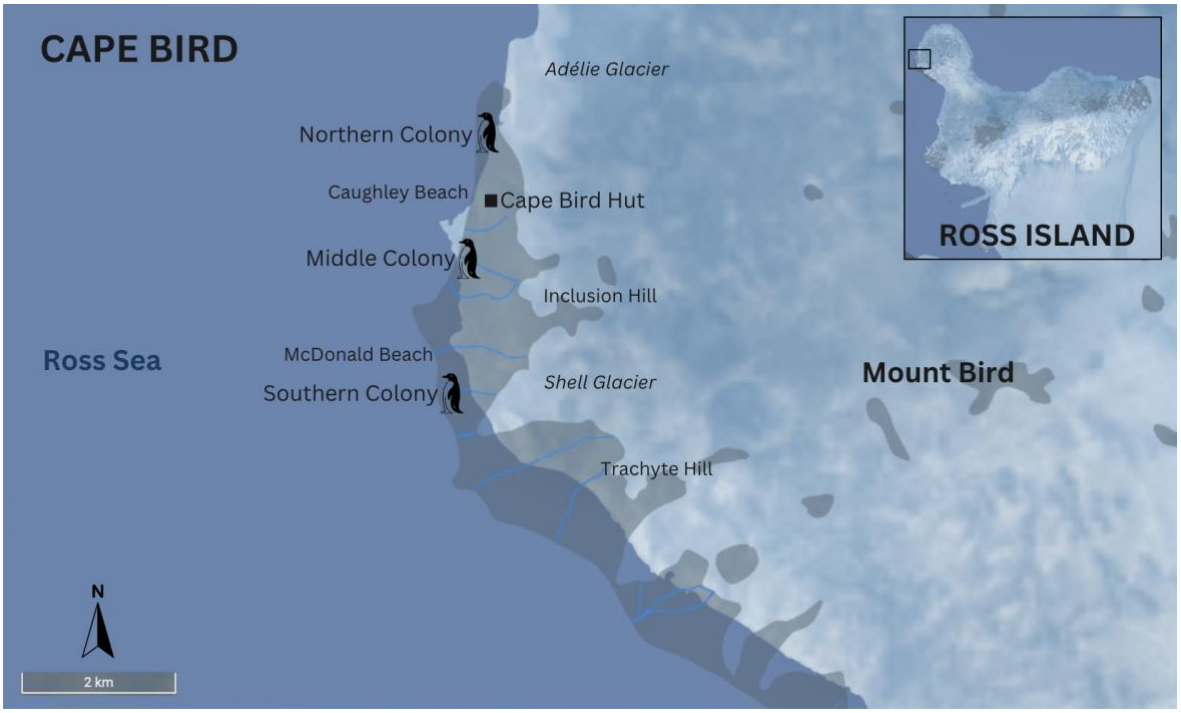

Figure 9: Map of Cape Bird, Ross Island, showing the Adélie penguin colonies and key geological features. Imagery sourced from Manaaki Whenua, Landcare research.

3.3 Experimental design

The Cape Bird northern Adélie penguin colony was chosen because of its position between a substantial ice cap (Bird Ice Cap) and the Southern Ocean, with several melt streams known to traverse directly through penguin habitat. Cape Bird is also an established and accessible location, featuring the Cape Bird hut initially constructed by Antarctica NZ in 1966, and subsequently rebuilt in 1991/92. This hut is situated approximately 250 meters from the northern penguin colony and undergoes frequent maintenance.

Field work occurred between 28 December 2022 to 10 January 2023, to coincide with the timeframe of melt stream formation by Downes et al. (1986) and Howard-Williams et al. (1986), and close to time of maximum soil thaw.

Water sampling, physiochemical measurements, and stream gauging were conducted on four separate days. Preliminary observations of the stream indicated substantial diurnal and daily fluctuations in stream discharge and sediment load. To capture these variations and therefore provide an accurate representation of the streams, sampling occurred on days spanning a range of temperatures and times. Additionally, soil samples were collected at three sites to attribute the origins of the water results to soil composition as a source of enrichment.

An array of methodologies was utilized to fulfil the research objectives. Given the complex chemical interactions, to which HM and nutrients are subject, a range of both in-situ and chemical analyses were used to understand these dynamic and changing stream environments. Further details on methods will be explained in section 3.5and 3.6, field and laboratory methods.

3.4 Site descriptions

Considering a colony stream length of 400 meters and a control stream length of 550 meters, it was determined that selecting five sampling sites along these streams would adequately encompass variations in stream HM and nutrient inputs. To determine if the penguin mounds are the source of enrichment, sites were selected along a gradient of ornithogenic influence. This included a site well above, on the colony boundary, and three sites within the penguin colony with the final site immediately before the stream discharges into the Ross Sea. For analytical comparisons, a matching number of sites were selected within the control stream.

3.4.1 Northern colony stream

The penguin-influenced stream transverses through the Cape Bird northern colony from east to west along a north-west facing aspect between the Bird Ice Cap and the Ross Sea (Figure 10 and 11).

Notably at all northern colony stream sites there was an absence of algae, moss, or lichens in or near streams. Water samples were collected in a transect spanning the length of the stream. Site summaries and GPS coordinates and stream details can be found in Table 7.

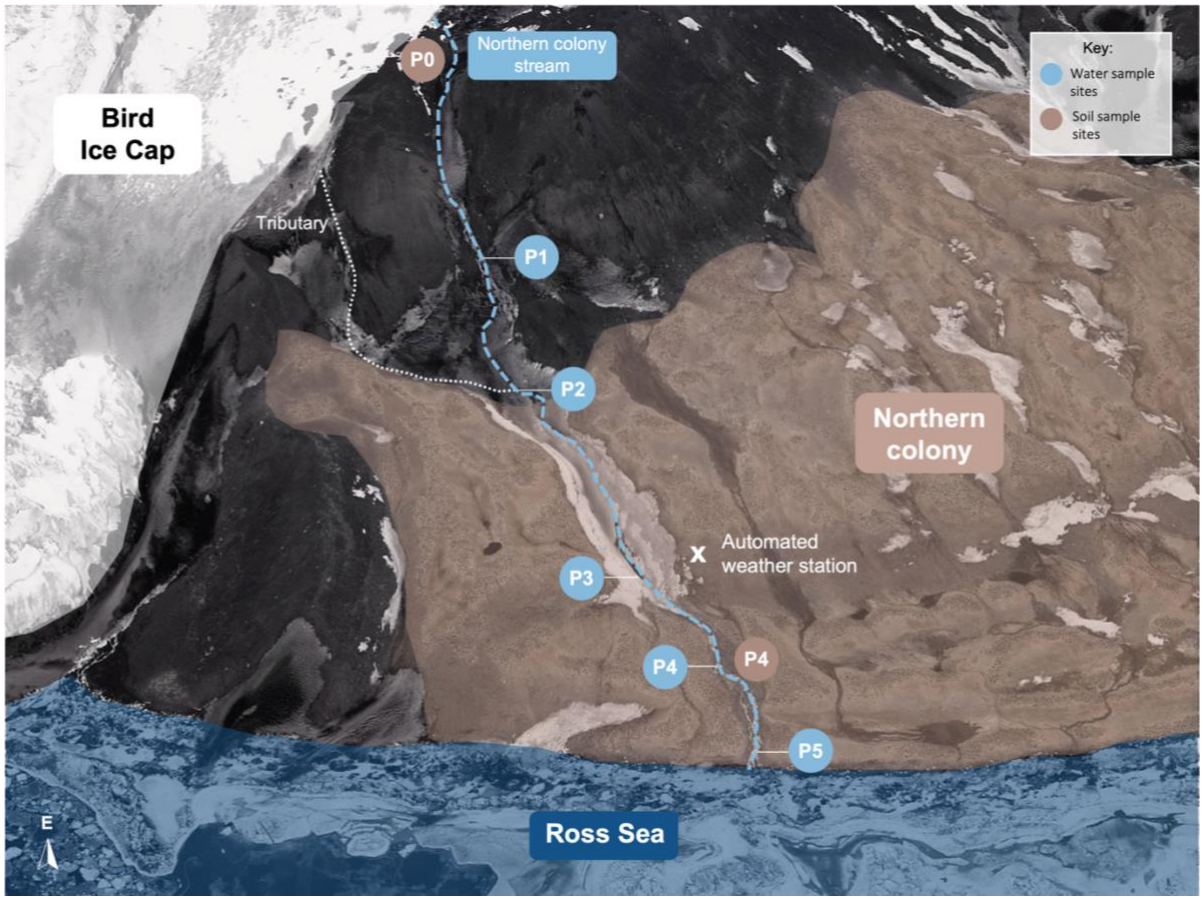

Figure 10: Map of stream water sampling and physiochemical measurement sites (P1 – P5) and soil sampling sites (P0 and P4) at the Cape Bird northern colony. Image from Kerry Barton.

P1 was the furthest upstream sampling site, situated above the penguin colony, thereby free from direct penguin influence. This section of stream was on a moderately steep, west-facing slope with an angle of 27°, characterised by a mixture of large rocks and finer albeit unstable sediment on a windy hill side. Despite the absence of penguin influence, the surrounding area was home to several skua with visible nests, with the nearest located approximately three meters away. Several penguin eggs were present in the vicinity indicating skua feeding activity.

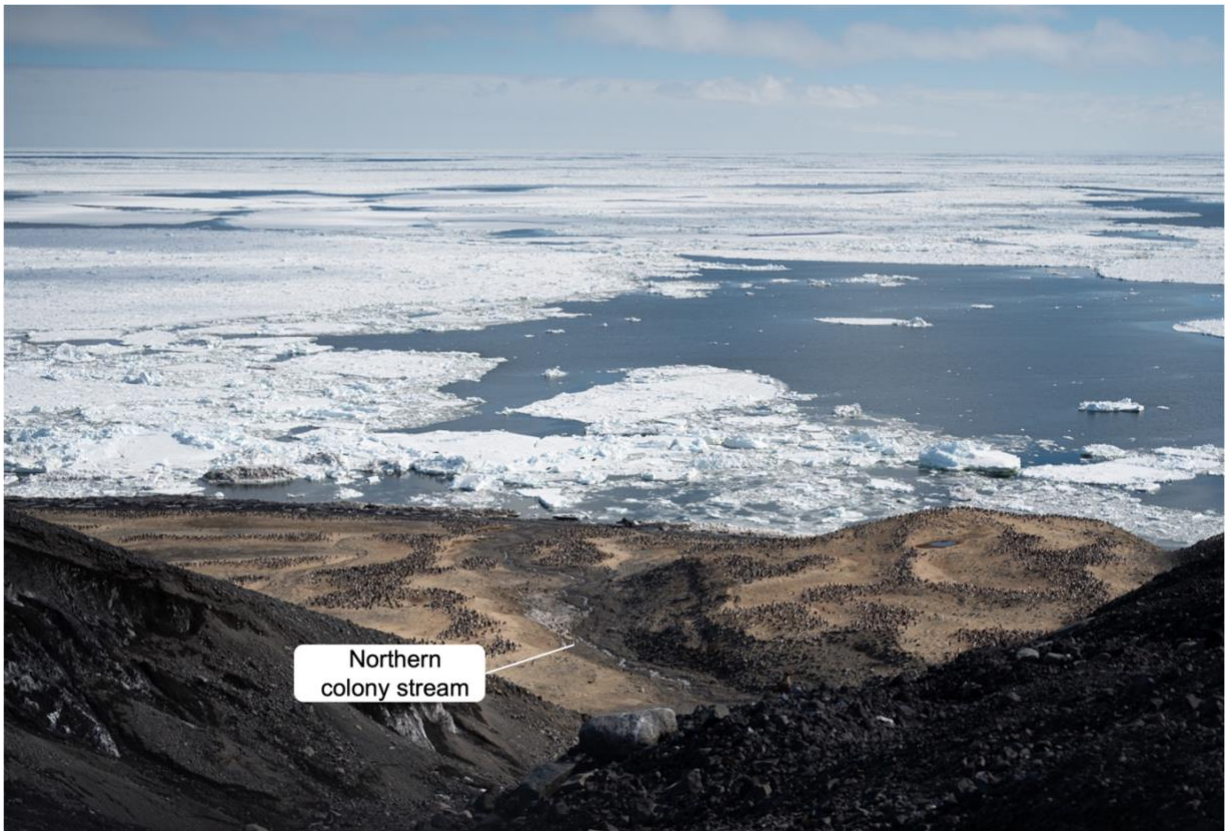

Figure 11: Image of the northern colony stream. Image taken facing downstream (west) between sites P0 and P1.

Site P2 site was approximately 50 m downstream and resided just below a confluence where the primary stream merged with a tributary from the north. This tributary runs along the upper perimeter of the penguin colony and therefore may introduce some biological inputs to the site, however, these are unlikely to be significant. This site offered a relatively sheltered environment with a stream width of 1.3 meters and a lower stream slope of 5°. The nearest active penguin nest from this site was approximately five meters to the north, just outside of the visible floodplain width of the stream which was three meters. Moving downstream, between sites P2 and P3 the stream channelises through steep stream-cut banks of ornithogenic soils reaching approximately four meters high.

P3 was positioned 80 m downstream of P2, at the base of this channel where the banks level out to a large inter-mound and opening to a broader floodplain. Here the stream exhibited a gentle slope of 3°, with the closest active nests two meters away, nesting within the five-meter floodplain.

This site is frequently traversed by penguins and with many feathers and carcasses in close proximity. This flat site was also considered suitable for the installation of the automated weather station adjacent to the stream. See section 3.4.4 for further details.

Approximately 40 m downstream at site P4, the stream further flattens to 2°, becoming more braided with a wide floodplain up to eight meters in width. Active penguin nesting sites were approximately three meters away with penguins nesting directly on the stream edge just upstream. As this section of the stream was braided, the specific sample location was chosen in the section of the braided stream which has the most flow and kept consistent throughout all measurements.

Site P5 was the furthest downstream measurement, a further 40 m downstream of site P4 and four meters before the stream emptied into the Ross Sea marine environment. This segment of the stream was braided with a broad floodplain visible as the stream descends the final few meters at a slope of 3°. The nearest active nesting site was three meters away with this section of the stream frequently used as a walkway for penguins moving up and down the coastline and returning from feeding.

Table 7: Water and soil sample site coordinates and key stream morphological and geographical features of a penguin-influenced (P0 – P5) and a control stream (C1 – C5) at Cape Bird, Antarctica.

Site code	GPS	Elevation	Stream slope	Stream width	Floodplain width	Braided
		m	°	m	m	Yes/No
P0	S 77 12.884 E 166 27.476	78	1	2	30	Yes
P1	S 77 13.260 E 166 25.834	54	27	1	-	No
P2	S 77 13.257 E 166 25.281	26	5	1.2	3	No
P3	S 77 13.250 E 166 25.800	11	3	1	5	Yes
P4	S 77 13.244 E 166 25.772	5	2	1	8	Yes
P5	S 77 13.245 E 166 25.746	2	3	1.5	3	Yes
C1	S 77 12.403 E 166 45.596	8	40	1	-	No
C2	S 77 12.811 E 166.27.268	6	34	1	-	No
C3	S 77.12.780 E 166 27.099	5	10	1.5	3	Yes
C4	S 77 12.759 E 166 26.986	4	5	2.2	6	No
C5	S 77 12.745 E 166 26.977	4	2	4	8	Yes

3.4.2 Control stream

The control stream was located 1.1 km to the south of the northern colony stream and 600 m away from the northern penguin colony boundaries. In its catchment area there were neither active nor historic penguin nests, however, some skua nests were present within meters of the stream waters. In the surrounding area there were also some penguin feathers, potentially transported from the strong and dominant northerly wind (University of Wisconsin, 2017). The control stream originates from the Bird Ice Cap, traversing over Cape Bird Drift before descending a volcanic scarp, and flows out onto an alluvial fan before entering the Ross Sea (Dochat et al., 2000). This stream follows an east to west course with the headwaters situated within New College Valley ASPA 116, thus our sampling was conducted in the lower and accessible portion of the stream with sample sites approximately 30 meters apart.

At the furthest upstream sample site, C1, the terrain was characterised by a steep slope through large rocks and boulders at the base of the volcanic scarp. Present on the northern side of the slope was an almost vertical friable breccia, while the southern side consisted of a south-west facing

colluvium. The stream gradient at this location was 40° with a stream width of approximately one meter.

Site C2 closely resembled site C1, albeit with increased exposure and a reduced gradient of 34°. Large rocks and unstable breccia continued to dominate the stream morphology. Between sites C2 and C3 the slope gradually levelled off to 10° with the stream became more braided.

For sampling at C3, the stream braid with the main water flow was selected and sampled consistently during the study throughout all samplings. Here, the parent material was noticeably smaller in size compared to upstream sites, with a higher proportion of cobbles, gravels, and sand forming a three-meter floodplain.

C4 was selected as a site just downstream of where the braids briefly converged into a single stream flow. Here, the slope continued to reduce with a gradient of 5° with a noticeable widening of the stream and an approximate width of 2.2 m. The floodplain expanded to approximately 6 m, with gravels and sand continuing to dominate the floodplain and stream bed material.

Site C5 was the mouth of the stream, situated just two meters upstream of where it discharged into the Ross Sea. Here the stream slope flattened further to 2°, with extensive braiding and floodplain reaching approximately 8 m. There was a near absence of boulders with sands and silts dominating the stream bed. As a result, the ground was often waterlogged, indicating a substantial volume of water was also moving through sub-surface stream flow. The stream braid with the highest and most consistent flow was chosen for sampling throughout this research.

3.4.3 Soil profile sites

Soil sampling was conducted at three sites which were deemed to be representative of the different soils adjacent to the control and penguin-influenced streams. The first site sampled, P0, was situated adjacent to the colony stream headwaters at the base of the Bird Ice Cap (Figure 10). Here waters coming from the glacial face were extensively braided with a very wide floodplain. Landforms at

this site consisted of glacial moraine and unconsolidated parent material which varied in size from boulders to silts with a lot of visible ground moisture.

Ornithogenic soil was sampled within the penguin colony, adjacent to water sampling site P4 (Figure 10). This location was the edge of the stream floodplain, where a previous year's melt stream had eroded the face of the ornithogenic soil mound (Figure 12). No penguins were nesting on the site directly atop the soil however, the closest nests active were approximately one to two meters away.

Figure 12: Site P4, ornithogenic soil sample site pre-sampling (Right) and post-sampling (Left).

The third soil sampling site was adjacent to the stream waters at site C5, near the mouth of the control stream on the alluvial fan. Full soil profile descriptions of all three soil sample sites may be found in Appendix 1.

3.4.4 Automated weather station site

The Automated Weather Station (AWS) (Figure 13) was positioned within the penguin colony adjacent to site P3 (Figure 10). The AWS was positioned on a large inter-mound composed of thick guano-topped ornithogenic soil on a relatively flat section of ground, suitable for the AWS.

Figure 13: Automated weather station set up within the Cape Bird northern colony from the 28th of December 2023 to the 10th of January 2023.

3.5 Field methods

All field work was conducted at the Cape Bird northern colony between the 28th of December 2022 and the 10th of January 2023. This included four days of water sampling, stream physiochemical measurements, dilution gauging, soil profile sampling, deployment, and collection of DGT and deploying the AWS.

3.5.1 Water sampling and physiochemical measurements

Stream water sampling and physiochemical measurements were conducted at all sites across the two streams on four days, 1st, 3rd, 7th, and 10th of January 2023. Water samples were taken mid-stream, with care not to disturb any stream bed sediments. On the first say of sampling at all sites, (P1-5 and C1-5) two 50 mL falcon tubes were filled with unfiltered stream water and a minimum of 300 mL was filtered using 0.45µm Minisart polyethersulfone syringe filter with 50 mL syringes into Nalgene

bottles. On the subsequent three sampling days, two 50 mL falcon tubes were filled with unfiltered stream water, and four 50 mL falcon tubes were filled with water filtered. A larger quantity of filtered water on day one was used for laboratory method development for nutrient analysis. New syringes and filters were used at each location to avoid cross-contamination. Before sampling, falcon tubes and syringes were rinsed with stream water twice at each sample site.

During the time of water sampling, physiochemical parameters (pH, temperature, electrical conductivity (EC) and dissolved oxygen) were measured with a YSI ProQuatro multiparameter meter, ensuring that the probe was completely submerged. The YSI probe was calibrated twice during the field campaign, on 28th December 2022, before sampling began and on 4th January 2023. Calibration used Merck Centipur Supelco pH 4, 7 and 10 buffer solutions and Merck Centupur 200 and 1000 μS cm^{-1} calibration fluid. Turbidity was measured with a Sper Scientific 860040 Turbidity meter which was calibrated with 0 NTU and 100 NTU calibration solutions each day of analysis. All physiochemical measurements were conducted mid-stream where the water was well mixed.

3.5.2 Stream discharge

Stream discharge was measured through dilution gauging, using a dilute tracer and measuring stream EC as a proxy for salt concentration. Due to Antarctica being a protected location, seawater was used as a tracer which naturally occurs instead of adding table salt (sodium chloride) or other chemical tracers. During the time of water sampling, dilution gauging was undertaken at one location on each stream. These locations were initially scoped out depending on stream morphology and braiding, and multiple sites were tested to see which locations provided reliable information. The final and only sites that were considered to have a sufficient length without braiding and excessive noise within conductivity measurements were sites P3 and C3.

At these sites, 1 L of seawater collected from the Ross Sea was injected into the centre of the stream. Approximately 100 meters downstream, a calibrated a YSI ProQuatro Multiparameter meter was situated mid-stream, recording stream EC at one-second intervals. Injections were completed

three times, ensuring that the EC had returned to baseline stream measurements between each injection. For calculation calibration, 150 mL of seawater and 3 L of stream water from each stream was collected on measurement days. Further information on calibration methods is found in section 3.6.10.

3.5.3 Diffusive gradients in thin-films

Diffusive gradients in thin-films for metals in solution with a Chelex binding layer, and for NO_3^- in solution with a SIR-100-HP binding layer, were purchased from DGT research UK (Product codes LSNM-NP and LSNN-AP for metal and NO_3^- DGT, respectively). DGT were transported to Antarctica as per DGT Research (n.d.) recommendations. Two metal and two NO_3^- DGT were mounted into plastic cages using cable ties and deployed at each sample sites in the northern colony and control stream with a waratah. Deployment took place on 29 December 2022, while handling with powder-free gloves to ensure there was no cross-contamination. HOBO pendant MX2201 temperature loggers were also deployed in cages at sites 1, 3, and 5 in both the northern colony and control stream for the duration of deployment. During the first few days of deployment, an unpredicted cold weather event saw some sections of the streams completely freeze for several hours overnight. Because of this and the requirement of the DGT to remain moist during the entire deployment period, any results from the DGT were deemed untrustworthy, thus no further analysis of DGT was conducted. Please refer to section 5.5.2 of the conclusion, pit-falls of DGT, for further discussions on the practicability of DGT in Cape Bird melt streams.

3.5.4 Soil sampling

Sampling of three different soil profiles was conducted on 2 January 2023. At sites P0 and C5, an approximately 30 x 30 cm pit was dug to reveal a vertical profile face. The depth of the profile was dug until the ice-cement was reached, which was at a depth of 35 cm for both P0 and C5 sites. Samples were placed into Whirl-Pak sterile sample bags. Digging was conducted with a trowel that was sanitised with Scott sanitizing wipes between the sampling of horizons. Care was taken to not contaminate other

horizons while taking the sample. Both P0 and C5 sites were very weakly developed with little visible horizonation, and as such, soil samples at the surface, subsoil and immediately above the ice-cement were taken. At site P0 a sample was taken at the surface (0 - 2 cm), at 18 - 20 cm depth and at 33 - 35 cm depth from soil immediately above the ice cement. At C5 samples were taken at the surface (0 - 2 cm) and 33 - 35 cm, above the ice-cement. At the penguin-influenced soil, site P4, a previously eroded nest site was sampled where a clean face with fresh-exposed soil was cleared (Figure 12). There were six visible horizons where samples were taken at 0 - 2 cm, 2 - 18 cm, 18 - 37 cm, 37 - 44 cm, 44 - 53 cm, and 53 - 65 cm. The ice-cement was not reached during sampling however, the depth of 65 cm was chosen because unconsolidated beach ridge material underneath the ornithogenic soils had been reached.

3.5.5 Automated weather station

A small, automated weather station (AWS) was installed at Cape Bird Northern colony from 28 December 2022 until 10 January 2023. This climate station was positioned adjacent to stream site P3 on a flat section of ornithogenic soil between penguin mounds. The AWS consisted of a Campbell Scientific 92000 ResponseONE weather transmitter which gave wind speed, wind direction, temperature, humidity, and air pressure. An Apogee SN-500-SS net radiometer gave the incoming and outgoing radiation, this was mounted on an extending bracket so the AWS shadows would not affect radiation measurements. There were also two T-type thermocouples to record temperature on the ground surface, and at 10 cm depth. Data was logged at 10-minute intervals and downloaded using the Campbell Scientific PC400 Datalogger Support Software (version 4.7).

3.5.6 Permitting and sample movement

During sampling days, upon returning to the Cape Bird hut, water and soil samples were frozen in a -20 °C freezer. All samples were helicoptered from Cape Bird to Scott Base within a chilly bin with freezer packs to keep cool. Upon arrival at Scott Base samples were returned to a -20 °C freezer.

Samples were transferred to the University of Waikato, Thermophile Research Unit (TRU) Ministry of Primary Industries (MPI) registered facility 1659 (2837) physical containment level 2 (PC2) laboratory in New Zealand on import permit number 2023081077. Samples were transported within a ventilated chilly bin and on dry ice. Once at the TRU water and soil samples were stored within a -80 °C freezer until further analysis.

Within New Zealand, work with biosecurity risk samples and potential new and/or unwanted organisms including any samples from Antarctica, must comply with the Biosecurity Act 1993 and the Hazardous Substances and New Organisms Act 1996. These Acts prohibit the release of these samples into the environment unless express approval has been given, and that samples must be held within containment. Samples imported from Antarctica must comply with the Act regulations and held within a New Zealand MPI physical containment Level 2 laboratory (PC2). Throughout this research, samples were handled within the University of Waikato, Thermophile Research Unit MPI registered facility 1659 PC2 laboratory. To be removed from the PC2 laboratory samples need to be pre-treated or have a MPI approved permit.

3.6 Laboratory methods and data analysis

Several laboratory analyses used to understand the relationship between HM and nutrients in penguin colonies and melt water streams. Melt stream samples were analysed separately for their total and dissolved HM content, nutrient anions, and NH_4^+ (Figure 14). Soils were analysed for their total HM content, nutrient anions, NH_4^+, TN, total carbon (TC), clay mineralogy, pH and EC (Figure 15). Laboratory methods were also required for the calibration of conductivity in discharge calculations, this is followed by load calculation and data analysis.

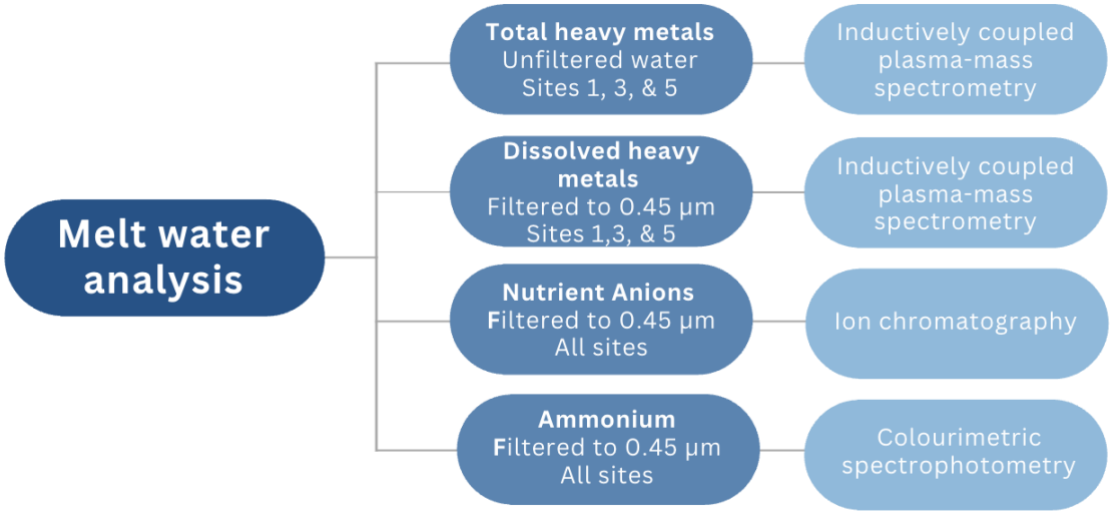

Figure 14: Flow chart summary of melt water laboratory analysis and methods.

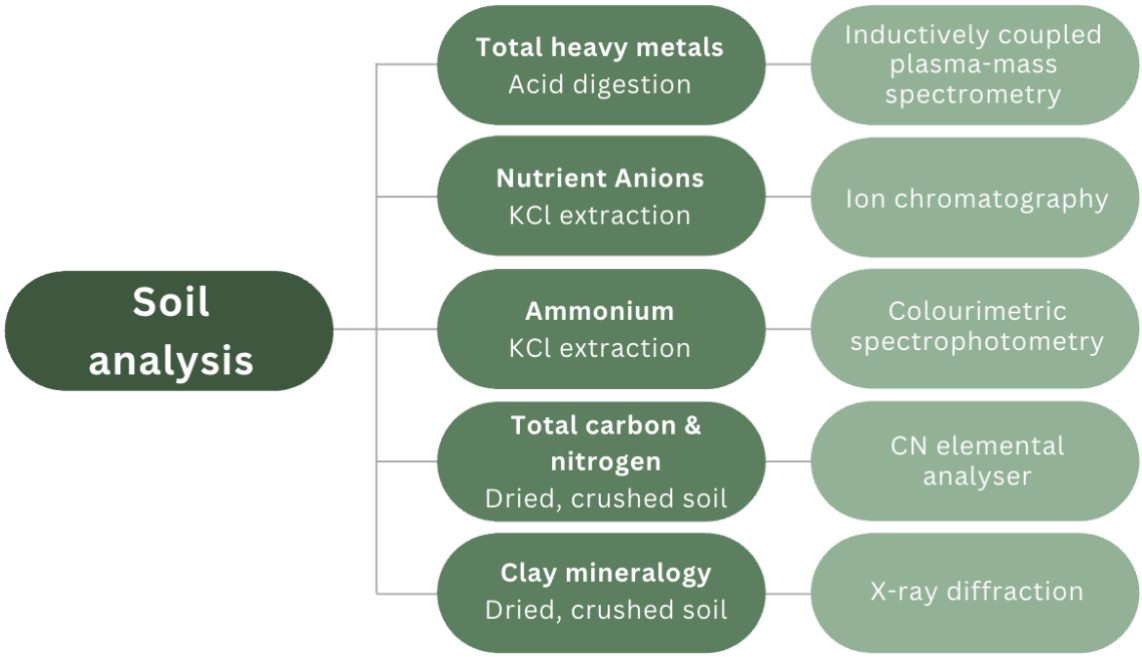

Figure 15: Flow chart summary of soil laboratory analysis and methods.

Sample preparation was conducted within a PC2 or physical containment level one laboratory in accordance with MPI regulations. Before analysis, water samples were removed from the -80 °C freezer 24 hours before analysis and left in a chilly bin to defrost until completely liquid. Soil samples

were removed from the -80 °C freezer for eight hours until completely thawed prior to analysis. Initial stages of sample preparation where there is a biological safety risk, were undertaken within a HERASafe HS12-ICN2 biological safety cabinet that had been cleaned with 70 % ethanol and UV sterilized for a minimum of 15 minutes. Throughout the laboratory methods, all Type 1 water used in laboratory processes was obtained from a Milli-Q direct water purification system and all glassware was hydrochloric acid (HCl) washed in 2 % HCl for a minimum of 15 minutes and rinsed thrice with Type 1 water.

3.6.1 Melt stream heavy metal analysis

For water elemental analysis sample sites P1, P3, P5, from the colony stream, and samples from C1, C3 and C5 sites in the control stream, were selected to be analysed. Samples analysed were reduced because of time constraints and the large volume of samples to be analysed. The three sites were chosen to give a representative of changes along the northern colony stream before (P1), in the middle (P2) and near the end (P3) of the penguin colony influence. The corresponding control stream sites were selected for comparison and consistency. The three samples analysed are also meant to indicate where any significant inputs and changes are occurring along the stream and where potential future research at sites P2 an P4 may be useful. In both types of HM analyses, samples were analysed in field duplicates.

Dissolved metals refers to the concentration of a metal analyte in a 0.45 μm filtered sample and were analysed according to EPA method 200.8 in US EPA (1994) for samples with <1 NTU with no obvious colouration or noticeable odour. Into a new 15 mL falcon tube, 10 mL of sample was aliquoted with a calibrated pipette with 0.2 mL of nitric acid. The samples were analysed in two batches along with two method blanks containing Type 1 water. After acidification, the samples were shaken to homogenize and stored in a refrigerator at 4 °C for two days until they were analysed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) with an Agilent 8900 triple quadrupole ICP-MS.

Total recoverable metals (EPA 200.2) refers to the concentration of a metal analyte in an unfiltered aqueous sample Martin et al. (1994). Defrosted unfiltered samples were shaken to homogenise, then 25 mL of each sample was decanted into a 50 mL calibrated digestion tube. Using a calibrated pipette, 0.5 mL of high-purity nitric acid and 0.25 mL of high-purity HCl was added. Samples were capped loosely and placed in a ThermoScientific Haake E3-W26 water bath at 90 °C for two hours. Samples were removed and allowed to cool for 30 minutes. Using Type 1 water, the sample was diluted to a final volume of 25 mL, the caps were then tightened, samples were shaken to mix. As there was visible particulate matter still within the samples, they were filtered with a 0.45 µm Minisart polyethersulfone syringe filter with new 15 mL syringes. In a new 15 mL falcon tube, 10 mL of sample was measured. This process was completed in two batches for ease of handling with a laboratory blank containing Type 1 water for each batch. Samples were stored in a refrigerator at 4 °C for approximately 24 hours until they were analysed by ICP-MS (Agilent 8900 triple quadrupole).

3.6.2 Melt stream nutrient anions

Duplicate samples from all five sample sites within the northern colony (P1 through P5) and the control stream (C1 through C5) were analysed for nutrient anions. Approximately 4 mL of defrosted field filtered sample was pipetted into IC vials with new Pasteur pipettes used per sample. Samples were run on a ThermoSceintific Dionex AS-DV and Dionex Integrion HPIC ion chromatography (IC) machine through a 35-minute isocratic gradient elution programme. The IC used integrated software, Chromeleon 7 chromatography data system (version 7.3.1). Calibration standards of three through to 10 ppm were run along with samples and blanks using ThermoScientific Dionex 7 Anion standard II. Samples were analysed in two batches with two blanks of Type 1 water per batch. Any samples waiting for analysis were stored at 4 °C in the refrigerator for a maximum of 12 hours, covered with parafilm to prevent evaporation.

3.6.3 Melt stream ammonium

Ammonium in water was measured using a colourimetric method using the indophenol blue reaction (EPA method 350.1) on all sample sites within both the northern colony (P1 through P5) and control stream (C1 through C5), in duplicate. Two reagents (solution A and solution B) along with NH_4^+ standards were prepared prior to analysis. Solution A, a phenol and sodium nitroprusside solution, was made with 10 g of phenol and 0.05 g of sodium nitroprusside dissolved into 200 mL of Type 1 water. This solution was then diluted to 1 L in a volumetric flask using Type 1 water. The solution was inverted 10 times, before being decanted into an amber Schott bottle. Solution B of sodium hypochlorite and sodium hydroxide was made with 10 g of sodium hydroxide dissolved into 16.8 mL of 5 % sodium hypochlorite. This was diluted to 2 L in a volumetric flask with Type 1 water and inverted 10 times before being decanted into an amber Schott bottle. Both solutions A and B were used within two weeks of being made and refrigerated at 4 °C until use. Ammonium standards used for making a calibration curve were made fresh each day. A stock solution of 100 ppm NH_4^+ was made within a 200 mL volumetric flask with 0.918 g of Merck NH_4^+ sulphate salt diluted with Type 1 water. From this 100 ppm solution, 0.25, 1.25, 2.5 and 12.5 mL of standard was transferred into four 250 mL volumetric flasks using a calibrated pipette and diluted with Type 1 water. This made a 0.1, 0.5, 1 and 5 ppm of NH_4^+ standard respectively.

Of the defrosted field filtered samples, standards and blanks with Type 1 water, 3 mL was added into a 15 mL falcon tube along with 3 mL of solution A and solution B with calibrated pipettes. Falcon tubes were capped and shaken on a vortex mixer for 3 seconds. Samples were placed in a ThermoScientific Haake E3-W26 water bath at 37 °C for exactly 15 minutes. After removal from the bath, they were inverted three times and poured into cuvettes. Samples were read immediately by a calibrated Pharmacia Biotech Ultrospec 3000, UV and visible spectrophotometer set to 625 nm wavelength. This process was conducted in batches of 10 so samples could be read within the spectrophotometer quickly due to colour development being a time sensitive reaction. As NH_4^+

concentration within the northern colony samples was higher than the 5 ppm standard, sites P1 and P2 were diluted two times with Type 1 water, and sites P3, P4 and P5 were diluted ten times. Results were multiplied by their respective dilution factors.

In Microsoft Excel (version 16.75.2) NH_4^+ standard concentrations were plotted against absorbance. An example of a calibration curve made during this research may be found in figure 16. All calibration curves had an R^2 value of >0.98 and therefore, the calibration standards were accepted.

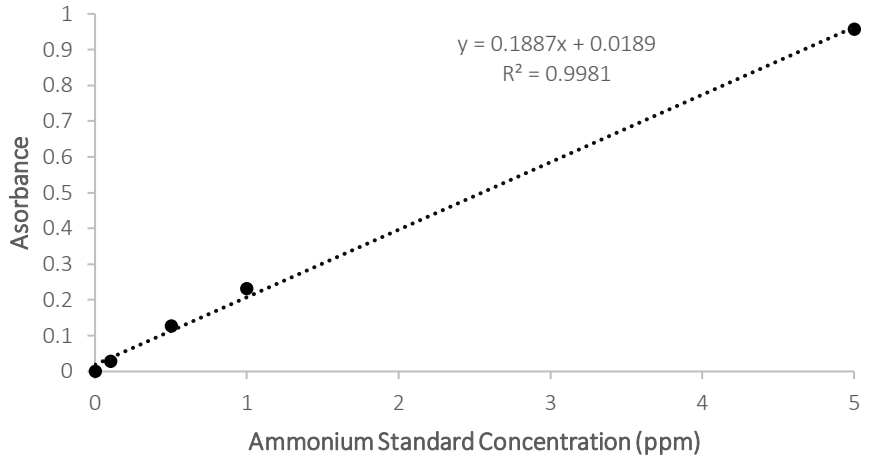

Figure 16: Ammonium spectrophotometer calibration curve using 0.1, 0.5, 1 and 5 ppm ammonium standards.

The linear equations from the calibration curve were then used to solve for the NH_4^+ concentration. An example calculation from the calibration curve in Figure 16 may be seen in Equation 1, where 'y' is the absorbance of the sample measured at 625 nm.

$$Ammonium\ concentration\ = \frac{(y-0.0189)}{0.1887} \qquad \text{Equation 1}$$

3.6.4 Soil heavy metal analysis

Soil elemental analysis was analysed using EPA method 200.2 on all soil samples in duplicate. After defrosting, soil samples were mixed with a spatula prior to weighing for homogeneity. Approximately 10 g of each soil sample was weighed using Kern EMB 600-2 scales, into a tinfoil dish.

Samples were oven dried at 60 °C for 72 hours to remove all moisture in an Ontherm 8150 oven that had been wiped with 70 % ethanol prior to use. Once the dried samples were cooled, samples were crushed with a mortar and pestle. This was wiped with 70 % ethanol, scrubbed with Diversey Pyroneg powder detergent and warm water, then rinsed with Type 1 water three times between each sample. The mortar and pestle were left to dry completely between each sample crushing. Of the dried and crushed sample, 1 g of each soil was weighed into a 50 mL falcon tube in duplicate using Kern EMB 600-2 scales. Into each sample, 10 mL of 1:5 ultrapure HCl acid to Type 1 water dilution, and 4 mL of a 1:2 ultrapure nitric acid with Type 1 water dilution was added. Samples were digested within a ThermoScientific Haake E3-W26 water bath at 90 °C for 3.5 hours. Each sample was transferred into a volumetric flask and diluted to 100 mL with Type 1 water (Figure 17). Samples were let stand for 12 hours and then filtered using a 0.45 µm Minisart polyethersulfone syringe filter with new 15 mL syringes. Of each sample, 10 mL was filtered into 50 mL volumetric flask which was further diluted to 50 mL with Type 1 water and inverted ten times. Into a 15 mL falcon tube, 10 mL of sample was aliquoted with a further 0.2 mL of concentrated nitric acid pipetted into each falcon tube. Samples were stored in a refrigerator at 4 °C for two days until they were analysed by ICP-MS (Agilent 8900 triple quadrupole).

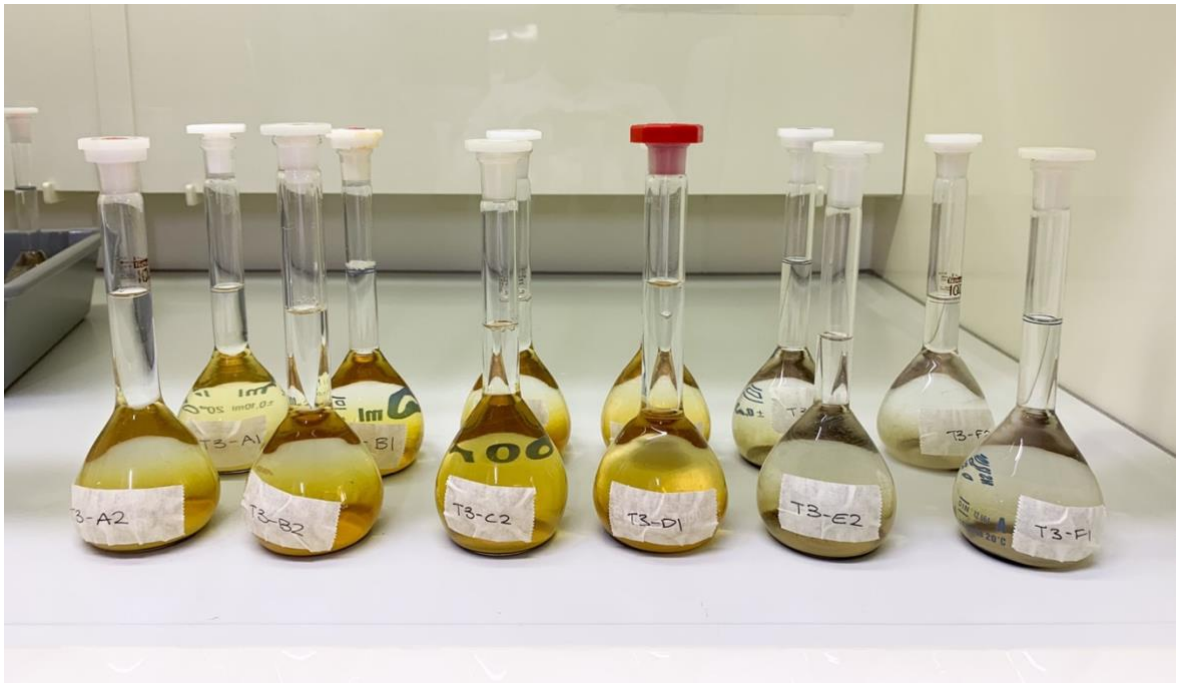

Figure 17: Site P4, ornithogenic soil, samples during heavy metal analysis preparation for ICP-MS. Samples on the left are surface soil samples, moving through the soil profile towards the right.

3.6.5 Soil nutrient anions

Soil nutrient anions were analysed through a potassium chloride (KCl) extraction method as outlined in Wang and Øien (1986). Throughout this process a 2 M KCl solution was used, made with 300 g KCl dissolved in Type 1 water, and made up 2 L.

Analysis was conducted on all soil samples in duplicate along with two blanks of Type 1 water. Sample was mixed with a spatula for homogeneity, then 10 g of soil was weighed into a 50 mL falcon tube. Into this, 50 mL of KCl solution was measured in a volumetric flask and added to the sample. These were then put on a Grant-Bio PS-M3D rocking bed for 1 hour at 30 orbital degrees (Figure 18). Suspensions were then vacuum filtered through a 1.2 µm pore size Whatman GF/C glass microfibre filter. Of the KCl extraction, 3-4 mL was pipetted into IC vials. Samples were run on a ThermoSceintific Dionex AS-DV and Dionex Integrion HPIC ion chromatography machine. This used Chromeleon 7 chromatography data system (version 7.3.1). The water was run through a 35-minute isochratic gradient elution programme. Calibration standards three ppm, through 10 ppm with ThermoScientific

Dionex 7 Anion Standard II, were run along with samples and blanks. Due to issues with the operation of the IC machine, reliable results of soil nutrient anions were unable to be produced. This research limitation is further discussed in section 5.5.3.

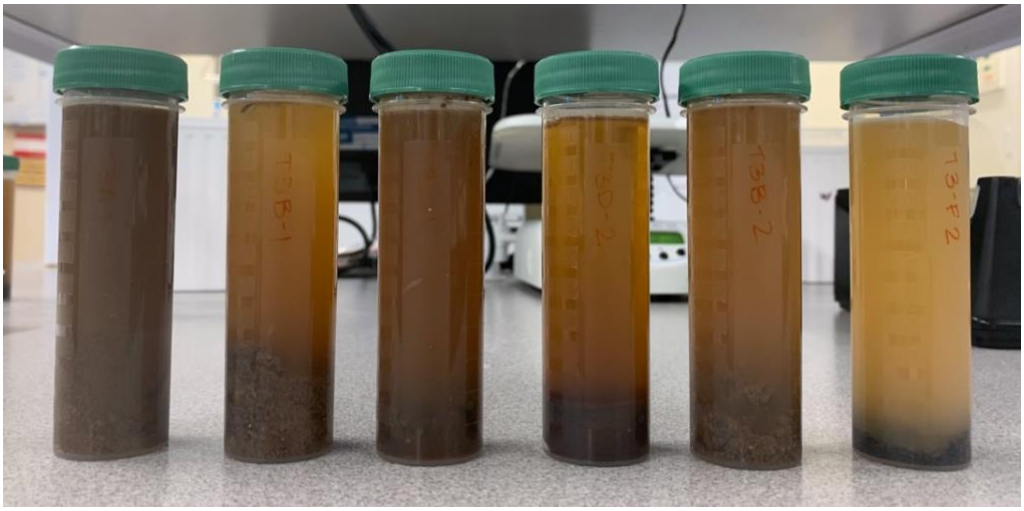

Figure 18: Ornithogenic soil samples during the KCl extraction prior to filtering.

3.6.6 Soil ammonium

Soil NH_4^+ was determined through a potassium chloride extraction of available NH_4^+ and analysis through spectrophotometry using the indophenol blue method as outlined in Wang and Øien (1986). Three reagents, sodium hydroxide-tartrate solution, alkaline phenol solution, and sodium hypochlorite solution, were made along with NH_4^+ standards were made prior to analysis. Within the hydroxide-tartrate solution, 0.5 g of sodium hydroxide and 5 g tartrate were dissolved in Type 1 water and made up to 500 mL in a volumetric flask. Alkaline phenol solution had 15.6 g phenol dissolved into 25 mL of 27 % sodium hydroxide. Then, 5 mL of acetone was added, and the solution was made up to 250 mL with type 1 water in a volumetric flask. This alkaline phenol solution was made fresh each day of analysis, stored in an amber Schott-bottle, and kept refrigerated (4 °C) until use. The sodium hypochlorite solution was made from 12.5 mL of sodium hypochlorite with 12 % available chlorine, diluted to 250 mL with Type 1 water. A 100 ppm NH_4^+ standard solution was made with NH_4^+ sulphate

salt as in 3.6.3 however, using KCl solution substituting Type 1 water as in section 3.6.5. From this, standards of 0, 0.5, 2, 5, 8 and 10 ppm were made up in 250 mL volumetric flasks with KCl solution.

Shaken and filtered soil from a KCl extraction, as conducted in soil nutrient anions method, section 3.6.5, from each soil sample was analysed in duplicate. Of the extractant, 10 mL was pipetted into a 50 mL falcon tube along with 10 mL of the sodium hydroxide-tartrate solution. This was mixed by shaking by hand for 3 seconds. Then 7 ml alkaline phenol solution and 5 ml sodium hypochlorite were pipetted into the sample and let stand for 30 min at room temperature (Figure 19). The absorbance was immediately read by a calibrated Pharmacia Biotech Ultrospec 3000, UV and visible spectrophotometer set to 635 nm wavelength. This process was conducted in batches of 10 so samples could be read within the spectrophotometer quickly due to colour development being a time sensitive reaction. The same procedure was followed with standard solutions and blanks of KCl solution. As NH_4^+ concentration within the northern colony soil samples was higher than the 10 ppm standard, samples from P4 0 - 2 cm, 2 - 18 cm, and 18 - 37 cm depths were diluted 160 times, the P4 37 - 44 cm depth was diluted 125 times, and the P4 44 - 53 cm and 53 - 63 cm were diluted 50 times. Results were multiplied by their respective dilution factors and a calibration curve was made to calculate NH_4^+ concentration as per melt stream NH_4^+ section 3.6.3.

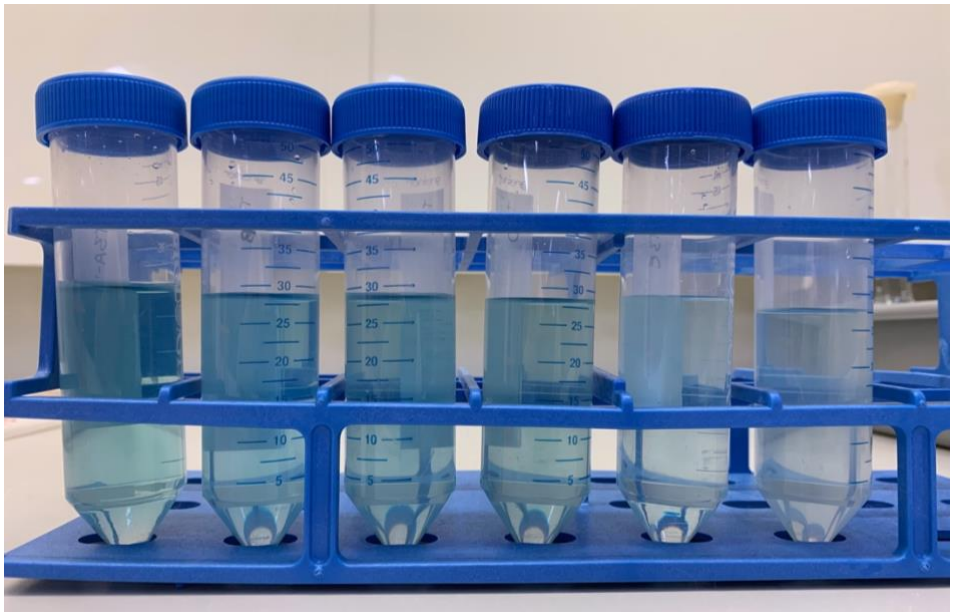

Figure 19: Colour development on ornithogenic soil samples during the indophenol blue method of testing soil ammonium.

Soil samples had an additional calculation (Equation 2) to convert the sample into mg g^{-1} where 'χ' is the NH_4^+ concentration calculated from Equation 1, and V_{EXT} is the volume of extractant in litres.

$$\text{Ammonium concentration} = \frac{(c \times V_{EXT})}{g\ of\ soil} \qquad \textbf{Equation 2}$$

3.6.7 Soil total nitrogen and carbon

Oven dried soil prepared in section 3.6.4, was crushed for approximately 30 seconds into a very fine and uniformly sized powder with a tungsten-carbide ring-mill. Of the dried and crushed soil, 10 mg of the ornithogenic soil from site P4 was weighed and sealed within tin capsules in duplicate and 100 mg of P0 and C5 soils were used for analysis. Capsules were combusted in an Elementar Vario EL Cube.

3.6.8 Soil clay mineralogy

All soil samples were analysed for clay mineralogy through X-ray diffraction (XRD). Oven dried soil as prepared in section 3.6.4, crushed with in a tungsten-carbide ring-mill (See section 3.6.7) were pressed into a palate mould (Figure 20). Samples were run in a PANalytical Empyrean Series 2 XRD at the University of Waikato with bulk samples run for 5-80 °2θ, at 50 seconds per step.

Figure 20: Preparation of soil samples for clay mineralogy analysis by X-ray diffraction. Left: Sample crushed within the tungsten-carbide ring mill. Right: Crushed soil prepared into a pressed palate mould.

3.6.9 Soil pH and electrical conductivity

Defrosted soil samples were mixed with a spatula to homogenise, then using a Kern EMB 600-2 scale 4 ± 0.02 g of sample was weighed into a 50 mL falcon tube. Into the falcon tube, 20 mL of Type 1 water added. Samples were capped and shaken for 1 minute with a Velp Scientifica 2x3 hand-vortex at 20 hertz. They were then put on a Grant-Bio PS-M3D rocking bed for 30 minutes at with 30 orbital degrees, 60 reciprocal degrees and no vibration. Immediately after removal, the EC and pH of the samples were measured using a ThermoScientific Orion 4-star benchtop pH and conductivity meter with automatic temperature compensation set for conductivity measured at the reference temperature of 25 °C. The pH and conductivity were calibrated within the hour of the analysis using Merck Centipur Supelco pH 4, 7, and 10 buffer solutions, and ThermoScientific Orion conductivity

standards 12.9 mS cm^{-1} and 1413 μS cm^{-1} at 25 °C. All buffers and standards were fresh an opened the day of analysis. Analysis of soil pH and EC was conducted in batches of five for ease of handling.

3.6.10 Melt stream discharge calibration

For calculating stream discharge, the EC needs to be calibrated using three standards of river and seawater. This was done twice for each stream while at Cape Bird. Using a volumetric pipette, 25 mL of collected seawater was added to a calibrated 1 L wide-mouth Nalgene bottle each. These were filled with stream-water, capped, and shaken to ensure complete mixing. While on ice to cool the water down and being continuously stirred, the electrical conductivity was recorded when it reached the actual stream temperature. This process was repeated with a 0 mL and 50 mL added seawater calibration fluid. The following calculations are based on Moore (2005) using Microsoft Excel (version 16.75.2). Results of the EC calibration (Equation 3) is used to calculate the calibration coefficient (*fc*). Where *v* is the volume of seawater (1 L), and *q* is the volume in mL of this solution used to make up each of the two calibration solutions.

$$EC\ calibration = v\ (\mathrm{ml\ l^{-1}}) \times \frac{q\ (\mathrm{ml})}{1000\ (\mathrm{ml})} \qquad \text{Equation 3}$$

The concentrations in mL L^{-1} were plotted on a calibration curve against conductivity, with the slope of the line being the calibration coefficient. An example calibration curve from the northern colony stream may be found in Figure 21.

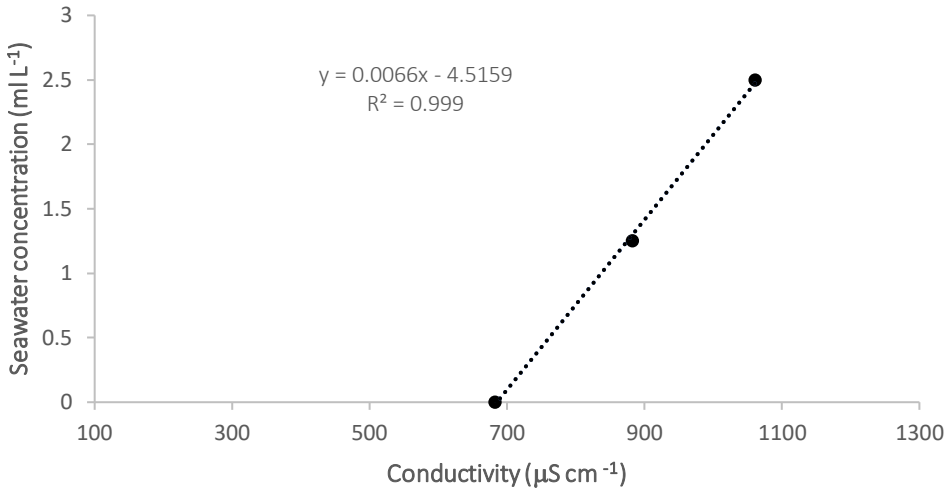

Figure 21: Calibration curve from northern colony stream discharge measurements on the 1st of January 2023 used to calculate the calibration coefficient (*fc* =0.0066).

Next the background conductivity (EC_0) of least 10 data points prior to the injection is plotted against the individual second measurements form the multiparameter probe (EC_t), to create a conductivity curve (Figure 22). This graph is checked for smoothness of data, without significant background shift.

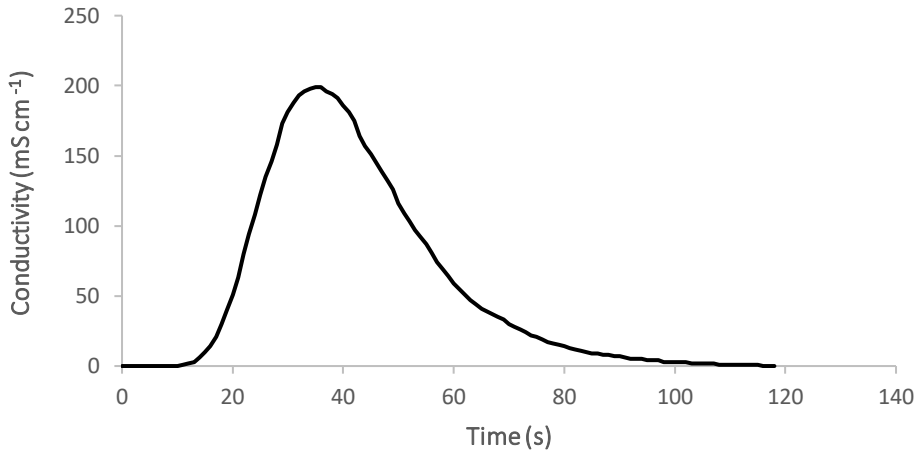

Figure 22: Conductivity curve after a 1 L sea water salt injection from the northern colony stream at site P3 on the 1st of January 2023.

Using the conductivity curve, stream discharge (Q) is then calculated using three equations (Equation 4 to 6). The first calculation works out the area underneath this curve (A_{EC}) where Δt is the time difference between measurements (1 second) and *n* is the number of measurements within a pulse.

$$A_{\mathrm{EC}} = \Delta t \times \sum\nolimits_{n} \left(\mathrm{EC}(t) - \mathrm{EC}_0\right) \qquad \text{Equation 4}$$

From this the integral of concentration over time can then be calculated, where *t* is time in seconds, t_1, t_2 are the start and end times of the tracer pulses, C_t is the tracer concentration at the sampling point at time *t*, C_0 is the background concentration, and *dt* represents an instantaneous change.

$$\int_{t_1}^{t_2} (C_t - C_0)dt = A_{\mathrm{EC}} \times f_C \qquad \text{Equation 5}$$

Then, using V_1, the volume of water injected, the discharge in L s^{-1} can then be calculated:

$$Q = \frac{V_I}{\int_{t_1}^{t_2} (C_t - C_0)dt} \qquad \text{Equation 6}$$

3.6.11 Calculation of load

The load of a particular analyte was calculated according to Harrison and Laxen (1984) (Equation 7). This was calculated using HM total recoverable and nutrient concentrations from the corresponding sites P3 and C3 where discharge was calculated for each of the four measurement days.

$$Load = Analyte\ concentration \times Q \qquad \text{Equation 7}$$

3.6.12 Statistical analysis

Inductively coupled plasma-mass spectrometry results from the dissolved and total recoverable soil and water analyses required some grooming prior to statistical analysis. Where any blanks returned

concentrations detected by instruments, their concentrations were checked for the relevant blank or average of the blanks where multiple were analysed, was subtracted from the sample concentrations.

Statistical tests were conducted using RStudio (version 2023.06.2 + 561) using the following packages: *car* version 3.1 (Fox & Weisberg, 2019)*, dplyr* version 1.1.3 (Wickham et al., 2023), and *ggplot2* version 3.4.3 (Wickham, 2016). A Shapiro-Wilk test and QQ-plots were used to test for normality. One-way ANOVA was used to compare sites with results returning a level of significance less than 5 % ($P<0.05$) then analysed with Tukey's Honest Significant Difference (HSD). A Pearson's Correlation was also conducted in R-studio using AWS air temperature to the nearest 10-minute recording at the time of discharge measurements.

Data collected by the AWS was analysed and summarised by Eva Bendix Nielsen of the University of Canterbury.

Heavy metal and nutrient concentrations were additionally compared to the Australia and New Zealand Freshwater Guidelines (ANZFG) for the protection for 99 % of species (ANZECC and ARMCANZ, 2000) and the Canadian Ecological Quality Guidelines (CEQG) (CCME, 1997). The CEQG for soil was selected as the Canadian Arctic environment, although not a perfect replica of the ice-free areas of Antarctica, are also subject to extreme cold and common freeze/thaw patterns. Where multiple threshold values were present, the lowest threshold values representing highest level of protection are chosen due to the comparatively reduced anthropogenic perturbation and high ecological value of Antarctica.

4 Transfer of toxic levels of heavy metals and nutrients from penguin colonies via Antarctic melt streams

This chapter presents the main findings of this research written in a paper format to be submitted as a journal article. As a result, not all analyses performed throughout this research are presented within this section. Concentrations and comparisons of key HM (As, Cd, and Pb) and nutrients (NH_4^+, NO_3^-, PO_4^3, TN, and TC) within soil and water are presented. This is in addition to soil and water physiochemical properties (pH and EC), discharge and its relationship with temperature, and key HM loads. Subsidiary content is found in the appendices, including analysis of additional total and dissolved melt water heavy metals (Appendix 2 and 3) and nutrients (Appendix 4), as well as additional soil heavy metals (Appendix 5) and nutrients (Appendix 6). Raw measurements of water physiochemical parameters (Appendix 7), discharge (Appendix 8), load (Appendix 9), and clay mineralogy (Appendix 10) may also be found. Summary information of the AWS data over deployment was analysed by Eva Bendix Nielsen, University of Canterbury, and is provided in Appendix 11, with raw AWS data in Appendix 12. Lastly, the ANOVA and Tukey's HSD comparisons are presented in Appendix 13.

Transfer of toxic levels of heavy metals and nutrients from penguin colonies via Antarctic melt streams

4.1 Abstract

In Antarctica, the escalating presence of heavy metals is of growing concern. While the biological transport of anthropogenically derived contaminants remains frequently overlooked, in the Arctic it has been shown to rival the atmospheric flux of contaminants. Penguin colonies have been identified as sites of heavy metal and nutrient accumulation. This research evaluated the role of seasonal melt water, as it flows through penguin colonies, in the redistribution of heavy metals, specifically arsenic (As), cadmium (Cd), and lead (Pb), along with the nutrients, ammonium (NH_4^+), nitrate (NO_3^-), and phosphate (PO_4^{3-}). Melt water and soil samples were collected from Adélie penguin-influenced and control streams at Cape Bird, Antarctica. Arsenic, Cd, and Pb, were elevated in melt water and soil within the Adélie penguin colony (p<0.05). Heavy metal water concentrations exceeded New Zealand freshwater guidelines for ecological health up to 37, 8, and 2 times for As, Cd, and Pb, respectively. Arsenic had a relatively high proportion within the dissolved metal fraction (35 – 72 %) indicating increased toxicity. Ammonium, nitrate, and phosphate were also elevated in penguin-influenced water compared to the control stream (p<0.05), surpassing water quality guidelines a maximum of 1038, 1017, and 551 times. When accounting for differences in stream discharge, load was significantly higher for heavy metals (p<0.05), with nitrate and phosphate showing the largest differences (p<0.01). Discharge was also strongly correlated with air temperature (P3 R=0.88, C3 R=0.81). This research suggests that seasonal melt streams play an important role in redistributing potentially toxic levels of heavy metals and nutrients from penguin colonies into the Southern Ocean. Given the inherent variability of melt streams, more research is needed to determine transfer over longer time scales. Moreover, the relationship between load and air temperature highlights the need for understanding how climate change induced temperature shifts affect the flow of melt streams and the associated heavy metal and nutrient transport may intensify.

4.2 Introduction

Owing to its geographical isolation and short history of occupation, Antarctica is generally considered as pristine. Contrary to this belief, it has been dramatically affected by anthropogenic perturbation (Bargagli, 2005). Recent research has revealed the presence of organochlorines, polychlorinated biphenyls, pesticides (Choy et al., 2010), flame retardants (Lewis et al., 2020), microplastics (Aves et al., 2022), and increasing concentrations of heavy metals (Webb et al., 2020). Due to human activity, heavy metal emissions have increased since the 1940s and have led to their inevitable deposition within the Antarctic marine and terrestrial environments (Nriagu, 1996; Tuohy et al., 2015). This issue is compounded by the fact that polar regions are known repositories of anthropogenic contamination (Corsolini, 2009; Xie et al., 2022).

Anthropogenically derived heavy metals accumulate in Antarctica through direct point sources, atmospheric deposition, and biological transportation (Webb et al., 2020). The latter is often overlooked, but in the Arctic, it has been shown to rival atmospheric fluxes (Blais et al., 2005). Seabirds, such as Adélie penguins (*Pygoscelis adeliae*), play a crucial role in the transport of nutrients and contaminants between the marine-terrestrial interface (De La Peña-Lastra et al., 2022; Sparaventi et al., 2021). Foraging on mostly krill in the open ocean, heavy metals within the food chain may be assimilated, bioaccumulated, and potentially biomagnified due to penguins' high trophic position (Chu et al., 2019; Xie & Sun, 2008). Metals are then deposited on ice-free areas through seabird related substrates such as guano, feathers, eggshells and carcasses (Brasso et al., 2012; De La Peña-Lastra et al., 2022). This effect is exacerbated within Adélie penguin colonies as birds return to the same nests for several millennia, facilitating the accumulation of extensive ornithogenic soils (Emslie et al., 2007; Emslie et al., 2014). As a result, Adélie penguin formed ornithogenic soils are recognized as sites for the accumulation of anthropogenically derived heavy metals (Ellis et al., 2018; Sun & Xie, 2001) and high concentrations of nutrients (Sun & Xie, 2001; Sun et al., 2020; Xie & Sun, 2008). This is especially significant in Antarctica, where background nutrient levels are low, and environments are typically considered oligotrophic. Antarctic penguins are a keystone species, and their colonies are known as

biological hotspots, supporting high biodiversity and abundances of mosses, lichens, and invertebrates (springtails, mites, roundworms) which comprises a sizeable portion of Antarctica's ecological diversity (Bokhorst et al., 2019; Lee et al., 2017).

Adélie penguin colonies are situated in scarce, ice-free areas along the Antarctic coast, often between large ice caps or glaciers and the sea (Emslie et al., 2007). In the austral summer, 24-hour radiation leads to the formation of glacial melt streams that persist for 6 to 12 weeks, with peak-flow coinciding with peak soil thaw in mid-January (Howard-Williams et al., 1986). Streams flow through penguin colonies and erode ornithogenic soils before flowing into the sea. Despite this, the movement of heavy metals and nutrients from penguin colonies into the wider environment has received limited attention.

To address this knowledge gap, this study aimed to investigate the role of seasonal melt streams in transporting heavy metals (As, Cd, Pb) and nutrients (NH_4^+,NO_3^-, nitrite, and PO_4^{3-},) from penguin colonies into the marine environment. Heavy metal and nutrient composition and contaminant risk were compared at several sites along the length of both a penguin-influenced and control melt streams. Stream discharge and contaminant load were determined, in addition to soil chemical composition to further quantify the influence of penguin activity on melt streams.

4.3 Methods

4.3.1 Study location and sampling

The Cape Bird northern colony (S: 77.21404, E: 166.44781) is located on the north-western tip of Ross Island, Antarctica (Figure 23). From October to February, approximately 50,000 breeding pairs of Adélie penguins' nest on beach ridges between the Bird Ice Cap and the Ross Sea (Davis et al., 2001; Lyver, 2020). Several melt streams flow through the colony, with penguins frequently nesting on the stream edges.

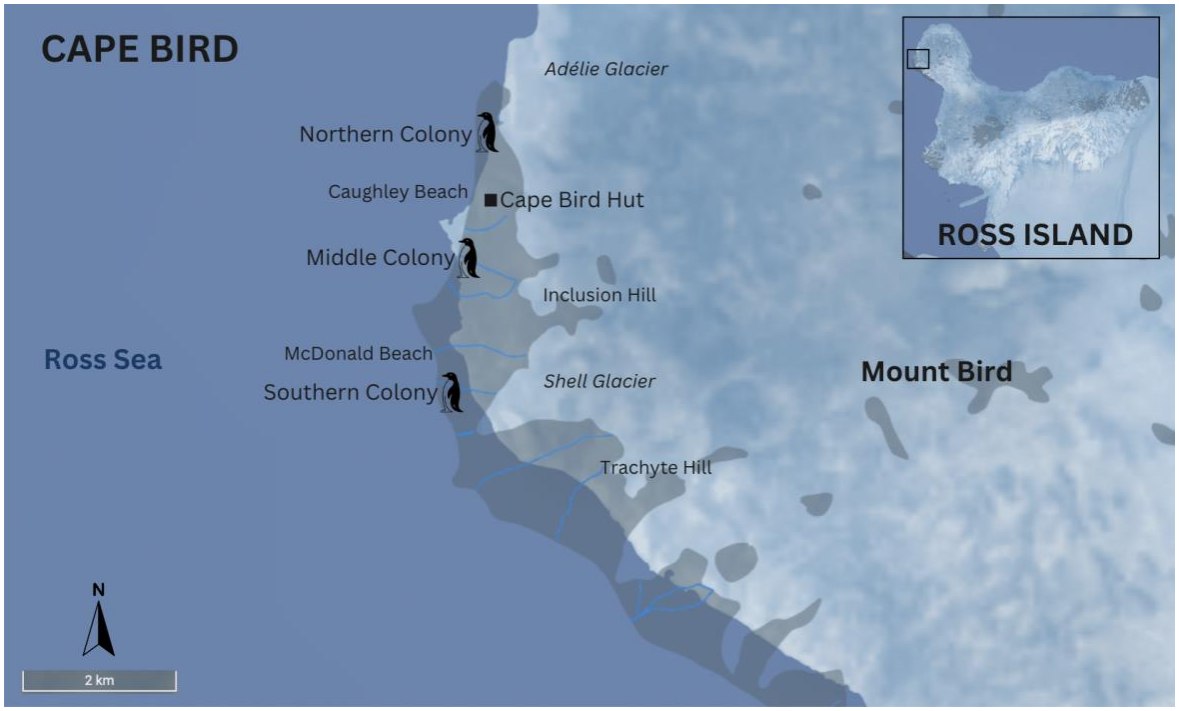

Figure 23: Map of Cape Bird, Ross Island, showing the Adélie penguin colonies and key geological features. Imagery sourced from Manaaki Whenua, Landcare Research.

This research focussed on two streams, one within the Cape Bird northern colony, and a control stream approximately one kilometre south with no ornithogenic soils within its catchment. Filtered (0.45 μm) and unfiltered water samples were taken mid-stream at five sites along these streams with sample sites in the northern colony, P1 to P5 (Figure 24), spanning the gradient of ornithogenic influence. Additionally, physiochemical parameters (temperature, pH, electrical conductivity (EC), and turbidity) were measured (YSI ProQuatro multiparameter and Sper Scientific 860040 Turbidity meter) at the time of sampling. Water samples were collected on four days on the 1st, 3rd, 7th, and 10th of January 2023.

Soil was sampled at three sites adjacent to the melt streams, P0 near the terminal face of the Cape Bird Ice Cap and the origin of the colony stream, P4 within the colony and C5 adjacent to the control stream right before it enters the sea. Surface samples were collected (0-2 cm) at all sites and subsequently at any visible horizons. Soil was sampled to the depth of ice-cement (frozen ground) at

sites P0 and C5 (both 35 cm), and at P4, samples were taken until the beach ridge parent material was reached (63 cm). Water and soil samples were frozen at -20 °C until subsequent analysis.

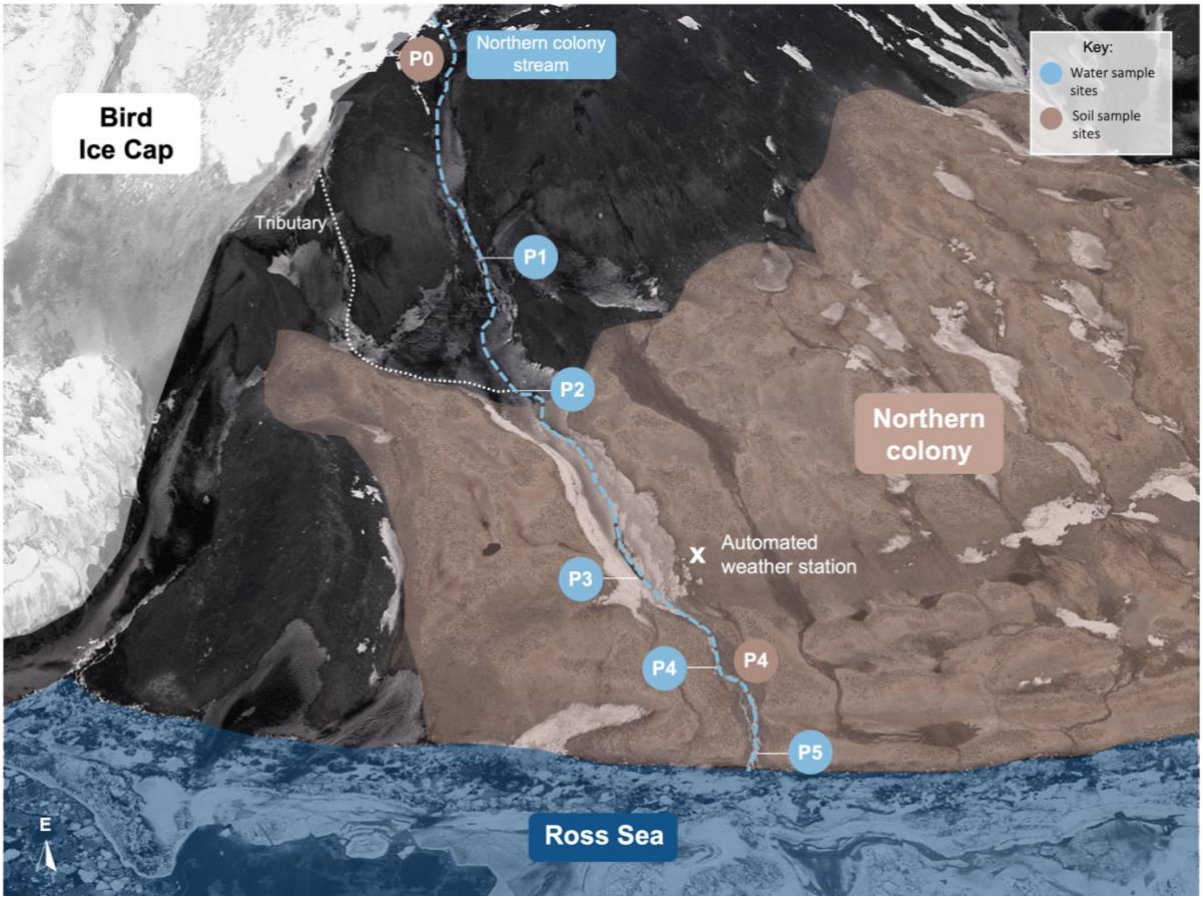

Figure 24: Map of stream water sampling and physiochemical measurement sites (P1 – P5) and soil sampling sites (P0 and P4) at the Cape Bird northern colony. Image from Kerry Barton.

4.3.2 Water chemical analysis

Metal analysis was conducted at sites 1, 3, and 5 within the penguin-influenced and control streams. These three sites were chosen to represent changes along the northern colony stream before (P1), in the middle (P2) and near the end (P3) of the penguin colony influence with corresponding control stream sites selected for comparison and consistency. Dissolved metals, those which have been passed through a 0.45 μm pore size filter, were analysed using field-filtered water samples and acidified with 2 % (V/V) ultrapure nitric acid (EPA 200.8) (US EPA, 1994). Total recoverable metal analysis includes the dissolved fraction and any metals associated within suspended sediment in the sample. Total

recoverable analysis involved sample digestion for two hours at 90 °C with 3 % (V/V) ultrapure 1:2 nitric acid to HCl mix (EPA 200.2) (Martin et al., 1994). Both dissolved and total recoverable metals were analysed through an Agilent 8900 triple quadrupole inductively coupled plasma-mass spectrometer (ICP-MS). Nutrient analysis was conducted at all five sites along the penguin-influenced (P1 through P5) and control stream (C1 through C5). Filtered water from all sites was measured for anionic nutrient concentration using an ion chromatographer (ThermoScientific Dionex Intregrion). The different anions were separated using an isocratic gradient elution method. Ammonium was measured using the colourimetric indophenol blue reaction. Filtered water samples were combined with a phenol and sodium nitroprusside solution and a sodium hypochlorite and sodium hydroxide solution. Samples were read by Pharmacia Biotech Ultrospec 3000 at 625 nm wavelength.

4.3.3 Stream discharge and load

Stream discharge was measured through dilution gauging using seawater as a chemical tracer as outlined in Moore (2004). Although numerous sites were tested along each stream, only one site within each stream, P3 and C3, were deemed to have sufficient length and thorough mixing, without the presence of braiding to ensure accurate results. Dilution gauging was undertaken on the same days as water sampling. The contaminant load was calculated using equation 8:

$$\text{Load} = \textit{Analyte concentration x discharge} \qquad \text{Equation 8}$$

4.3.4 Soil chemical analysis

Soil samples were oven-dried at 60 °C and crushed. A subsample of 1 g of soil was digested with 14 mL of ultrapure 5:2 nitric to HCl. The extracting solution was refluxed at 90 °C for 3.5 hours. The resulting extract was filtered to 0.45 μm and diluted before analysis (EPA 200.2) (Martin et al., 1994). Water and soil were analysed using ICP-MS at the University of Waikato, Hamilton, New Zealand. Soil pH was measured with 1:5 (W/V) samples and Type 1 water extraction. This was followed by

vigorous mixing, and subsequent measurement of the aqueous phase by a ThermoScientific Orion 4-star benchtop pH meter. Soil ammonium was measured after extracting 10 ± 0.02 g soil with a 0.3:2 (W/V) potassium chloride to Type 1 water mix and filtered using Whatman GF-C paper. A sodium hydroxide tartrate solution, sodium hypochlorite and alkaline phenol solution were added to the soil extract and the absorbance of the solution was measured at 635 nm according to Wang and Øien (1986). Total soil nitrogen and total carbon were measured by combustion. Briefly, oven-dried soil was crushed within a tungsten-carbide ring mill, and subsequently, 10 mg of the ornithogenic soil was weighed into tin capsules. For the control site, 100 mg of soil was used for analysis. Capsules were combusted in an Elementar Vario EL Cube.

4.3.5 Automated weather station

On the 28th of December 2022 an automated weather station was installed at the northern colony, adjacent to the stream site P3, and later disestablished on the 10th of January 2023. The automated weather station consisted of a Campbell Scientific 92000 ResponseONE weather transmitter, which measured windspeed and direction, temperature, humidity, and air pressure. An Apogee SN-500-SS net radiometer measured the incoming and outgoing radiation. Data was logged at 10-minute intervals and downloaded using the Campbell Scientific PC400 Datalogger Support Software (version 4.7).

4.3.6 Data analysis

Differences in the concentration of heavy metals, nutrients, and contaminant loads along the length of streams and between streams were compared using one-way ANOVA and subsequent Tukey's HSD. Pearson's correlation test was conducted between discharge and air temperature as measured by the automated weather station. All statistical analysis was conducted in RStudio (version 2023.06.2+561).

Heavy metal and nutrient concentrations in soil and water were additionally compared to the Australia and New Zealand Freshwater Guidelines (ANZFG) for the protection for 99 % of species (ANZECC and ARMCANZ, 2000) and the Canadian Ecological Quality Guidelines (CEQG) (CCME, 1997). These were selected as Antarctica does not have water or soil toxicity values based on relevant species, environmental, and toxicological interactions. The Canadian Arctic environment, although not a perfect replica of the ice-free areas of Antarctica, are also subject to extreme cold and common freeze/thaw patterns. Where multiple threshold values were present, the lowest threshold values representing the highest level of protection were chosen due to the comparatively reduced anthropogenic perturbation and high ecological value of Antarctica. It should also be noted that not all analytes measured within this research have CEQG guideline values.

4.4 Results

4.4.1 Stream water chemical composition

P-values of ANOVA and Tukey's HSD comparisons of heavy metal (sites 1, 3 and 5) and nutrient (sites 1 through 5) concentrations can be found in Appendix 13. Sites within the Cape Bird northern colony with direct penguin influence (P3 to P5) had significantly higher total recoverable As, Cd, Pb, ammonium, and nitrate ($p<0.05$) compared to upstream sites (P1 and P2), and all sites in the control stream (C1 through C5) (Table 8). Maximum concentrations of As (2.92 μg As L^{-1}) and ammonium (10.38 mg NH_4^+ L^{-1}) were recorded at site P3. Whereas maximum concentrations of nitrate (20.34 mg NO_3^- L^{-1}) were recorded at site P4, while maximum concentrations of Cd (0.46 μg Cd L^{-1}) and Pb (1.8 μg Pb L^{-1}) were at site P5. Phosphate within the northern colony stream was significantly higher from sites P2 through P5 than the upstream P1 site ($p<0.05$), with a maximum of 4.96 mg PO_4^{3-} L^{-1} recorded at P4. Phosphate concentrations in sites P2 through P5 were also significantly higher compared to the control stream sites C1 through C5 ($p<0.01$). There were no statistical differences in total recoverable metals or nutrient concentrations between sites along the control stream (C1 through C5) ($p>0.05$).

Total recoverable As, Cd, and Pb exceeded the ANZFG threshold values by up to 37, 8 and 2 times, respectively, the threshold value within penguin-influenced sites (P3 and P5). Ammonium and nitrate exceeded the ANZFG threshold values at all sites within both the penguin-influenced and control stream, with a maximum exceedance 1038 times higher for ammonium at site P3 and 1017 times higher at site P4. Phosphate exceeded guideline values within the northern colony stream only (from sites P2 to P5), with a maximum of 551 times the ANZFG threshold value at site P4.

Table 8: Average heavy metal and nutrient concentrations over duplicate samples from four sampling days in January 2023, along the length of the northern colony and control stream at the Cape Bird, Ross Island. Concentrations in bold have exceeded the ANZFG threshold values for 99 % species protection (ANZECC and ARMCANZ, 2000).

Site	pH	EC	As	Cd	Pb	NH_4^+	NO_3^-	PO_4^{3-}
		$\mu S\ cm^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$
Northern colony stream								
P1	8.07	702.68	0.53	0.03	0.09	**0.24**	**3.08**	0.00
P2	7.78	524.73	-	-	-	**0.27**	**5.10**	**1.24**
P3	**6.86**	532.18	**2.94**	**0.27**	**1.65**	**10.38**	**14.12**	**4.78**
P4	**7.09**	546.80	-	-	-	**8.47**	**20.34**	**4.96**
P5	8.07	504.50	**2.61**	**0.46**	**1.80**	**9.15**	**13.74**	**4.55**
Control stream								
C1	7.50	408.38	0.37	0.01	0.17	**0.13**	**1.40**	0.00
C2	7.38	429.68	-	-	-	**0.08**	**1.51**	0.00
C3	7.31	430.63	0.19	0.01	0.09	**0.09**	**1.66**	0.00
C4	7.31	431.25	-	-	-	**0.14**	**1.56**	0.00
C5	**7.25**	436.25	0.18	<0.01	0.07	**0.12**	**1.99**	0.00
ANZFG	7.30 - 8.50	ND	0.80	0.06	1.0	0.01	0.02	<0.01

' – ' = Not analysed, 'ND' = No data

The pH of both streams was circumneutral to slightly basic ranging from 6.86 – 8.07. Electrical conductivity was higher at all sites within the northern colony stream (504.5 – 702.68 $\mu S\ cm^{-1}$) compared to the control stream (408.3 – 436.38 $\mu S\ cm^{-1}$). At sites P3, P4 and C5, average pH was lower than the ANZFG threshold of 7.3 to 8.5.

The proportion of dissolved versus total recoverable metals varied between the different elements with As having a significantly higher dissolved fraction (up to 72 %) within both the northern colony and control streams compared to Cd (up to 22 %) and Pb (up to 11 %) (Figure 25).

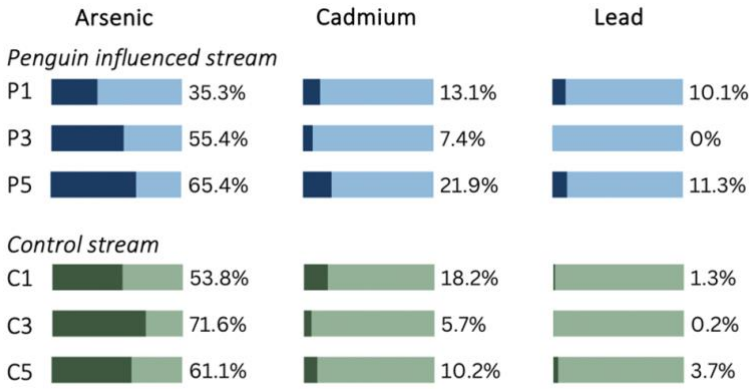

Figure 25: Average percentage of dissolved heavy metals (filtered to 0.45 mm) compared to total recoverable metals over four sampling days in January 2023 at sites along a penguin-influenced (P1, P3, and P5) and control stream (C1, C3, and C5), Cape Bird, Ross Island.

4.4.2 Stream discharge and load

Stream discharge measured at sites P3 and C3, had large daily variations, particularly within the penguin-influenced stream (16.7 - 52.3 L s^{-1}), compared to the control stream (10.8 - 14.7 L s^{-1}) (Figure 26). The highest discharges were recorded between 2 pm and 4 pm on the 1st of January in the penguin-influenced stream (52.3 L s^{-1}) and on the 10th of January in the control stream (14.7 L s^{-1}), which coincides with peak daily temperatures.

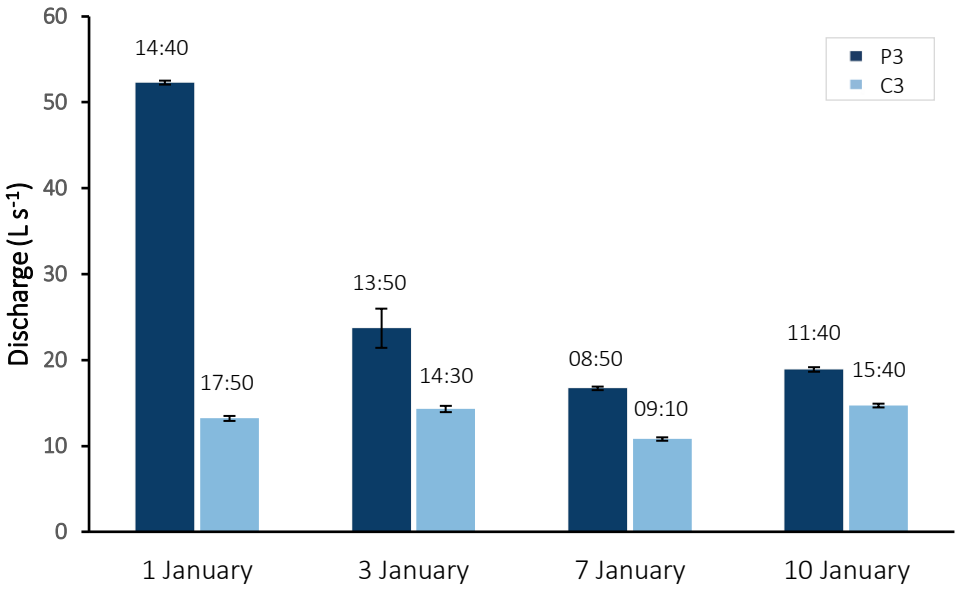

Figure 26: Average discharge measurements of three injections made at site P3 (northern colony stream), and C3 (control stream) over four sampling days in January 2023 at Cape Bird, Ross Island. Discharges are an average of three measurements. The time of day during measurements is displayed above discharges.

Load was calculated at the sites where discharge was measured to account for the difference discharge may have on concentration (Table 9). The average load of As, Cd, Pb and ammonium was 103.49 µg As s^{-1}, 9.98 µg Cd s^{-1}, 53.22 µg Pb s^{-1}, and 404.04 µg NH_4^+ s^{-1} at site P3. These loads were significantly higher (p<0.05) than that of site C3, 1.68 µg As s^{-1}, 0.09 µg Cd s^{-1}, 0.43 µg Pb s^{-1}, and 21.30 µg NH_4^+ s^{-1}. Notably, nitrate and phosphate showed the most significant differences in stream load between sites (p<0.01) with 349.55 mg NO_3^- s^{-1} and 147.37 mg PO_4^{3-} s^{-1} at P3, compared to 1.2 mg NO_3^- s^{-1} and no phosphate detected at C3. Pearson's correlation between discharge and air temperature, as measured by our automated weather station, had a strong positive correlation (P3 R=0.88, C3 R=0.81).

Table 9: Average heavy metal and nutrient load measurements at P3 (northern colony stream), and C3 (control stream) over four sampling days in January 2023 at Cape Bird, Ross Island.

Site	As	Cd	Pb	NH_4^+	NO_3^-	PO_4^{3-}
	µg s^{-1}	µg s^{-1}	µg s^{-1}	mg s^{-1}	mg s^{-1}	mg s^{-1}
P3	103.49	9.98	53.22	404.04	349.55	147.37
C3	1.68	0.09	0.43	21.30	1.20	0.00

4.4.3 Soils

Within the ornithogenic soil (P4), As, ammonium, total carbon, and total nitrogen had the highest concentrations within surface soils (0 – 2 cm) with 14.54 μg As g^{-1}, 8.59 μg NH_4^+ g^{-1}, 14.53 % C, and 8.19 % N (Table 10). Concentrations decreased with depth to 2.73 μg As g^{-1}, 1.11 μg NH_4^+ g^{-1}, 0.21 % C, and 0.24 % N at 53 – 65 cm depth. Cd and Pb, however, had their highest concentrations at 18 – 37 cm (2.87 μg Cd g^{-1}) and 2 – 18 cm (3.96 μg Pb g^{-1}), respectively, before decreasing with depth. Concentrations of all analytes were significantly higher within the P4 soil compared to the P0 and C5 control soils (p<0.05), which had significantly lower concentrations and very little variation down the profile. Soil As within the P4 surface soil, and Cd within P4 surface to 44 cm depth exceeded the CEQG threshold guidelines.

Table 10: Average heavy metal and nutrient content within three soils at Cape Bird, Ross Island. Concentrations in bold have exceeded the CEQG guidelines (CCME, 1997). Samples are an average of laboratory duplicates.

Depth	pH	EC	As	Cd	Pb	NH_4^+	TN	TC
cm		mS cm^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}	mg g^{-1}	%	%
Site P4, an ornithogenic soil								
0 - 2	7.78	30.00	**14.54**	**1.40**	1.04	8.59	8.19	14.53
2 - 18	8.43	31.26	9.04	**2.43**	3.96	8.01	6.92	10.75
18 - 37	8.32	22.48	10.29	**2.87**	2.37	5.95	2.07	4.89
37 - 44	8.33	11.20	6.07	**2.50**	1.90	4.52	0.51	1.17
44 - 53	8.39	4.03	3.34	0.33	1.53	2.04	0.46	1.06
53 - 65	8.57	1.66	2.73	0.15	1.83	1.11	0.24	0.21
Site P0, a control soil above penguin colony								
0 - 2	9.47	0.12	1.31	0.26	1.55	<0.01	<0.01	0.04
18 - 20	9.86	0.16	0.96	0.09	1.23	<0.01	<0.01	0.07
33 - 35	9.51	0.11	0.88	0.10	1.15	<0.01	<0.01	0.03
Site C5, a control soil								
0 - 2	9.27	1.85	0.59	0.04	0.64	<0.01	<0.01	0.03
33 - 35	8.14	0.09	0.54	0.09	0.77	<0.01	<0.01	0.03
CEQG	ND	ND	12.00	1.40	70.00	ND	ND	ND

'ND' = No data available

Soil pH was circumneutral to basic within the P4 soil, with pH increasing with depth (7.78 to 8.57). Site P0 (9.47 to 9.86) and C5 (8.14 to 9.27) also had circumneutral to basic pH. Electrical conductivity was notably higher within the top 44 cm of P4 soil (11.2 to 31.26 mS cm^{-1}) than at site P0 (0.11 to 0.16 mS cm^{-1}) or C5 (0.09 to 1.85 mS cm^{-1}).

4.5 Discussion

4.5.1 Heavy metal enrichment in penguin-influenced melt streams

Our findings support research highlighting the biogenic enrichment of As, Cd, and Pb from seabirds (Brimble et al., 2009; Castro et al., 2021; Metcheva et al., 2011) (Table 8). Studies of Arctic waters influenced by seabirds revealed Cd and As concentrations ranging from 0.22 - 3.3 μg As L^{-1}, and 0.01 - 0.03 mg Cd L^{-1}, respectively (Brimble et al., 2009). Our results show a similar concentration range for As at the penguin-influenced sites (2.61 - 2.94 μg As L^{-1}), however, Cd levels were notably up to 15 times higher (0.27 – 0.46 μg Cd L^{-1}). Previous research has consistently identified elevated Cd levels within the tissues of Antarctic birds and mammals (Metcheva et al., 2011; Szefer et al., 1993; Szefer et al., 1994). The upwelling of Cd-rich waters in the Ross Sea has been suggested as an additional source of Cd, and therefore a driver of increased bioaccumulation in Antarctic and Southern Ocean biota (Metcheva et al., 2011; Sanchez-Hernandez et al., 2000; Szefer et al., 1993; Szefer et al., 1994). Krill also has a high affinity for As and Cd, with concentrations three to four times higher in krill than in the surrounding waters (Mirzoeva et al., 2022). This subsequently increases the potential for As and Cd bioaccumulation and biomagnification by penguins (Xie & Sun, 2008). Pb within the northern colony stream (1.65 – 1.80 μg As L^{-1}) was within the range recorded by Nędzarek et al. (2014) of 1.46 – 10.41 μg Pb L^{-1} in penguin-influenced surface waters. Sun and Xie (2001) investigated historical increases of Pb within penguin guano-formed sediments. Results increased significantly post the industrial revolution, with particular increases within the last 50 years (Sun & Xie, 2001). Despite global heavy

metals increasing rapidly due to anthropogenic activities, heavy metals can also have natural sources, therefore, it is difficult to attribute results to a specific source without further investigation.

Arsenic, Cd and Pb exceeded ANZFG threshold values within penguin-influenced waters (Site P3 and P5), being up to 27, eight and two times higher than the control stream, respectively. This indicates the potential for toxic and adverse effects on biota within these ecosystems, such as reduced reproduction, behavioural changes, and increased mortality (Jaishankar et al., 2014). While these guidelines are useful for characterizing potentially hazardous substances, actual chemical toxicity may vary due to the chemical species, bioavailability, physiochemical conditions, exposure, and species-specific physiology. As melt streams connect the terrestrial and marine ecosystems, it is also important to consider that melt streams are transporting potentially toxic loads to the nearshore environment, however, more research into dilution effects and the potential impacts on benthic communities within the nearshore marine environment is recommended.

The low proportion of Cd and Pb within the dissolved metal fraction indicates these metals are predominantly in a solid phase (Figure 25) (Cotter-Howells, 1996). It can be assumed, as in Nędzarek et al. (2014), that Cd and Pb are adsorbed or complexed to minerals and organic matter suspended within waters, which is common in Antarctic melt waters (Sheppard et al., 1997). Conversely, the higher portion of dissolved As indicates increased bioavailability. The interaction of multiple factors such as pH, speciation, EC, and particulate matter surfaces determines metal binding and subsequently affects toxicity (Préndez & Adriana Carrasco, 2003). The neutral to basic stream pH (colony stream: pH 6.86-8.07, control stream: pH 7.31-7.50) favours Cd binding (Kubier et al., 2019), however, As solubility is increased in alkaline conditions, potentially explaining differences in dissolved metal proportions (Gersztyn et al., 2013). Cadmium and Pb are further known to be immobilized when present with elevated levels of organic matter, such as what is found in ornithogenic soils (Castro et al., 2021; Malik et al., 2021; Simas et al., 2007), as demonstrated by the high total carbon content in the P4 ornithogenic soil with up to 14.5 % carbon in the guano rich upper horizons. Despite this, our ability to determine

factors controlling the proportions of dissolved versus total recoverable metals is limited without detailed analysis of the parent material and organic matter present (Nędzarek et al., 2014). Further work would be required to analyse the mechanisms controlling dissolved metal fractionation.

4.5.2 Nutrient enrichment in penguin-influenced melt streams

Ammonium and nitrate concentrations exhibited enrichment several orders of magnitude higher within the penguin colony (8.47 – 10.38 mg NH_4^+ L^{-1}, 13.74 – 20.34 NO_3^- L^{-1}), surpassing levels found upstream of the colony and in the control stream (Table 8). These concentrations were consistent with earlier studies conducted by Lindeboom (1984) on ammonium (0 - 70 mg NH_4^+ L^{-1}) and Tatur and Myrcha (1983) on nitrate in penguin-affected water (0 – 43 mg NO_3^- L^{-1}). High nitrate levels within this study (up to 20 mg L^{-1}) may be attributed to its mobility within soils, leading to rapid leaching (Speir & Cowling, 1984), typically coinciding with peak thaw events (Yano et al., 2010). Notably, nitrite was not detected in this study or in Lindeboom (1979). The absence of nitrite suggests that the shallow and turbulent waters are well-oxygenated and that the source of forms of nitrogen, the adjacent ornithogenic soils being eroded by the melt water stream, also maintain oxygen-rich conditions (Lamba et al., 2017).

All sites measured within both streams (P1-P5 and C1-C5) exceeded the ANZFG threshold concentration for 99% species protection for ammonium and nitrate. Interestingly, this included sites beyond the northern colony (sites P1 and C1 through C5) despite the lack of direct nitrogen inputs. While some level of nutrients is expected in the control waters due to its origin of glacial ice (comprising ground-up rock, wind-blown sand and silts, salts, and atmospherically deposited nutrients), concentrations are well above what is seen in oligotrophic melt streams within the McMurdo Dry Valleys which lack in penguin influence (Howard-Williams et al., 1986). Within guano, urea is the dominant form of nitrogen, which has been shown to be rapidly volatilised (Hadas & Rosenberg, 1992; Lindeboom, 1979, 1984). The subsequent redeposition of ammonia has been shown to affect an area up to 240 times the size of the colony boundaries (Bokhorst et al., 2019). Data from the long-term

University of Wisconsin Madison weather station at Cape Bird has shown a prevailing north to north-east wind, which may facilitate redeposition of ammonia towards the control stream (University of Wisconsin, 2017). The high pH within the colony soils also supports ammonia volatilisation of guano urea (Erskine et al., 1998; Rochette et al., 2013).

Phosphate was only detected in melt stream sites P2 through P5 with concentrations exceeding ANZFG thresholds at these sites. Penguin colonies have been known to redistribute phosphorous through phosphine emissions (Zhu, Liu, Ma, Sun, Xu, & Sun, 2009; Zhu, Wang, et al., 2014), however a lack of phosphates outside of colony boundaries aligns with Nedzarek (2007), and therefore, redistribution is low.

1.1.1 Stream discharge and contaminant load

There were large variations seen between both measurement days and time, particularly within the northern colony stream (Figure 26). Discharge measurements at P3 fell within the range of what was measured at the Cape Bird northern colony by Howard-Williams et al. (1986). However, it should be noted that our maximum discharge (52.3 L s^{-1}) was only half of the Howard-Williams et al. (1986) recorded maximum (162 L s^{-1}). This leads us to believe that our fieldwork may not have coincided with the annual peak thaw period, potentially resulting in measurements taken outside the peak erosive and transport capacity of the streams.

Load was calculated at P3 and C3 to account for the influence of stream discharges on heavy metal and nutrient concentration in stream waters (Table 9). Loads of As, Cd, Pb, ammonium, nitrate and phosphate remained significantly higher (p<0.05) at P3 within the colony stream. The significant chemical contrasts in both load and concentrations, evident not only between streams but along their lengths, indicate that the northern colony stream is experiencing substantial enrichment originating from the penguin colony. It is important to acknowledge that while levels of heavy metals and nutrients within the penguin-influenced stream exceed what the control stream presents as background levels, this study reflects a relatively short timeframe due to constraints in conducting Antarctic fieldwork.

Given the extreme seasonality in Antarctica and recorded variations in discharge, the results are likely to exhibit considerable variability over longer timescales. Fluxes within streams may also vary with the seasonal presence and size of the penguin population and the degree of soil thaw (Finne et al., 2022; Xie & Sun, 2008). Nevertheless, the contamination of heavy metals and high nutrients is predicted to impact biota surrounding penguin-enriched melt streams.

Streams also serve a crucial role in connecting terrestrial and marine ecosystems, facilitating the exchange of nutrients between the two. Their impacts extend beyond their immediate boundaries, with potentially toxic levels of heavy metals and nutrients carried into the Southern Ocean. This may have significant consequences for biota living within the receiving environment. This is particularly important as keystone species, such as phytoplankton, are amongst some of the most sensitive to As toxicity (Abbas et al., 2018; Neff, 1997). However, future studies would be required to quantify these impacts. Despite the majority of transported metals being in particulate form, which lowers their potential for toxicity, it is also important to account for how future oceanic changes, such as warming temperatures and increased acidity, may increase solubility and thus toxicity of these heavy metals within the Southern Ocean.

The relationship between air temperature and discharge also brings into question how these streams will change within a warming world, where higher temperatures and longer summers will influence the melt stream discharge, and the duration of seasonal flow, both of which may increase heavy metal and nutrient transport.

4.5.3 Soils as sources of melt stream enrichment

As predicted, ornithogenic soil (P4) exhibited significant enrichment of heavy metals and nutrients, with the most noticeable effects within the upper 44 cm of soil (Table 10). Among the heavy metals reported, Cd was particularly enriched (p<0.05) with concentrations in P4 (2.87 μg Cd g^{-1} dry weight) surpassing the maximum Cd concentration of 2.38 μg Cd g^{-1} reported by Santamans et al.

(2017). The neutral to basic pH of soils (7.78 to 9.86) is likely a reflection of Cape Bird basalt parent material (Speir & Cowling, 1984).

Cd within soils at P4 from 0-44 cm, exceeded Canadian soil guideline values. Arsenic also showed remarkable enrichment at site P4, with concentrations up to 27 times higher than those within control soils (P0 and C5) (p<0.01), reaching a maximum concentration of 14.54 μg As g^{-1} dry weight. While this was twice as high as values reported in penguin ornithogenic soils by Santamans et al. (2017), it fell within the range of penguin guano-influenced sediments (Xie & Sun, 2008). The presence of high levels of As, even at a depth of 63 cm (within the underlying beach ridge sediment), suggests it is in solution and mobile, which is likely due to the basic pH (P4 = 7.78 - 8.57). Concentrations of As were highest in the surface soil (0 - 2 cm) of P4 exceeded Canadian soil guidelines for ecological health. This likely reflects recent guano deposition as As has been shown to be excreted at a higher rate by penguins compared to other top predators, such as seals (Metcheva et al., 2011; Xie & Sun, 2008). The colony soil had higher Pb concentrations compared to P0 and C5 (p<0.05), and concentrations were consistent with those reported by Santamans et al. (2017), however, did not exceed the CEQG.

Ammonium levels within the P4 profile displayed a decreasing trend with increasing depth, starting at 8.59 mg NH_4^+ g^{-1}, and were significantly higher compared to the control soils (p<0.01). It is worth noting that our maximum ammonium was almost five times lower than the maximum value reported by Speir and Cowling (1984), which was 47.2 mg NH_4^+ g^{-1}. Total nitrogen was also higher in P4 soil (p<0.05) and exhibited a similar decreasing trend with depth. The presence of high nitrogen compounds in ornithogenic soils is well-documented, owing to the substantial nitrogen content in guano inputs (Bokhorst et al., 2019; Santamans et al., 2017; Speir & Cowling, 1984). There are currently no Canadian soil quality guidelines for ammonium or total nitrogen levels within soil. Total carbon was high within the ornithogenic soil at site P4, with enrichment within the surface soil (14.5 %) and decreasing with depth. Total carbon concentrations aligned with other research on ornithogenic soils

(Santamans et al., 2017; Tatur & Mayrcha, 1984), and had results consistent with high levels of soil organic matter (Finne et al., 2022).

Our results support research that penguin-influenced soils are hotspots of nutrient accumulation and biogeochemical cycling, which have further been correlated with the stimulation of greenhouse gas emissions (Ball et al., 2015; Liguang et al., 2002; Zhu, Liu, Ma, Sun, Xu, & Sun, 2009). Liguang et al. (2002) measured a nitrous oxide flux which was two orders of magnitude higher in ornithogenic soils compared to those dominated by mosses, largely due to mineralisation of ammonium. High soil carbon content and associated increases in bacterial abundance within ornithogenic soils, result in higher carbon dioxide emissions than in otherwise carbon-poor desert soils (Zhu, Bao, et al., 2014). When considering climate change impacts, a potential increase in ambient temperatures is predicted to increase greenhouse gas fluxes, and enhanced thawing of ornithogenic soil is likely to significantly increase nitrous oxide, methane, and carbon dioxide production (Zhu, Liu, Ma, Sun, Xu, & Sun, 2009; Zhu et al., 2011).

Microbial activity, and therefore nutrient cycling, within soils is highly temperature and moisture dependant, with higher activity during the warmest summer temperatures and peak soil thaw (Yergeau & Kowalchuk, 2008). Therefore, nutrient cycling and associated emissions are likely to contribute to variable seasonal fluxes. Regardless, ornithogenic soils are serving as a primary source of heavy metals and nutrients to melt streams, contributing to potentially toxic loadings of heavy metals and nutrients into the Ross Sea near-shore environment.

4.6 Conclusions

Potentially toxic concentrations of heavy metals and nutrients within ornithogenic soil and the subsequent enrichment of penguin-influenced melt streams over background levels highlight that ornithogenic soils may be acting as secondary sources of contamination via seasonal melt streams, with ecological effects that likely propagate through terrestrial and marine food webs.

However, it is important to note that the transport of heavy metals and nutrients is likely to exhibit variations on daily and seasonal cycles due to the inherently variable nature of Antarctic melt streams, fluctuating depth of the thawed soil layer and extreme changes in temperature. Transport variability is also dependent on the seasonal presence of penguins during the breeding season for the deposition of new heavy metals and nutrients to be incorporated within ornithogenic soils.

Climate change in the Ross Sea region of Antarctica, with warmer, potentially wetter, and longer summers, is likely to have important implications for penguin-driven fluxes of nutrients and heavy metals. Increased temperatures and melt water within the colony system have the potential to increase microbial activity and nutrient cycling within ornithogenic soils. This increases nutrient run-off and particulate transport by melt water streams and could enhance fluxes to the coast. However, with the predicted declining Adelie penguin populations across Antarctica as a result of reduced sea ice extent (and therefore krill), these complex and dynamic nutrient and heavy metal fluxes are likely also changing. There is, therefore, the need for further studies to unravel the role of penguin colonies in the release of penguin-derived nutrients to the coast, better quantify nutrient and heavy metal load within streams with respect to current strong diurnal and seasonal cycles, and changes to transport and erosive capacity of melt water streams with climate change. Finally, our research showed that melt water streams flowing through penguin colonies are an important point source for nutrients and heavy metals to coastal waters, but further research is vital to understand the potential impacts of these inputs to the Southern Ocean ecosystem.

4.7 References

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5 Conclusions

Penguins play an important role in transferring HMs and nutrients from the marine to terrestrial ecosystems in Antarctica. Previous works have demonstrated that colonies are hot spots where HMs and nutrients accumulate within ornithogenic soils. Several studies have investigated HM and nutrient content within penguin formed ornithogenic soils, however, very few have focused on waters impacted by penguin colonies, and none on the role of Antarctic glacial melt water streams in the redistribution of HMs and nutrients.

The main aim of this thesis was to investigate the role of seasonal melt water streams in the transfer of HMs and nutrients in an Adélie penguin colony, Cape Bird, Antarctica, during the austral summer of 2022/23. Two streams were selected, one flowing through the northern penguin colony and the other as a control site, and at multiple points along each stream, and on multiple occasions, water samples were taken for chemical analysis, the physiochemical characteristics (stream temperature, pH, EC and turbidity) were measured, and stream gauging undertaken to determine discharge. Moreover, to determine the chemical inputs from surrounding soils to the melt water streams, colony soils and control soils were analysed for chemical content, physiochemical characteristics, and crystal structure. The two streams were then compared to determine if melt streams are transporting HMs and nutrients, and whether ornithogenic soils from the Adélie penguin colony are the source.

5.1 Heavy metal and nutrient transport

Total recoverable HMs, As, Cd and Pb, measured at sites within the Adélie penguin colony, were several orders of magnitude higher than the control stream (one-way ANOVA, $p<0.01$) exceeding guidelines for ecological health. Along the length of the streams, concentrations of As, Cd and Pb increased up to six, 15 and 20 times higher within the penguin colony (sites P3 and P5) compared to upstream of penguin influence (P1). Concentrations of HMs did not change along the length of the control stream. The proportion of dissolved As, Cd, and Pb was not different between streams or along

the length. Trends in stream nutrient enrichment were similar to those seen with HM, with significantly increased nutrients within the northern colony stream compared to the control stream (one-way ANOVA, $p<0.01$). Within the northern colony stream, NH_4^+, NO_3^-, and PO_4^{3-} increased significantly at the colony sites P3 through P5 compared to the further upstream sites P1 and P2. Concentrations of NH_4^+, NO_3^-, and PO_4^{3-} did not change or have any statistical differences along the control stream. Ammonium and NO_3^- exceeded ANZFG values of 10 μg NH_4^+ L^{-1} and 17 μg NO_3^- L^{-1} at all sites within the northern colony and control stream. Phosphate guideline values (9.00 μg PO_4^{3-} L^{-1}) were exceeded at P2 through P5 in the penguin colony stream only.

Our findings support research highlighting the biogenic enrichment of As, Cd, and Pb from seabirds. Sites with direct penguin influence showed stark chemical contrasts to those outside of the northern colony boundaries, becoming significantly enriched with potentially toxic levels of HMs and nutrients. This indicates the potential for toxic and adverse effects on biota within these ecosystems such as, reduced reproduction, behavioural changes, and increased mortality. Living in these high nutrient areas may ironically, also expose these species to potentially toxic levels of some heavy metals in addition to the risk of 'over manuring'. It should be noted that while comparisons to guideline values such as the ANZFG, are useful for characterizing potentially hazardous substances, actual chemical toxicity may vary due to the chemical species, bioavailability, physiochemical conditions, exposure, and species-specific physiology. It should also be noted that Antarctica does not have water or soil toxicity values based on relevant species, environmental, and toxicological interactions and not all analytes measured within this research have guideline values.

The higher portion of dissolved As in both streams, compared to Cd and Pb, indicates that Cd and Pb are in a solid phase, bound or complexed to suspended organic matter and minerals. This reduces toxicity, however, their presence, however, is no less important as if stream conditions should change, such as lowering of stream pH, their release from particulate matter may have ecological repercussions.

5.2 Stream physiochemical properties

Stream physiochemical measurements at the time of sampling showed both streams had circumneutral to basic pH (pH 6.86-8.07). The dissolved ion content, measured as EC, and turbidity were up to 1.5 and 7 times higher, respectively, within the northern colony stream compared to the control, with highest levels seen in site P1. Differences in stream EC and turbidity appear to be a result of the glacial origin as opposed to being from penguin influence, as melt streams are commonly associated with turbid and conductive waters due to high levels of suspended sediment.

On their own, stream physiochemical characteristics provide a limited view of stream functioning, however, when looked at in association with chemical concentrations, physiochemical properties provide important context. The difference between the proportions of dissolved As, Cd, and Pb, may be due to factors such as pH or organic matter content, which influences solubility and thus metal toxicity. However, our ability to determine factors controlling the proportions of dissolved versus total recoverable metals is limited without a detailed analysis of the parent material and organic matter present.

5.3 Stream discharge and load

Stream discharge in the northern colony stream was higher on all four measurement days (16.7 L s^{-1} to 52.3 L s^{-}1) compared to the control stream (10.8 L s^{-}1 to 14.7 L s^{-1}). There was a high variability in stream discharge between measurement days, particularly within the penguin-influenced stream. This may be partially explained by fluctuations in air temperature which is known to greatly impact glacial melt. Stream discharge, as expected, was strongly correlated with air temperature at both the penguin-influenced (R=0.88) and control (R=0.82) streams.

Our measured discharge was half of that measured previously within the northern colony stream, captured on January 18th and 19th. Therefore, it is supposed that our sampling was not conducted at maximum thaw. Consequently, it is likely that the full erosive and transport capacity of

the northern colony stream, with respect to HM and nutrient load, may not have been captured within these results and transport within this stream may be greater than the results reported in this study.

The calculated load of HMs and nutrients was statistically higher in the penguin-influenced stream than the control (As, Cd, Pb, NH_4^+: $p<0.05$; NO_3^- and PO_4^{3-}: $p<0.01$). This indicates that differences between stream HM and nutrient concentration were attributed to penguin influence and not due to differences between stream discharge.

5.4 Ornithogenic soils

Our research supports previous findings that penguin-influenced soils are hotspots of HM and nutrient accumulation within an otherwise oligotrophic environment. Total recoverable metals within the P4 ornithogenic soil had up to 26, 72, and six times higher concentrations of As, Cd, and Pb compared to the control soil, with particularly high concentrations in the upper 44 cm. Site P4 concentrations of As within the ornithogenic topsoil (P4 0-2 cm) and Cd at depths 0-44cm were present in concentrations that exceeded the CEQG. Toxic levels have the potential for adverse effects on biota, however, this is likely to be spatially heterogeneous. Results within this study also supported previous research that As, Cd, and Pb are biogenically enriched within penguin colony soils.

Ammonium, TN, and TC levels within the colony soil, P4, were highest in the topsoil with 8.59 NH_4^+ mg g^{-1}, 8.19 % TN, and 14.53 % TC, and decreased depth. P4 soil nutrients were also significantly higher compared to the control soils ($p<0.01$). High concentrations of nutrients in penguin colony soils have been associated with increased greenhouse gas emissions (carbon dioxide, methane, and nitrous oxide), as well as high levels of NH_3 volatilisation and subsequent redeposition. As a result, ornithogenic soils can affect an area several times greater than the colony boundaries. Ammonia volatilisation is further encouraged by the circumneutral to basic soil pH within P4 soil 7.78 – 8.57. However, with the seasonal presence of penguins and changes in the depth of soil thaw, this is likely highly temporally variable.

5.5 Limitations and recommendations for future research

5.5.1 Sampling constraints

When conducting field research within remote locations within Antarctica, there are many practical constraints, such as extreme weather, limited capability for transporting equipment, and very limited time in the field. Because of this, adaptability is essential, and as a result, sampling was limited to four days. Although this research has provided clear evidence of HM and nutrient transport via melt streams, these results justify the need for further research with increased sampling over longer time frames. This would help capture the daily and seasonal variations in transport (including during maximum glacial thaw) to provide accurate long-term data and transport trends. Such research would provide precise baseline data and allow future predictions to be made in a changing climate (see section 5.5.6). It is also important to consider the scale at which melt water transport was assessed within one stream in a single Adélie penguin colony of approximately 50,000 breeding pairs. Therefore, future work could investigate impacts continent-wide incorporating the estimated 3.79 million breeding pairs and could involve climate models.

5.5.2 Pit-falls of DGT

DGT have proven to be extremely useful during their few applications at investigating analytes within Antarctic soil and sediment. However, their application in-situ during this research was unsuccessful. At Cape Bird, short term weather forecasts are vague and often inaccurate, which meant that during their deployment there was an unpredicted weather event which caused the freezing of the DGT samplers. It was also noted that the extreme variability of the Cape Bird melt streams in terms of discharge, changes in stream depth, and changes of stream pattern and braiding, makes the deployment of DGT, which are required to be fully submerged throughout, difficult. Due to this, we do not believe that DGT are a suitable technique for measuring water analytes within the Cape Bird melt streams.

5.5.3 Soil nutrient anion analysis

Due to instrument breakdown and technical compilations of the running of the IC machine, reliable results of soil nutrient anions were unable to be produced within the timeframe of this research. Because of this, we employed an alternative nutrient analysis of soil TN and TC. However, it would have been beneficial to analyse soil nutrient anions to allow comparisons between soil and water nutrient concentrations. This would have allowed a more confident determination of their source from ornithogenic soils. Information on anion concentration within soil would also provide further insights into the cycling of nutrients within penguin colonies.

5.5.4 Heavy metal sources

Anthropogenic activity has resulted in the global increase of As, Cd, and Pb emissions, several times higher than what would occur from natural sources. Despite this, it is difficult to determine if concentrations found within the results of this research are from an anthropogenic source alone. As a result, further research, such as isotopic fingerprinting, is recommended to be able to attribute metals from the northern colony to a specific source.

5.5.5 Impacts to the marine environment

Melt streams are the connection between terrestrial and marine ecosystems, it is also important to consider that melt streams are transporting potentially toxic loads to the nearshore environment. However, to better quantify impacts, research into the chemical interactions of HMs and nutrients within seawater and the potential impact on nearshore benthic communities is recommended. This could include the analysis of HM and nutrient uptake in sessile bivalves within the vicinity of streams and investigating impacts on health.

5.5.6 Future impacts of climate change

There has been limited research into penguin and seabird-impacted waters, and while our research contributed to advancing our understanding of HM and nutrient transport in penguin colonies, there is a lot still unknown about these dynamic ecosystems. This is particularly true when considering the future effects of climate change. There is a myriad of ways in which global warming has and is predicted to continue to have clear ramifications on many aspects of the terrestrial and marine environment. An increase in air temperature may increase the melting of the Bird Ice Cap, cause changes in melt water volume and seasonal duration, and increase soil temperatures deepening the active layer of soils. This may increase the potential for run-off from ornithogenic soils, increase the leaching of nutrients, enhance biogeochemical cycling and greenhouse gas emissions, and increase the erosive capability of melt streams. Climate change is also predicted to influence the receiving marine environment via ocean acidification, which may influence bioavailability and hence, toxicity of transported HMs and nutrients. Because of this suite of potential changes, it is imperative that we gain a full understanding of the complex interactions taking place in penguin colonies between soil, sediment, melt water, and the microbes within, to be able to predict how these environments will respond to climate change. Furthermore, understanding how future changes will influence the receiving marine environment and potentially increase HM toxicity is critical for these protected ecosystems.

Given the access constraints of undertaking fieldwork in Antarctica, and the fact that the management of science research relies on cost-benefit analysis of negative environmental impact versus positive scientific gain while undertaking research, we decided to collect additional data for a future research student. The AWS was installed to provide accurate weather information within the northern colony stream during our field campaign, with the possibility that the data could be used for future climate change modelling of melt stream transport and its relationship with weather. The modelling of changes to nutrient and heavy metal transport with respect to climate variables and

climate change was outside the scope of this research; however, data has been collected for future analysis.

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Appendices

Appendix 1: Soil profile descriptions

Profile of soil sample sites from P4 (ornithogenic soil), P0 (control soil above the penguin colony), and C5 (control soil) at the Cape Bird northern Adélie penguin colony, Ross Island on the 2nd and the 5th January 2023.

Site P4: An ornithogenic soil profile

Date:	2 January 2023
Location:	S 77 12.759 E 166 26.986
Elevation:	5 m
Slope:	2°
Aspect:	N
Weather:	Cloudy, wind of 5 knots, very occasional and light snow flurries
Location description:	Cape bird northern penguin colony. Site is approximately 3 m from the northern colony stream and is contiguous with the stream floodplain. Taken on the eroded face of an active penguin mound.
Drainage:	Moderately
Ice cement:	Not reached
Parent lithology:	Basalt and guano
Samples taken:	At all horizons

Horizons	*1*	*2*	*3*	*4*	*5*	*6*
Base (cm)	2	18	37	44	53	65
Thickness (cm)	2	16	19	7	9	12
Sample no.	P4/1	P4/2	P4/3	P4/4	P4/5	P4/6
Field moisture	Dry	Slightly moist	Very moist	Very moist	Dry	Slightly moist
Boundary distinctness	Abrupt	Indistinct	Abrupt	Abrupt	Abrupt	
Boundary shape	Wavy	Irregular	Wavy	wavy	Wavy	
Colour	5YR 6/3 Light reddish brown	2.5YR 4/4 Reddish brown	2.5YR 2.5/3 Dark reddish brown	7.5YR 6/6 Reddish yellow	5YR 2.5/1 Black	5YR 4/1 Dark grey
Texture	Medium to fine gravel	Medium to fine gravel	Medium to fine gravel	Medium gravel	Medium gravel to medium sand	Coarse gravel to medium sand
Gravel	80 % Sub rounded	60 % Sub rounded	45 % Sub rounded	50 % Rounded	75 % Sub rounded	85 % Angular
Boulders	n/a	n/a	n/a	n/a	n/a	n/a

0 - 2 cm	Guano cemented layer, with a crust of yellow grey compacted guano. Penguin stones commonly embedded in soil.
2 - 18 cm	Reddish-brown with eggshell fragments clearly visible. High amounts of penguin guano and material with a sticky texture.
18- 37 cm	Dark brown with a decomposing adult bird at 28-36 cm depth. Just above this decomposing bird was an extra wet layer.
37 - 44 cm	Light yellow brown soil with moderate amounts to guano. Soil was drier with a more friable consistency.
44 - 53 cm	A potential flood deposit of dark brown and sandy soil that was slightly greasy.
53 - 65 cm	Un-weathered beach deposit. Dark gravelly material with more angular stones than previous sites. Material appeared to have a slightly greasy coating.

Site P0: A control soil profile from above the penguin colony

Date:	5 January 2023
Location:	S 77 12.884 E 166 27.476
Elevation:	78 m
Slope:	1°
Aspect:	W
Weather:	90 % cloud cover, no wind
Location description:	At the source of the penguin colony stream at the base of Bird Ice Cap on an undulating surface of glacial moraine. Site is approximately 4 m from water on moraine floodplain.
Drainage:	Moderately
Ice cement:	35 cm
Parent lithology:	Basalt moraine
Samples taken:	0 - 2 cm, 18 - 20 cm, and 33 - 35 cm

Horizons	*1*
Base (cm)	35 (Ice cement)
Thickness (cm)	35
Sample no.	P0/1, P0/2, P0/3
Field moisture	Moist
Boundary distinctness	Distinct
Boundary shape	Smooth
Colour	5YR 4/41 Dark grey
Texture	Boulders to silt
Gravel	40 % Sub angular
Boulders	40 % Sub angular

0-35 cm

Raw, uniform soil with no horizonation on the ice cored moraine. No change down the profile with ice cement reached at 35 cm (Right).

Site C5: Control soil profile

Date:	5 January 2023
Location:	S 77 13.245 E 166 25.746
Elevation:	2 m
Slope:	2°
Aspect:	W
Weather:	90 % cloud cover, no wind
Location description:	Adjacent to the control stream site C5 on the stream floodplain
Drainage:	Poor
Ice cement:	35 cm
Parent lithology:	Basalt moraine and floodplain deposit
Samples taken:	0 – 2 cm, 33 – 35 cm

Horizons	*1*
Base (cm)	35 (Ice cement)
Thickness (cm)	35
Sample no.	C5/1, C5/2
Field moisture	Very moist
Boundary distinctness	Distinct
Boundary shape	Smooth
Colour	5YR 4/41 Dark grey
Texture	Medium gravel to silt
Gravel	50 % Sub rounded
Boulders	n/a

0 – 35 cm Raw, uniform soil of basaltic scoria with no horizonation on floodplain deposit. No change down the profile with ice cement reached at 35 cm. Ground water table reached at 33 cm.

Appendix 2: Melt stream total recoverable metal concentrations

Stream total recoverable metal concentrations within duplicate samples taken from the northern colony stream (P1 to P5) and the control stream (C1 to C5) at Cape Bird, Ross Island. Samples were collected on four sampling days in 2023, the 1st January (1), 3rd January (2), 7th January (3), and the 10th January (4). Metals analysed through ICP-MS.

Site	Sample Day	Na	Mg	Al	K	Ca	P	S	Cr	Mn
		μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}
P1	1	179546.29	30177.05	16256.92	12974.90	31461.33	945.86	24294.30	4.73	263.64
	1	185607.86	30971.20	16604.88	12975.71	31518.14	966.69	25944.45	4.99	265.48
	2	132091.83	25960.49	2765.52	7519.42	22749.75	283.29	16704.33	0.67	52.91
	2	130295.19	24664.00	1249.95	6848.33	21049.28	163.80	17279.47	0.28	26.91
	3	67359.81	8156.43	146.70	3011.90	6003.55	41.78	8816.13	0.00	7.14
	4	140016.45	27851.04	14397.30	10159.10	27028.30	871.48	16830.35	3.81	225.50
	4	143605.68	28065.09	14265.47	10312.89	27573.10	1005.91	19979.16	3.44	218.01
P3	1	104657.20	19536.16	3169.64	9871.08	27272.03	4093.15	15817.24	0.89	96.50
	1	117128.22	22154.62	3288.36	10636.61	28862.50	4303.98	18429.09	0.70	107.68
	2	87599.58	13007.34	1344.04	7693.56	16999.63	1946.16	11936.69	0.35	49.63
	2	83221.54	12349.40	1421.46	7319.60	16133.96	1988.18	11413.91	0.32	48.97
	3	26423.81	3446.42	137.94	1314.82	3698.70	123.23	3654.36	0.00	6.16
	3	86867.02	11125.80	132.92	4924.67	11386.46	345.52	14234.86	0.13	13.73
	4	83150.78	11703.45	612.88	6090.38	15871.78	855.69	10874.29	0.13	30.44
	4	56869.79	8112.80	449.98	4105.74	12666.17	671.09	6931.03	0.00	18.12
P5	1	66074.83	16170.91	30724.45	10442.51	23826.72	4047.51	6713.12	6.03	426.59
	1	93480.70	19435.10	28410.39	12144.72	27198.10	4664.46	11886.82	6.49	419.04
	2	89801.59	13030.75	602.54	7266.63	16382.58	1065.52	12997.93	0.24	42.77
	2	91022.41	25700.05	16915.32	9737.01	27328.68	3328.27	10507.32	4.06	489.73
	3	61278.90	7940.79	295.69	3816.77	8343.19	332.48	8442.51	0.02	14.31
	3	34317.15	4492.02	177.31	2033.75	5332.83	306.50	5298.59	0.00	9.44

Site	Sample Day	Na	Mg	Al	K	Ca	P	S	Cr	Mn
		µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
P5	4	63491.05	9145.07	244.44	5128.72	11503.16	603.14	9232.03	0.17	15.01
	4	80819.67	11547.06	260.07	6562.03	15777.80	998.56	11904.81	0.00	28.96
C1	1	40157.18	6909.44	5609.17	3076.09	7770.98	338.00	3809.59	1.44	86.50
	1	24610.54	4749.67	5480.85	2256.39	5646.87	311.36	2123.03	1.41	80.66
	2	81060.74	10970.63	1528.65	4438.82	13375.04	169.07	9676.19	0.42	24.24
	2	67419.10	9617.01	91.39	3452.78	10044.92	27.25	7795.84	0.00	2.38
	3	75356.55	9738.98	216.02	3901.11	10727.73	48.95	10559.67	0.08	5.46
	3	77911.41	9333.03	124.89	3855.33	10055.59	52.47	11748.65	0.00	5.13
	4	76624.56	10488.50	9864.38	5780.23	13263.57	612.51	8495.11	2.47	151.75
	4	82369.19	11556.38	11723.22	7217.06	13985.53	749.23	8819.56	4.19	187.15
C3	1	29108.27	4940.59	3525.56	2044.20	5670.48	213.14	2734.99	0.68	54.58
	1	64748.98	10327.57	4162.61	4127.52	11724.82	274.36	6905.68	1.12	64.29
	2	72014.03	9833.20	336.25	3732.26	11369.60	44.45	6604.67	0.21	7.26
	2	100121.14	14335.84	251.49	5025.12	15730.08	58.72	10924.05	0.21	5.89
	3	80219.00	9981.48	337.29	3951.76	11245.45	78.93	14622.36	0.10	9.15
	3	78744.43	9683.83	117.92	3800.14	10662.93	49.93	11778.85	0.08	5.55
	4	44429.73	5604.71	468.70	2149.32	5621.50	72.51	8279.86	0.01	8.56
	4	28601.02	3903.71	680.56	1332.93	4815.17	50.51	3974.20	0.21	10.63
C5	1	49611.93	7572.47	2549.23	3173.32	9125.39	187.22	5236.07	0.61	43.11
	1	61045.52	9321.35	3090.14	3793.98	10415.99	226.96	6653.68	0.70	47.81
	2	59659.10	8379.02	173.88	2902.37	9030.25	38.35	6466.57	0.05	4.42
	2	20868.91	2970.69	148.83	872.41	3165.53	15.20	2029.50	0.12	2.85
	3	77966.24	9440.50	142.19	3728.91	10308.79	52.76	12005.21	0.12	4.93
	3	77749.51	9632.79	455.69	3736.89	10230.81	97.09	11938.28	0.26	11.45
	4	32659.60	4347.89	672.94	1578.69	5244.37	65.19	4726.50	0.03	11.77
	4	86478.66	11050.65	751.62	4264.27	12440.34	95.75	12032.10	0.25	13.69
Detection limit		10	10	10	500	100	1	500	0.1	0.1

Site	Sample Day	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	U
		μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}
P1	1	11002.34	5.26	8.25	12.38	31.33	1.48	0.06	0.22	0.85
	1	11102.68	5.30	8.25	12.33	28.78	1.52	0.00	0.22	0.84
	2	1893.36	0.98	2.43	2.27	13.34	0.45	0.00	0.22	0.27
	2	832.24	0.38	0.74	1.23	8.15	0.39	0.00	0.02	0.22
	3	110.55	0.01	0.04	0.26	9.34	0.00	0.00	0.00	-0.02
	4	8809.35	4.24	7.01	8.80	19.40	0.10	0.05	0.02	0.58
	4	8399.69	4.05	6.94	9.10	20.73	0.30	0.06	0.02	0.56
P3	1	2137.96	1.60	4.95	7.90	32.16	5.16	0.76	2.02	0.18
	1	2233.08	1.88	6.10	7.99	31.06	5.47	0.56	3.12	0.18
	2	907.98	0.79	3.53	4.54	11.92	3.50	0.36	1.02	0.09
	2	968.76	0.84	2.61	4.52	9.59	3.07	0.36	1.22	0.10
	3	91.49	0.02	0.13	0.42	5.61	0.70	0.16	0.42	-0.02
	3	87.42	0.06	0.40	1.38	9.99	0.84	0.16	2.32	-0.01
	4	444.58	0.38	1.43	2.55	53.90	2.60	0.26	1.42	0.04
	4	328.41	0.26	1.02	2.13	8.92	2.20	0.36	1.62	0.02
P5	1	16959.69	8.81	18.52	21.32	61.29	4.50	0.86	3.06	1.19
	1	16540.99	8.33	16.84	21.23	62.64	4.17	0.86	2.87	1.15
	2	455.56	0.49	1.83	2.96	8.70	2.61	0.56	1.32	0.03
	2	14918.64	10.47	32.09	11.83	27.47	3.21	0.56	1.15	0.77
	3	163.96	0.12	0.56	1.69	15.60	1.00	0.36	2.22	-0.01
	3	89.97	0.07	0.26	0.81	9.75	0.90	0.26	0.42	0.01
	4	197.17	0.26	1.56	2.65	5.33	2.40	0.66	2.72	0.01
	4	160.66	0.25	1.28	2.50	2.55	3.00	0.56	2.82	0.02
C1	1	3654.06	1.82	3.20	4.50	10.25	0.41	0.00	0.47	0.17
	1	3506.34	1.77	3.12	4.56	10.76	0.36	0.00	0.49	0.16
	2	911.08	0.42	0.63	1.29	4.04	0.23	0.00	0.06	0.07

Site	Sample Day	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	U
		µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
C1	2	59.93	0.00	0.00	0.23	2.96	0.10	0.00	0.00	0.02
	3	192.50	0.05	0.60	0.68	5.40	0.14	0.00	0.00	0.01
	3	92.14	0.05	0.32	0.88	7.54	0.20	0.00	0.00	0.04
	4	6396.72	3.22	6.17	7.49	16.58	0.68	0.05	0.30	0.37
	4	7634.03	5.36	9.25	11.23	23.46	0.83	0.06	0.02	1.96
C3	1	2225.40	1.12	2.07	2.90	8.38	0.24	0.00	0.26	0.10
	1	2699.58	1.35	2.38	3.39	7.17	0.35	0.00	0.33	0.15
	2	239.21	0.08	0.12	0.43	4.24	0.11	0.00	0.00	0.03
	2	184.21	0.04	0.03	0.33	4.95	0.14	0.00	0.00	0.05
	3	294.38	0.17	0.30	0.59	5.19	0.20	0.04	0.04	0.08
	3	81.85	0.08	0.19	0.45	4.31	0.17	0.03	0.03	0.07
	4	347.30	0.15	0.27	0.47	2.00	0.18	0.00	0.00	0.02
	4	487.37	0.22	0.45	0.65	2.45	0.10	0.00	0.05	0.02
C5	1	1776.51	0.89	1.55	2.46	5.62	0.28	0.00	0.20	0.08
	1	2016.99	0.99	1.70	2.63	5.84	0.32	0.00	0.25	0.11
	2	125.52	0.02	0.00	0.20	5.26	0.10	0.00	0.00	0.01
	2	108.10	0.01	0.00	0.14	2.12	0.03	0.00	0.00	0.00
	3	105.65	0.07	0.15	0.35	7.93	0.17	0.02	0.05	0.06
	3	319.65	0.17	0.45	0.48	1.54	0.19	0.01	0.02	0.09
	4	487.13	0.23	0.45	0.89	3.48	0.12	0.00	0.05	0.03
	4	539.29	0.27	0.51	1.12	5.31	0.20	0.01	0.00	0.09
Detection limit		5	0.1	0.1	0.1	1	0.3	0.1	0.1	0.1

Appendix 3: Melt stream dissolved metal concentrations

Stream dissolved metal concentrations within duplicate samples taken from the northern colony stream (P1 to P5) and the control stream (C1 to C5) at Cape Bird, Ross Island. Samples were collected on four sampling days in 2023, the 1st January (1), 3rd January (2), 7th January (3), and the 10th January (4). Metals analysed through ICP-MS.

Site	Sample Day	Na	Mg	Al	K	Ca	P	S	Cr	Mn
		μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}
P1	1	248264.23	35605.24	3.14	11700.09	46743.54	83.30	28457.04	0.35	35.40
	1	269663.05	38459.47	14.22	13128.09	51041.84	124.42	36559.92	0.82	40.31
	2	32830.42	6345.13	3.10	1628.88	15603.05	31.82	5129.50	0.09	6.88
	2	33090.51	6407.78	2.73	1678.04	16013.96	36.83	4823.92	0.07	7.05
	3	53788.86	6667.14	2.30	2634.91	9790.27	31.41	7503.30	0.19	5.58
	3	55803.71	6994.47	2.60	2786.72	10361.88	29.82	7480.59	0.08	6.03
	4	140978.56	24018.83	2.75	7552.91	35076.60	49.39	17167.43	0.08	25.65
	4	139478.46	24076.48	2.68	7400.32	34526.06	52.21	17451.15	0.09	25.13
P3	1	196557.82	30237.36	13.20	13933.16	52853.57	2147.26	26007.69	0.13	49.13
	1	195544.58	30564.94	8.94	13951.79	52716.40	2199.52	24740.33	0.10	48.15
	2	51067.42	7631.79	14.00	4411.40	22550.42	1005.76	6749.69	0.08	18.57
	2	46802.52	6916.35	7.98	4105.72	20767.19	1035.99	7002.74	0.14	16.77
	3	53043.01	7060.28	4.00	3198.07	15619.12	174.91	7682.19	0.07	10.60
	3	52762.17	6912.86	4.15	3142.96	15196.48	177.68	7747.66	0.08	10.54
	4	88786.14	12089.53	4.61	6647.64	26792.55	708.78	11659.76	0.05	29.93
	4	85782.14	11867.22	7.58	6450.74	27632.43	697.30	11807.71	0.09	29.19
P5	1	124948.60	17584.27	32.99	9499.71	30682.72	1411.14	14374.44	1.37	35.04
	1	117842.31	16116.06	20.85	8228.52	28547.62	1265.73	13185.13	0.06	30.57
	2	90414.23	13013.80	6.03	7819.58	28764.88	988.01	12050.60	0.08	30.68
	2	88839.56	12659.76	8.54	7577.72	27819.63	976.55	11905.90	0.09	30.04
	3	68526.49	9011.12	3.32	4419.51	20918.77	395.13	9504.90	0.32	16.26
	3	74062.94	9784.44	25.26	5476.54	23517.09	435.73	9578.26	1.46	21.17

Site	Sample Day	Na	Mg	Al	K	Ca	P	S	Cr	Mn
		µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
P5	4	72460.03	10258.52	9.67	5955.91	14401.04	895.40	11035.86	0.09	29.79
	4	72135.38	10236.64	6.27	5964.81	14122.19	895.77	11199.61	0.12	29.72
C1	1	122615.43	17155.08	2.66	6729.95	18097.29	101.20	13080.58	0.10	8.85
	1	123146.17	17355.44	3.13	6676.40	17600.80	97.66	12992.29	0.05	8.68
	2	85408.32	12116.25	2.19	4396.65	13472.15	49.54	10061.85	0.09	5.29
	2	87715.65	12538.24	2.51	4479.47	13910.42	40.36	9916.44	0.08	5.50
	3	67051.94	8593.40	2.80	3718.45	10219.07	41.44	8950.92	0.10	4.69
	3	64722.49	8187.78	2.47	3518.42	9341.54	41.44	10443.46	0.08	4.50
	4	81211.08	10821.65	3.28	4302.12	12303.44	56.40	11625.12	0.13	4.59
	4	76378.08	10180.34	2.83	4025.21	11862.92	51.74	10447.94	0.07	4.31
C3	1	90627.06	12659.37	3.46	4961.69	12475.36	69.83	9523.06	0.03	6.51
	1	91883.71	12853.97	4.50	4990.38	12636.96	71.75	9718.50	0.06	6.54
	2	77050.70	10606.93	2.80	4383.48	11743.94	119.07	13289.40	0.08	6.10
	2	77588.80	10935.73	2.60	4402.56	12051.71	81.24	9286.52	0.13	6.14
	3	75966.13	9614.13	2.59	4086.22	10191.42	40.14	12076.38	0.10	5.09
	3	74737.09	9446.23	2.38	4085.33	10138.59	60.40	14320.52	0.06	5.10
	4	43806.99	5811.03	2.83	2344.06	7695.63	36.26	6383.19	0.09	2.52
	4	43619.21	5745.56	2.65	2316.79	7836.86	35.94	6276.07	0.06	2.54
C5	1	95284.79	12986.47	2.65	5119.21	13102.60	68.92	9225.90	0.11	6.42
	1	92894.30	12700.55	2.89	5077.96	13049.69	64.56	9060.22	0.11	6.29
	2	54353.14	7597.03	33.68	2792.13	10367.88	47.37	7236.07	0.06	3.91
	2	52287.49	7253.55	3.22	2681.30	9637.91	45.53	7292.24	0.07	3.27
	3	73195.10	9270.39	2.35	3942.83	10246.27	47.88	11477.96	0.09	4.75
	3	77961.44	9829.10	2.40	4157.86	10299.06	47.77	11402.65	0.19	5.08
	4	65629.47	8573.24	2.97	3458.50	10152.03	48.04	9464.36	0.06	3.42
	4	62392.46	8200.68	2.87	3373.04	10203.03	45.87	9430.71	0.08	3.30
Detection limit		10	10	10	500	100	1	500	0.1	0.1

Site	Sample Day	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	U
		µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
P1	1	1.94	0.04	0.15	0.99	2.75	0.47	0.01	0.00	0.34
	1	24.19	0.74	0.91	2.31	4.84	0.78	0.00	0.10	1.04
	2	1.12	0.03	0.14	0.28	4.46	0.09	0.04	0.05	0.06
	2	0.23	0.01	0.09	0.25	2.73	0.06	0.00	0.00	0.02
	3	0.46	0.01	0.05	0.25	1.62	0.00	0.00	0.00	0.000
	3	0.81	0.02	0.06	0.27	3.18	0.00	0.03	0.03	0.03
	4	0.07	0.02	0.05	0.39	2.10	0.15	0.00	0.00	0.05
	4	0.13	0.02	0.09	0.38	1.29	0.18	0.00	0.00	0.05
P3	1	12.75	0.42	1.79	3.70	4.11	3.35	0.07	0.00	0.16
	1	8.28	0.42	1.75	3.62	3.12	3.35	0.08	0.01	0.16
	2	13.12	0.25	1.10	2.79	5.36	1.58	0.04	0.00	0.03
	2	6.81	0.23	1.03	2.63	3.75	1.64	0.03	0.01	0.02
	3	1.46	0.05	0.28	0.56	3.64	0.37	0.00	0.00	0.00
	3	1.56	0.05	0.24	0.52	6.20	0.37	0.00	0.00	0.00
	4	2.60	0.24	1.12	2.14	2.89	1.46	0.02	0.00	0.02
	4	5.98	0.23	1.12	2.02	3.44	1.48	0.02	0.00	0.02
P5	1	50.80	1.38	2.24	4.52	8.43	1.77	0.70	2.11	1.15
	1	18.89	0.22	0.88	2.32	3.77	1.51	0.04	1.90	0.06
	2	4.25	0.29	1.30	3.00	4.81	2.21	0.03	0.00	0.04
	2	6.69	0.29	1.25	2.81	5.91	2.15	0.04	0.00	0.04
	3	2.41	0.10	0.54	1.11	4.63	0.40	0.01	0.10	0.01
	3	46.08	1.39	1.93	3.59	11.77	0.50	0.10	0.20	1.16
	4	7.48	0.25	1.24	2.29	3.74	1.58	0.02	0.00	0.02
	4	4.39	0.25	1.19	2.28	2.09	1.60	0.03	0.00	0.02
C1	1	0.32	0.01	0.11	0.37	1.28	0.21	0.000	0.00	0.05
	1	0.31	0.01	0.07	0.34	2.79	0.20	0.00	0.00	0.05

Site	Sample Day	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	U
		µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
C1	2	0.48	0.01	0.11	0.99	4.41	0.11	0.01	0.01	0.02
	2	0.22	0.01	0.09	2.31	4.84	0.14	0.01	0.00	0.02
	3	0.59	0.01	0.17	0.28	4.17	0.11	0.01	0.01	0.02
	3	0.56	0.01	0.10	0.25	4.05	0.12	0.01	0.01	0.02
	4	0.61	0.01	0.12	0.25	2.44	0.14	0.00	0.00	0.02
	4	0.23	0.01	0.07	0.27	3.22	0.13	0.00	0.00	0.02
C3	1	1.20	0.02	0.03	0.39	1.77	0.18	0.01	0.01	0.05
	1	0.80	0.01	0.07	0.38	1.05	0.18	0.01	0.00	0.04
	2	0.24	0.04	0.31	3.70	4.77	0.10	0.01	0.00	0.02
	2	0.21	0.04	0.30	3.62	5.91	0.10	0.01	0.01	0.02
	3	0.40	0.01	0.03	2.79	3.97	0.15	0.01	0.00	0.01
	3	0.23	0.01	0.16	2.63	2.00	0.19	0.01	0.00	0.01
	4	0.46	0.01	0.09	0.56	2.90	0.06	0.00	0.00	0.01
	4	0.17	0.01	0.07	0.52	3.74	0.09	0.00	0.00	0.01
C5	1	0.55	0.02	0.07	2.14	1.05	0.16	0.01	0.01	0.04
	1	0.56	0.02	0.10	2.02	2.10	0.17	0.01	0.00	0.04
	2	23.75	0.01	0.01	4.52	2.84	0.08	0.00	0.00	0.01
	2	0.11	0.00	0.03	2.32	1.93	0.00	0.00	0.00	0.01
	3	0.31	0.01	0.06	3.00	1.98	0.12	0.01	0.00	0.02
	3	1.10	0.01	0.07	2.81	2.58	0.11	0.00	0.01	0.01
	4	0.37	0.01	0.14	1.11	4.04	0.11	0.00	0.01	0.03
	4	0.12	0.01	0.11	3.59	4.44	0.10	0.00	0.00	0.01
Detection limit		5	0.1	0.1	0.1	1	0.3	0.1	0.1	0.1

Appendix 4: Water nutrient concentrations

Nutrients within duplicate samples taken from the northern colony stream (P1 to P5) and the control stream (C1 to C5) at Cape Bird, Ross Island. Samples were collected on four sampling days in 2023, the 1st January (1), 3rd January (2), 7th January (3), and the 10th January (4). Ammonium was analysed through colourimetric spectrophotometry and nitrate, sulphate and phosphate through IC.

Site	Sample Day	Ammonium	Nitrate	Sulphate	Phosphate
		mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
P1	1	0.327	3.803	98.268	0.000
	1	0.294	3.864	98.082	0.000
	2	0.316	3.655	60.200	0.000
	2	0.140	3.631	60.287	0.000
	3	0.250	2.245	19.537	0.000
	3	0.228	2.219	19.457	0.000
	4	0.217	2.578	56.927	0.000
	4	0.140	2.715	56.838	0.000
P2	1	0.316	5.559	26.565	0.000
	1	0.305	5.486	26.212	0.000
	2	0.393	5.035	20.516	3.343
	2	14.741	5.032	20.582	3.345
	3	0.250	5.255	65.993	0.000
	3	0.305	5.534	71.173	0.000
	4	0.217	4.462	18.344	0.000
	4	0.206	4.459	18.392	3.190
P3	1	16.338	14.295	56.726	6.305
	1	16.669	14.227	56.704	6.258
	2	14.741	18.849	35.504	5.297
	2	14.796	18.836	35.493	5.304
	3	3.893	8.318	37.187	3.403
	3	4.224	8.316	37.075	3.392
	4	6.206	15.144	30.990	4.151
	4	6.206	14.998	30.840	4.166
P4	1	12.483	9.252	40.980	5.514
	1	12.483	9.306	41.320	5.548
	2	7.528	14.620	24.223	4.745
	2	9.069	14.591	24.268	4.765
	3	4.058	15.081	73.873	3.663
	3	4.113	15.101	73.820	3.656
	4	9.235	42.570	69.843	5.927
	4	8.794	42.228	69.546	5.874
P5	1	12.814	8.341	35.854	5.195
	1	13.089	8.327	35.795	5.174
	2	4.939	22.259	35.494	4.718
	2	4.884	22.281	35.562	4.757
	3	10.501	8.159	28.728	3.803
	3	9.950	8.189	28.649	3.811
	4	8.629	16.199	27.949	4.467
	4	8.409	16.140	27.912	4.452

Site	Sample Day	Ammonium mg L^{-1}	Nitrate mg L^{-1}	Sulphate mg L^{-1}	Phosphate mg L^{-1}
C1	1	0.085	1.602	28.809	0.000
	1	0.080	1.521	28.732	0.000
	2	0.350	1.459	26.584	0.000
	2	0.350	1.400	26.517	0.000
	3	0.054	1.163	9.954	0.000
	3	0.048	1.183	9.929	0.000
	4	0.032	1.399	40.831	0.000
	4	0.038	1.436	40.883	0.000
C2	1	0.101	1.458	26.206	0.000
	1	0.117	1.425	26.142	0.000
	2	0.175	1.462	35.874	0.000
	2	0.080	1.471	35.747	0.000
	3	0.043	1.539	61.181	0.000
	3	0.038	1.538	61.355	0.000
	4	0.016	1.230	22.138	0.000
	4	0.085	1.218	22.134	0.000
C3	1	0.064	1.447	23.882	0.000
	1	0.075	1.363	23.931	0.000
	2	0.075	1.947	35.020	0.000
	2	0.276	1.930	33.852	0.000
	3	0.027	1.504	57.151	0.000
	3	0.064	1.527	57.717	0.000
	4	0.054	1.513	49.279	0.000
	4	0.064	1.556	49.387	0.000
C4	1	0.085	1.562	32.274	0.000
	1	0.122	1.503	32.301	0.000
	2	0.197	2.939	41.330	0.000
	2	0.393	2.983	41.365	0.000
	3	0.138	1.207	17.036	0.000
	3	0.091	1.307	33.463	0.000
	4	0.054	1.245	25.596	0.000
	4	0.075	1.248	25.485	0.000
C5	1	0.091	1.522	27.816	0.000
	1	0.096	1.502	27.880	0.000
	2	0.085	1.313	17.546	0.000
	2	0.191	1.259	17.677	0.000
	3	0.160	1.307	33.463	0.000
	3	0.032	1.261	33.389	0.000
	4	0.133	1.380	35.839	0.000
	4	0.154	2.344	35.138	0.000

Appendix 5: Soil metal concentrations

Stream total recoverable metal concentrations within duplicate samples taken from the northern colony stream (P1 to P5) and the control stream (C1 to C5) at Cape Bird, Ross Island. Samples were collected on four sampling days in 2023, the 1st January (1), 3rd January (2), 7th January (3), and the 10th January (4). Metals analysed through ICP-MS.

Site	Sample Depth	Na	Mg	Al	K	Ca	P	S	Cr	Mn
	cm	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}
P4	0 - 2	7320.622	3856.779	3908.396	3032.033	13305.642	1855.543	7320.622	2.537	96.739
	0 - 2	11239.933	5746.248	5897.807	4865.999	21142.185	2457.832	11239.933	3.638	150.342
	2 - 18	13786.651	15602.465	17556.371	11279.530	37478.313	3515.205	13786.651	11.434	403.435
	2 - 18	9865.265	10605.139	11909.927	8329.675	27202.224	2878.293	9865.265	7.665	276.673
	18 - 37	13636.228	10908.616	17295.303	9051.215	32276.563	3336.611	13636.228	7.156	330.079
	18 - 37	14542.867	11412.677	17601.046	9855.171	34330.952	3516.138	14542.867	6.734	343.724
	37 - 44	6408.954	3415.785	12718.698	4793.530	28316.154	2750.188	6408.954	6.385	309.170
	37 - 44	8818.347	4259.394	15405.697	6695.659	34707.328	3173.757	8818.347	8.028	386.846
	44 - 53	8641.084	9655.973	22678.444	5907.463	12559.895	5147.780	8641.084	9.238	408.659
	44 - 53	8108.945	6464.001	12635.445	5816.881	8791.871	3348.067	8108.945	8.669	279.196
	53 - 65	7864.078	11074.755	21998.981	5066.498	11595.686	4169.692	7864.078	8.764	408.541
	53 - 65	5122.284	6399.806	11087.306	3539.482	6900.950	4055.248	5122.284	7.011	259.003
P0	0 - 2	15058.150	10210.840	25101.947	5190.218	11911.471	6627.756	15058.150	4.997	452.410
	0 - 2	20013.965	15413.149	35342.155	7123.916	16330.234	7601.395	20013.965	7.437	659.380
	18 - 20	9691.168	7786.055	18581.584	4444.542	9934.198	6109.884	9691.168	4.900	378.573
	18 - 20	13872.636	11685.156	28078.713	6559.295	15117.903	6773.712	13872.636	7.806	543.785
	33 - 35	9645.003	7414.994	17999.526	4853.030	10049.654	6079.111	9645.003	4.122	371.071
	33 - 35	11644.088	8426.293	21385.243	5747.420	12013.692	5655.483	11644.088	5.045	426.184
C5	0 - 2	6446.707	4957.748	9703.877	2236.652	5638.025	4139.517	6446.707	2.295	215.061
	0 - 2	8700.038	6977.166	13091.756	3208.375	8293.248	4257.485	8700.038	2.540	305.166

Site	Sample Depth	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	U
	cm	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}
C5	33 - 35	7029.984	6364.630	11901.830	2984.774	7431.008	4585.261	7029.984	3.372	286.892
	33 - 35	6432.104	5511.624	11321.665	2760.211	6636.708	4692.306	6432.104	3.201	256.013
P4	0 - 2	3737.735	2.683	15.323	16.212	46.605	13.974	1.515	0.996	0.495
	0 - 2	5786.557	3.700	15.778	17.645	72.239	15.100	1.287	1.077	0.345
	2 - 18	17118.837	11.751	46.647	35.907	132.212	9.168	2.465	3.883	0.762
	2 - 18	11740.699	7.847	39.621	31.280	100.405	8.908	2.397	4.035	0.526
	18 - 37	13794.121	7.976	24.135	38.856	116.786	9.800	2.930	2.327	1.279
	18 - 37	14359.084	7.983	24.429	40.794	124.920	10.784	2.805	2.403	0.997
	37 - 44	11576.689	7.095	21.652	27.775	136.058	5.430	2.179	1.791	0.729
	37 - 44	14215.271	8.791	26.014	34.353	166.136	6.705	2.818	2.000	0.905
	44 - 53	17846.448	11.289	35.975	17.781	37.557	3.586	0.367	1.675	1.175
	44 - 53	10533.530	7.827	30.021	18.454	28.524	3.099	0.295	1.381	0.712
	53 - 65	18649.658	11.810	36.275	18.652	27.955	2.599	0.180	1.765	1.152
	53 - 65	11258.430	7.435	29.230	11.500	14.070	2.854	0.125	1.905	0.588
P0	0 - 2	13618.845	8.280	20.123	11.722	21.154	1.100	0.369	1.332	1.205
	0 - 2	20023.120	11.995	31.099	15.836	31.501	1.529	0.159	1.774	1.703
	18 - 20	11844.973	6.868	17.635	10.516	21.116	0.760	0.081	1.228	0.910
	18 - 20	17108.289	9.938	25.221	15.068	25.253	1.168	0.101	1.230	1.402
	33 - 35	11780.131	6.962	16.994	11.796	19.096	0.798	0.096	1.179	0.887
	33 - 35	13719.108	7.899	18.047	13.000	22.749	0.968	0.104	1.128	1.057
C5	0 - 2	7514.151	5.190	14.810	7.459	7.785	0.510	0.044	0.663	0.477
	0 - 2	11052.495	7.485	21.104	10.066	15.070	0.663	0.039	0.618	0.626
	33 - 35	9727.919	6.927	18.899	10.752	15.315	0.525	0.050	0.822	0.619
	33 - 35	8764.644	6.172	16.417	10.494	16.048	0.549	0.137	0.720	0.572

Appendix 6: Soil nutrients

Nutrients in duplicate samples taken from site P4 (ornithogenic soil), P0 (control soil above the penguin colony), and C5 (control soil) at Cape Bird, Ross Island. Samples from P4 were collected on the 2nd January 2023, and P0 and C5 were collected on the 5th January 2023. Ammonium was measured through colourimetric spectrophotometry and total nitrogen and carbon through combustion.

Depth	Ammonium	Total nitrogen	Total carbon
cm	mg g^{-1}	%	%
Site P4, an ornithogenic soil			
0 - 2	8.261	8.181	14.468
0 - 2	8.922	8.193	14.592
2 - 18	8.096	6.969	10.826
2 - 18	7.931	6.872	10.676
18 - 37	5.947	2.080	4.943
18 - 37	5.947	2.055	4.836
37 - 44	4.646	0.744	2.056
37 - 44	4.388	0.273	0.288
44 - 53	1.962	0.721	1.974
44 - 53	2.117	0.199	0.151
53 - 65	1.187	0.295	0.265
53 - 65	1.032	0.188	0.149
Site P0, a control soil above penguin colony			
0 - 2	0.000	0.006	0.035
0 - 2	0.001	0.007	0.035
18 - 20	0.003	0.006	0.074
18 - 20	0.004	0.005	0.074
33 - 35	0.003	0.005	0.047
33 - 35	0.002	0.002	0.021
Site C5, a control soil			
0 - 2	0.000	0.007	0.029
0 - 2	0.002	0.005	0.028
33 - 35	0.003	0.007	0.030
33 - 35	0.002	0.007	0.029

Appendix 7: Water and soil physiochemical measurements

Water

Physiochemical measurements taken in the northern colony stream (P1 to P5) and the control stream (C1 to C5) at Cape Bird, Ross Island. Measurements were conducted on the four sampling days in 2023, the 1st January (1), 3rd January (2), 7th January (3), and the 10th January (4).

Site	Sample Day	Temp.	pH	EC	Dissolved oxygen	Turbidity
		°C		µS cm^{-1}	%	NTU
P1	1	0.10	8.07	942.00	105.70	377.00
	2	0.00	7.78	724.00	118.30	21.58
	3	0.00	6.86	401.70	113.20	1.52
	4	0.00	7.09	743.00	112.50	37.38
P2	1	2.30	8.33	808.00	95.40	256.00
	2	0.90	7.72	461.00	115.90	15.12
	3	0.10	7.07	391.70	110.00	2.39
	4	1.25	6.94	438.20	108.00	28.15
P3	1	4.20	8.08	788.00	100.30	183.00
	2	1.30	7.71	510.00	106.30	29.69
	3	0.10	6.68	402.00	103.20	3.81
	4	2.70	6.75	469.10	116.00	30.90
P4	1	5.70	7.88	694.00	104.80	185.33
	2	1.00	7.67	512.00	109.00	22.04
	3	0.30	6.79	432.20	105.30	5.48
	4	5.00	6.89	549.00	112.60	27.19
P5	1	5.10	7.72	538.00	107.30	271.33
	2	1.00	7.69	515.00	104.80	23.51
	3	0.70	6.74	383.00	112.00	5.86
	4	6.60	7.04	582.00	114.00	35.04
C1	1	0.10	7.95	347.90	108.50	80.00
	2	0.00	8.50	544.00	112.00	4.11
	3	0.00	6.79	305.60	111.00	1.59
	4	0	6.76	436	113.00	2.17
C2	1	0.30	7.75	365.40	115.00	63.67
	2	0.00	7.88	534.00	117.90	4.23
	3	0.00	6.93	390.60	105.70	0.79
	4	0.1	6.96	428.7	114.30	14.47
C3	1	0.50	7.77	382.20	118.00	58.00
	2	0.00	7.88	527.00	119.60	4.29
	3	0.00	6.92	380.20	111.70	1.57
	4	0.3	6.93	433.1	115.60	15.73
C4	1	0.80	7.73	386.50	118.80	58.00
	2	0.30	7.72	532.00	120.20	4.11
	3	0.00	6.92	383.00	112.10	1.09
	4	0.6	6.88	423.5	115.8	31.73
C5	1	0.90	7.67	389.80	119.90	56.33
	2	0.40	7.63	531.00	122.20	4.15
	3	0.00	6.91	383.70	114.00	1.29
	4	0.8	6.8	440.5	115.7	33.97

Appendix 8: Stream Discharge

Stream discharge measurements measured within a penguin-influenced (P3) and a control (C3) meltwater stream at Cape Bird, Ross Island. Measurements were made over four sampling days in 2023, the 1st January (1), 3rd January (2), 7th January (3), and the 10th January (4). Discharge measured through dilution gauging.

Site	Injection	1	2	3	4
		L s^{-1}	L s^{-1}	L s^{-1}	L s^{-1}
P3	1	48.5	24.0	16.4	20.0
	2	57.4	23.3	16.7	18.3
	3	51.2	23.8	17.2	18.4
C3	1	13.1	13.5	10.0	14.3
	2	12.7	14.6	11.3	14.8
	3	13.9	14.8	11.0	15.0

Appendix 9: Water nutrient and heavy metal load

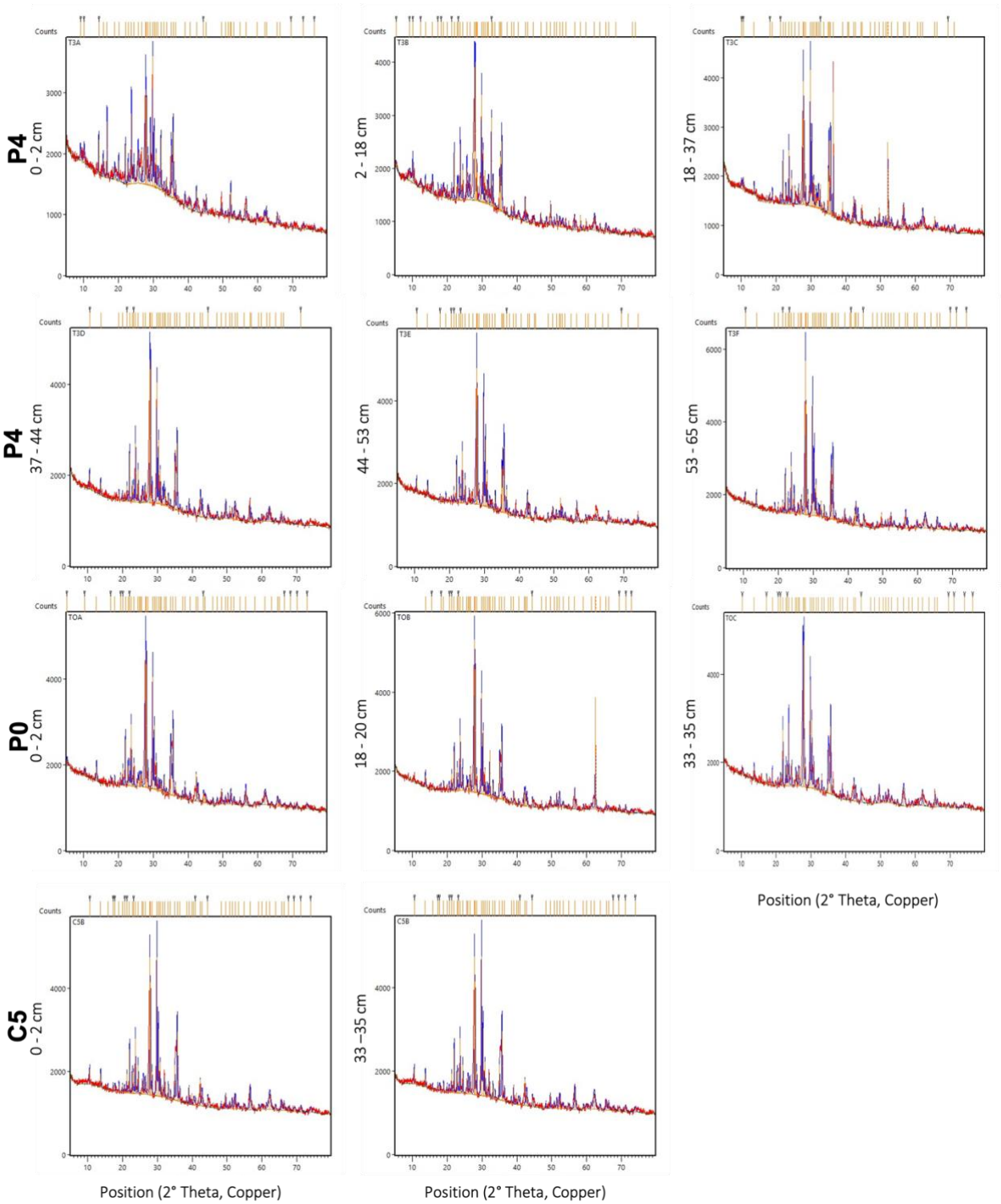
Heavy metal and nutrient load in samples taken from the northern colony stream (P1 to P5) and the control stream (C1 to C5) at Cape Bird, Ross Island. Samples collection and stream discharge was measured on four sampling days in 2023, the 1st January (1), 3rd January (2), 7th January (3), and the 10th January (4). Load is calculated through analyte concentration multiplied by stream discharge.

Site	Sample Day	Ammonium mg s^{-1}	Nitrate mg s^{-1}	Sulphate mg s^{-1}	Phosphate mg s^{-1}
P1	1	17.102	198.913	5139.390	0.000
	1	15.376	202.092	5129.668	0.000
	2	7.489	86.616	1426.738	0.000
	2	3.318	86.062	1428.809	0.000
	3	4.175	37.485	326.273	0.000
	3	3.808	37.052	324.935	0.000
	4	4.101	48.722	1075.915	0.000
	4	2.646	51.317	1074.236	0.000
P2	1	16.527	290.751	1389.339	0.000
	1	15.952	286.897	1370.893	0.000
	2	9.314	119.320	486.232	79.227
	2	4.622	119.247	487.796	79.277
	3	4.175	87.753	1102.078	0.000
	3	5.094	92.416	1188.581	0.000
	4	4.101	84.330	346.698	0.000
	4	3.893	84.279	347.614	60.299
P3	1	854.477	747.639	2966.775	329.736
	1	871.789	744.072	2965.614	327.283
	2	349.362	446.724	841.454	125.546
	2	350.665	446.416	841.186	125.707
	3	65.013	138.907	621.016	56.822
	3	70.541	138.879	619.144	56.645
	4	117.293	286.216	585.711	78.461
	4	117.293	283.462	582.870	78.730
P4	1	652.861	483.864	2143.228	288.398
	1	652.861	486.719	2161.057	290.139
	2	178.414	346.489	574.083	112.464
	2	214.935	345.807	575.154	112.921
	3	67.769	251.853	1233.681	61.170
	3	68.687	252.193	1232.787	61.062
	4	166.207	804.573	1320.040	112.011
	4	174.542	798.111	1314.412	111.020
P5	1	670.172	436.208	1875.143	271.678
	1	684.555	435.497	1872.084	270.600
	2	117.054	527.545	841.203	111.824
	2	115.751	528.069	842.824	248.796
	3	175.367	136.260	479.753	63.512
	3	166.165	136.760	478.442	199.315
	4	163.088	306.152	528.244	84.417

Site	Sample Day	Ammonium mg s^{-1}	Nitrate mg s^{-1}	Sulphate mg s^{-1}	Phosphate mg s^{-1}
P5	4	158.930	305.040	527.533	84.143
C1	1	1.126	21.142	380.277	380.277
	1	1.056	20.075	379.260	379.260
	2	5.009	20.857	380.155	380.155
	2	5.009	20.017	379.197	379.197
	3	0.578	12.558	107.502	107.502
	3	0.521	12.771	107.232	107.232
	4	0.475	20.559	600.222	600.222
	4	0.553	21.109	600.973	600.973
C2	1	1.336	19.251	345.921	345.921
	1	1.546	18.805	345.073	345.073
	2	2.508	20.907	512.991	512.991
	2	1.144	21.031	511.182	511.182
	3	0.464	16.620	660.755	660.755
	3	0.406	16.613	662.634	662.634
	4	0.241	18.084	325.430	325.430
	4	1.254	17.902	325.371	325.371
C3	1	0.846	19.104	315.238	315.238
	1	0.986	17.988	315.893	315.893
	2	1.069	27.838	500.785	500.785
	2	3.948	27.595	484.085	484.085
	3	0.292	16.240	617.233	617.233
	3	0.693	16.491	623.346	623.346
	4	0.787	22.244	724.403	724.403
	4	0.943	22.872	725.982	725.982
C4	1	1.126	20.612	426.019	426.019
	1	1.616	19.833	426.375	426.375
	2	2.811	42.023	591.016	591.016
	2	5.615	42.653	591.512	591.512
	3	0.979	13.036	183.993	183.993
	3	1.723	14.111	361.398	361.398
	4	0.787	18.304	376.266	376.266
	4	1.098	18.351	374.631	374.631
C5	1	1.196	20.086	367.165	367.165
	1	1.266	19.821	368.017	368.017
	2	1.220	18.770	250.911	250.911
	2	2.736	17.999	252.787	252.787
	3	1.723	14.111	361.398	361.398
	3	0.349	13.618	360.599	360.599
	4	1.955	20.285	526.836	526.836
	4	2.267	34.455	516.530	516.530

Appendix 10: Soil clay minerology

Soil clay minerology results of soil samples from P4 (ornithogenic soil), P0 (control soil above the penguin colony), and C5 (control soil) at the Cape Bird northern Adélie penguin colony, Ross Island on the 2nd and the 5th January 2023. Clay minerology measured through X-ray diffraction.

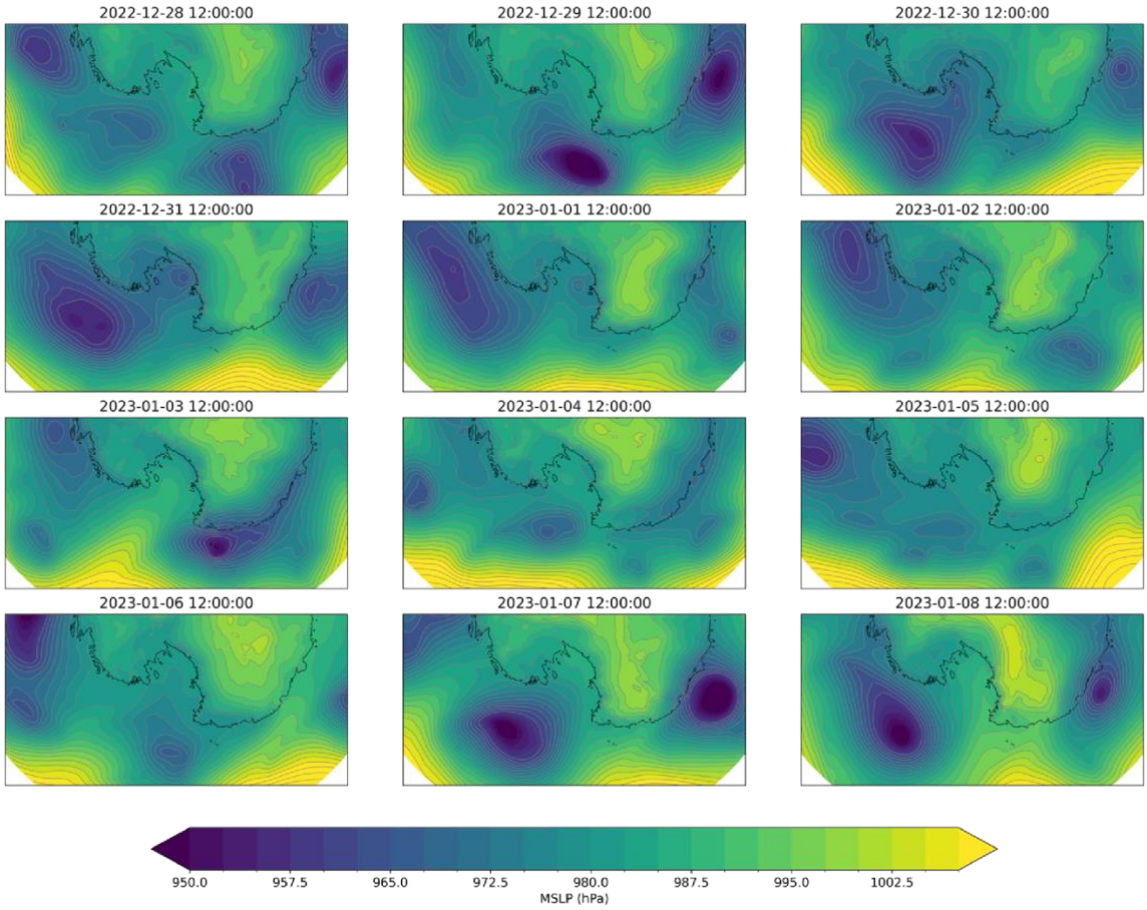


Appendix 11: Automated weather station summary by Eva Bendix Nielsen

Synoptic conditions

Below shows the mean sea level pressure from ERA5 over the Ross Sea Region. A low-pressure system was passing the Ross Sea on the 29th to the 31st of December moving toward the Amundsen Sea. A high-pressure system stabilizes on the 1st of January 2023 until a low-pressure system is developing on the 6th of January and strengthens on the 7th of January passing around the coast and creating a strong pressure gradient across the Ross Ice Shelf possibly leading to strong winds

Mean sea level pressure from ERA5

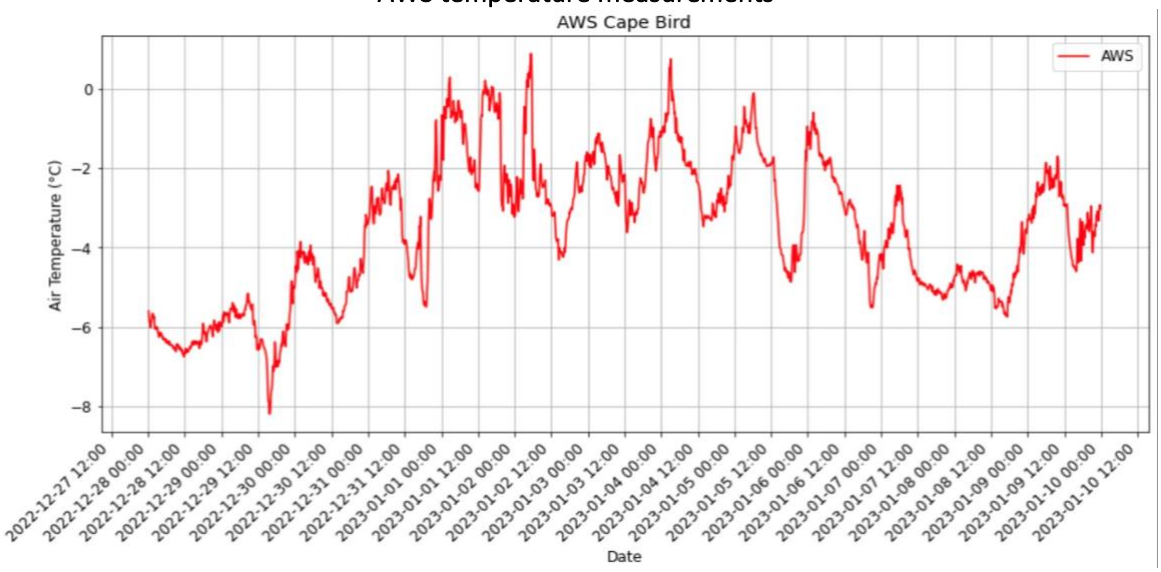


AWS observations

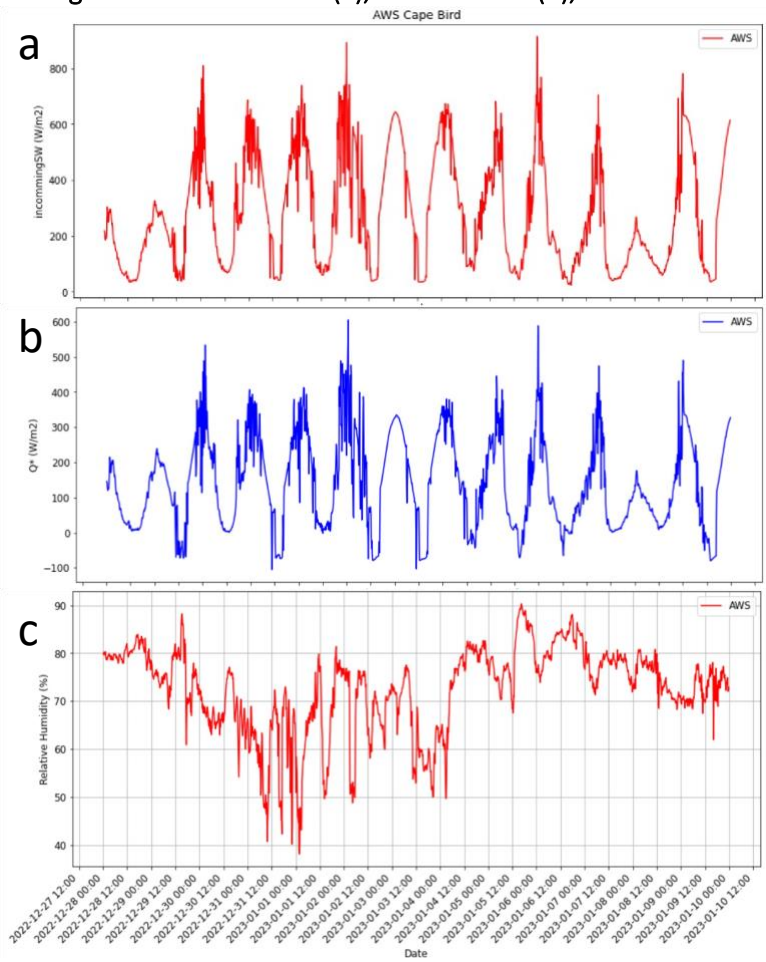
The air temperature in the figure below shows a clear diurnal circle with the highest temperature mid-day correlating well with the incoming shortwave radiation measurements. The incoming short-wave radiation shows that we have cloudy conditions from the 28th and 29th of December and again on the 8th of January. During these days there is a high relative humidity. There is a clear warming phase from the 1st to the 6th of January with high solar radiation during the daytime and a maximum temperature of 1°C on the 4th of January. On the 1st, 2nd, and 4th the temperature reaches above 0 °C. This corresponds to the stable high-pressure system in the Ross Sea. On the 1st of January around midnight, we see a warming trend in the air temperature not related to the incoming solar radiation. There is also a big drop in relative humidity which indicates that this could be related to

wind driven warming processes such as foehn warming. Since we do not have wind data for this day, this is not possible to confirm.

AWS temperature measurements



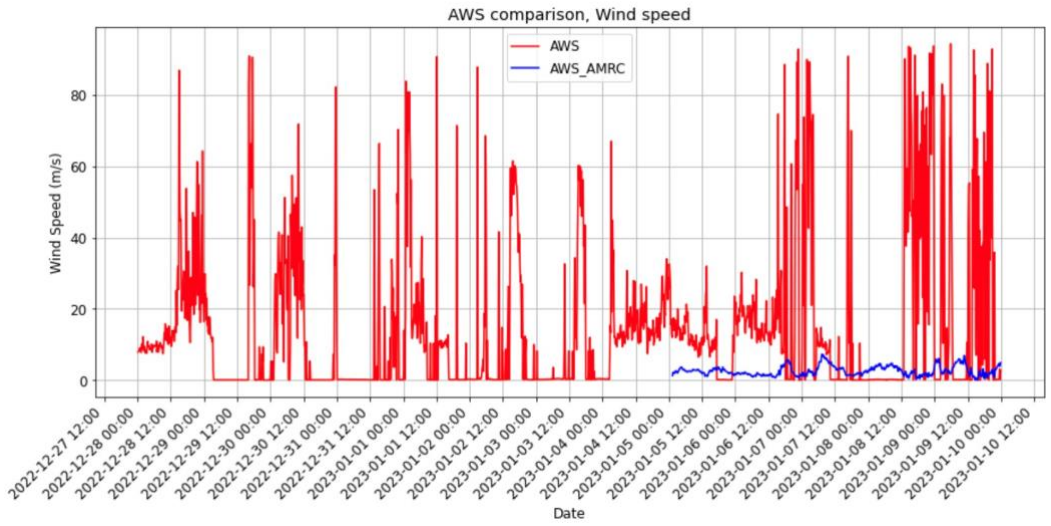
AWS incoming shortwave radiation (a), net radiation (b), and relative humidity (c)



Wind data

Due to dust and/or icing, the UC AWS did not give any useful results. The AMRC AWS did only have measurements from the 5th of January and onwards. Stronger winds of 7 m/s on the 7th of January are most likely due to the low-pressure system in the Ross Sea.

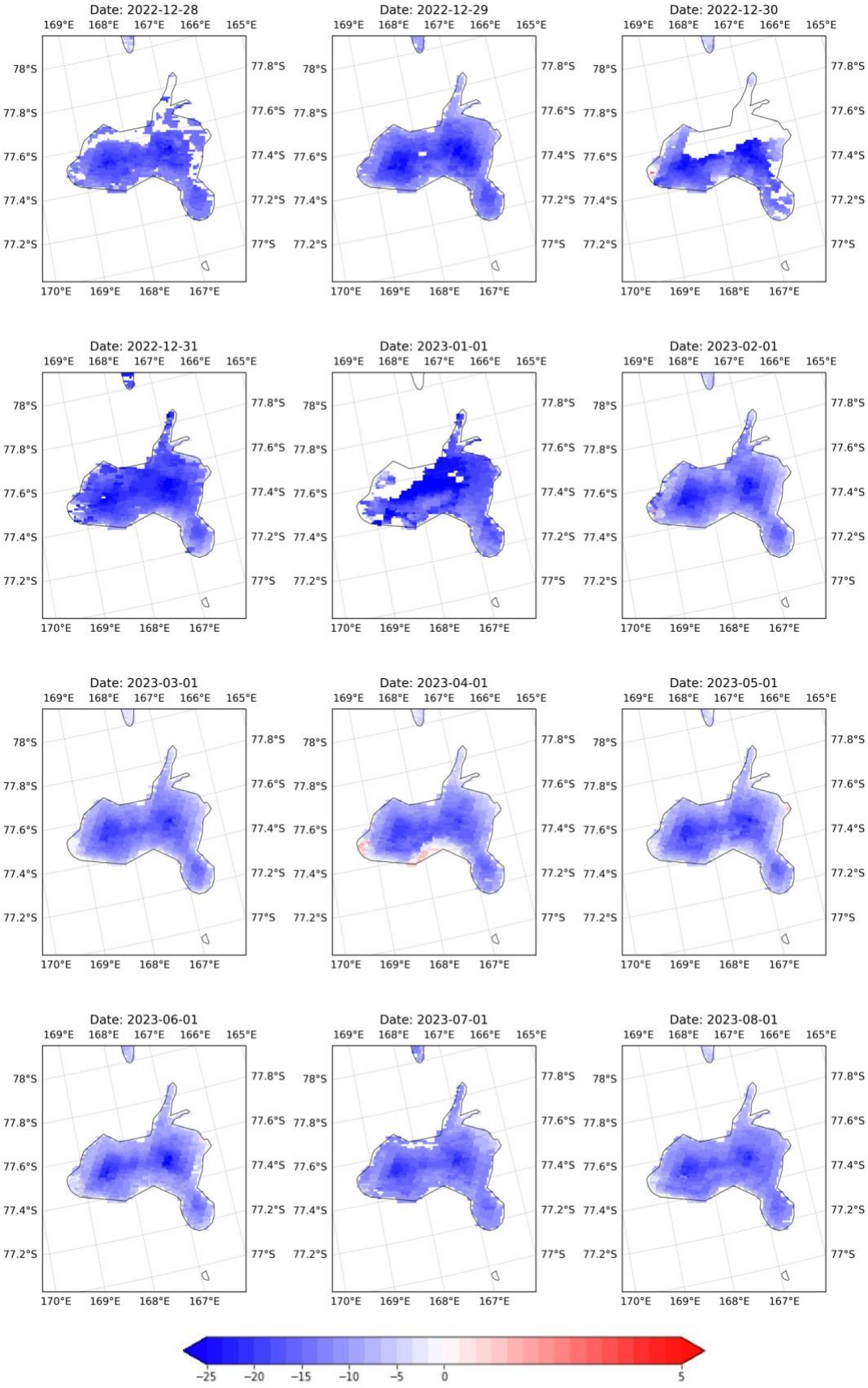
This researched AWS (red) and the University of Wisconsin AWS (AWS_AMRC,blue)



AntAirICE

In the daily mean air temperature from AntAir ICE, we see a warming pattern from the 2nd of January to the 6th of January across Ross Island. The 4th of January Lewis Bay and Cape Crozier have a strong warming signature with a daily mean air temperature above 0 °C.

AntAirICE daily mean air temperature for Ross Island



Appendix 12: Automated weather station raw data

Data recorded form the AWS deployed from the 28th of December 2022 to 10th of January 2023, at site P3 within the northern colony, Cape Bird, Ross Island. Data presented is the hourly average and includes shortwave (SW) and longwave (LW) radiation. Wind speed data not included due to issues with dust and icing.

Time stamp	Air temp	Relative humidity	Incoming SW radiation	Outgoing SW radiation	Incoming LW radiation	Outgoing LW radiation	Soil temp
	°C	%	W/m2	W/m2	W/m2	W/m2	°C
28/12/22 11:00	-4.112	75.18	239	35.94	288.8	326.7	1.061
28/12/22 12:00	-5.112	78.85	214.5	31.37	282.8	325.9	-0.243
28/12/22 13:00	-5.36	79.23	224.8	32.58	283.1	325.1	-0.057
28/12/22 14:00	-5.85	79.88	199	28.57	281.8	321.6	-0.482
28/12/22 15:00	-5.733	79.1	255.6	37.03	282.4	325.1	0.086
28/12/22 16:00	-6.034	79.38	275.6	40	281.1	326.7	0.021
28/12/22 17:00	-6.181	79.27	271.4	39.52	279.9	326.9	0.199
28/12/22 18:00	-6.232	78.86	207.1	29.93	279.1	322.1	-0.413
28/12/22 19:00	-6.345	79.66	161.8	22.99	279.7	316.7	-1.053
28/12/22 20:00	-6.393	79.29	128.8	18.26	278.7	314.2	-1.168
28/12/22 21:00	-6.464	78.52	100.9	14.37	278.1	311.6	-1.536
28/12/22 22:00	-6.554	79.39	74.71	10.65	278	308.5	-1.9
28/12/22 23:00	-6.484	78.4	63.7	9.25	278.4	306.9	-1.994
29/12/22 0:00	-6.555	79.66	64.99	9.84	277.4	306.1	-1.611
29/12/22 1:00	-6.691	81.4	60.04	9.89	276.6	304.2	-1.755
29/12/22 2:00	-6.603	79.76	40.3	6.036	278	303.9	-1.926
29/12/22 3:00	-6.555	80.3	38.46	5.69	279.4	304.2	-1.739
29/12/22 4:00	-6.431	80.5	41.13	6.835	279.4	304.6	-1.562
29/12/22 5:00	-6.394	81.2	41.48	8.42	280.1	304.1	-1.531
29/12/22 6:00	-6.451	83.1	50.64	16.79	280	301.9	-1.767
29/12/22 7:00	-6.255	82.7	91.2	38.85	280.3	301.3	-1.325
29/12/22 8:00	-6.177	82.4	132	58.15	281.2	299.8	-0.517
29/12/22 9:00	-6.15	82.5	161	62.06	279.8	301.3	0.166
29/12/22 10:00	-6.034	81.1	180	43.31	280.5	308.6	0.082
29/12/22 11:00	-5.984	78.42	222.3	32.37	278.5	316.4	0.231
29/12/22 12:00	-6.02	79.55	229.3	25.67	279	320.9	0.112
29/12/22 13:00	-5.942	77.82	239.4	24.96	278	323.6	-0.204
29/12/22 14:00	-5.803	76.13	286.2	29.53	277.3	326.9	-0.401
29/12/22 15:00	-5.675	75.31	311.7	33.47	276.9	330	-0.218
29/12/22 16:00	-5.711	75.9	281.9	32.02	277.2	328.1	-0.578
29/12/22 17:00	-5.514	74.79	276.5	33.46	276.9	326.8	-0.834
29/12/22 18:00	-5.614	73.3	283.6	36.23	271.5	327.6	-0.728
29/12/22 19:00	-5.739	74.25	264.6	34.83	266.6	326.7	-0.807
29/12/22 20:00	-5.715	75.16	234.5	31.44	262.5	323.5	-1.042
29/12/22 21:00	-5.604	75.19	209.9	28.48	258.9	320.2	-1.289
29/12/22 22:00	-5.292	70.3	173.4	23.6	254.7	316.6	-1.516
29/12/22 23:00	-5.482	72.41	173.8	23.73	247.2	313.8	-1.948

Time stamp	Air temp	Relative humidity	Incoming SW radiation	Outgoing SW radiation	Incoming LW radiation	Outgoing LW radiation	Soil temp
	°C	%	W/m2	W/m2	W/m2	W/m2	°C
30/12/22 0:00	-5.827	78.32	158	24.67	203.7	309.3	-2.841
30/12/22 1:00	-6.416	80.6	119.2	10.89	188.7	299.7	-4.188
30/12/22 2:00	-6.429	79.55	57.92	6.068	191.4	295.7	-4.42
30/12/22 3:00	-6.42	80.3	65.63	8.08	197.3	295.3	-4.455
30/12/22 4:00	-6.737	81.4	45.42	5.452	190.2	292.8	-4.747
30/12/22 5:00	-7.963	86.7	83	8.52	211.7	293.6	-5.306
30/12/22 6:00	-7.409	81.4	230.4	18.16	184.8	296.3	-3.743
30/12/22 7:00	-6.83	68.5	324.7	38.28	186.3	305.3	-1.249
30/12/22 8:00	-6.913	69.85	380.4	51.23	188	312.2	0.591
30/12/22 9:00	-6.49	69.32	441.8	65.27	190.8	324.7	3.43
30/12/22 10:00	-6.32	73.61	420.9	65.14	193.4	325.1	2.796
30/12/22 11:00	-6.032	75.8	517.7	82.5	219.1	329.4	0.713
30/12/22 12:00	-5.388	74.95	551.6	90.2	232.2	341.3	1.032
30/12/22 13:00	-5.104	72.38	425.5	70.33	207.9	341.9	2.24
30/12/22 14:00	-4.458	71.36	613	101.2	233.6	362.4	3.823
30/12/22 15:00	-4.185	69.23	610.8	100.9	235.6	375.1	5.568
30/12/22 16:00	-4.154	68.07	470.5	71.03	268.3	372.4	5.806
30/12/22 17:00	-4.274	67.47	385.2	56.74	271.7	364.9	5.412
30/12/22 18:00	-4.23	66.25	345	50.52	276.1	361.2	5.19
30/12/22 19:00	-4.209	64.38	356.7	53.46	275.4	355	3.154
30/12/22 20:00	-4.582	66.7	275.5	40.83	268.9	348.6	2.18
30/12/22 21:00	-4.667	66.03	194.2	28.68	264	339.8	1.611
30/12/22 22:00	-4.978	65.2	136.3	20.18	267.3	332.6	1.123
30/12/22 23:00	-5.164	66.32	107.7	16.09	259.5	325.8	0.622
31/12/22 0:00	-5.281	65.09	86	12.96	257.8	321.2	-0.26
31/12/22 1:00	-5.433	66.66	82.9	12.63	252.4	317.8	-1.001
31/12/22 2:00	-5.56	68.11	74.25	11.21	254.3	313.9	-1.975
31/12/22 3:00	-5.79	73.87	70.19	10.53	254.1	310.1	-2.659
31/12/22 4:00	-5.847	76.42	79.99	11.86	254.2	308.9	-2.83
31/12/22 5:00	-5.707	75.68	103.9	15.27	253.6	309.8	-2.664
31/12/22 6:00	-5.414	74.86	177.9	24.82	255.2	313.6	-2.199
31/12/22 7:00	-4.947	67.62	350	47.41	249.7	322.6	-1.287
31/12/22 8:00	-5.077	69.57	277.3	40.23	251.7	323.2	-1.275
31/12/22 9:00	-4.662	60.41	262.7	38.28	257.2	325.1	-0.917
31/12/22 10:00	-4.858	68.28	264.4	38.39	260.2	325	-1.065
31/12/22 11:00	-4.493	64.3	419.9	66	236.7	334.6	-0.391
31/12/22 12:00	-4.166	65.33	563.3	96	211.8	355.8	1.082
31/12/22 13:00	-3.343	64.43	608.1	105.1	220.1	369.7	2.92
31/12/22 14:00	-3.013	62.4	559.5	95.8	224.4	362	2.424
31/12/22 15:00	-2.988	63.98	507.3	85.8	220.9	355.6	2.065
31/12/22 16:00	-2.95	63.61	582.8	100.2	223.7	365.1	3.059
31/12/22 17:00	-2.994	63.21	485.1	82.5	222.2	362.1	3.239

Time stamp	Air temp	Relative humidity	Incoming SW radiation	Outgoing SW radiation	Incoming LW radiation	Outgoing LW radiation	Soil temp
	°C	%	W/m2	W/m2	W/m2	W/m2	°C
31/12/22 18:00	-2.752	60.63	507	87.9	214.7	362.4	3.754
31/12/22 19:00	-2.691	58.24	463.1	79.85	202.8	358.1	4.154
31/12/22 20:00	-2.387	55.31	434.6	73.24	199.9	357	5.252
31/12/22 21:00	-2.681	56.35	372.2	59.35	197.9	347.8	4.641
31/12/22 22:00	-2.465	48.49	317.3	46.26	196.5	339.4	3.888
31/12/22 23:00	-2.259	45.75	265.5	35.04	194.7	331.1	1.919
1/01/23 0:00	-2.765	52.51	164.3	25.25	193.9	323.6	0.122
1/01/23 1:00	-3.813	64.57	198.2	15.77	194.3	315.6	-1.149
1/01/23 2:00	-3.959	66.35	78.47	5.723	193.3	306.3	-1.855
1/01/23 3:00	-4.618	70.1	50.96	6.619	195	303.9	-2.029
1/01/23 4:00	-4.748	66.86	46.23	6.198	192.7	301.5	-2.297
1/01/23 5:00	-4.404	55.32	47.41	5.539	190.3	299.5	-2.27
1/01/23 6:00	-3.799	47.29	189.2	17.04	191	302.3	-1.546
1/01/23 7:00	-4.564	63.65	312.2	38.99	191.9	313.3	2.176
1/01/23 8:00	-5.402	71.95	362.3	51.43	192.5	319.8	4.543
1/01/23 9:00	-4.282	63.86	378.7	58.7	202	331	-
1/01/23 10:00	-3.04	64.61	465.2	75.67	212.6	348.3	9.46
1/01/23 11:00	-2.186	54.01	533.7	89.5	225.2	365.3	9.91
1/01/23 12:00	-1.736	57.73	514.4	88.9	224.9	373.3	9.72
1/01/23 13:00	-2.154	64.76	515	90.2	225.6	375.8	9.65
1/01/23 14:00	-1.049	52.74	511.7	89.1	219.9	382.9	9.59
1/01/23 15:00	-0.486	42.46	563.7	95.7	245.6	393.5	9.31
1/01/23 16:00	-0.086	45.83	666.7	119.3	238.9	409.8	11.2
1/01/23 17:00	-0.598	56.5	597.6	104.7	245.8	403.8	11.75
1/01/23 18:00	-0.634	60.42	533	91.7	242.4	398.2	10.76
1/01/23 19:00	-0.487	64.08	498	86.6	214.9	391.5	-
1/01/23 20:00	-0.758	66.46	425.5	71.53	209.9	382.2	15.99
1/01/23 21:00	-1.039	67.49	371.2	58.42	216.8	367.7	NAN
1/01/23 22:00	-1.641	68.01	233.3	35.03	240.8	351.9	7.761
1/01/23 23:00	-1.98	70.78	105.2	15.96	286.4	343.7	5.534
2/01/23 0:00	-1.953	70.53	88.4	13.45	288.7	340	4.966
2/01/23 1:00	-2.458	77.95	87.8	13.45	277.3	335.6	4.294
2/01/23 2:00	-1.778	72.6	62.51	9.41	286.6	331.4	2.778
2/01/23 3:00	-0.297	57.21	77.45	11.65	278.9	330	3.094
2/01/23 4:00	0.029	50.85	91	13.74	278	331.7	3.691
2/01/23 5:00	-0.228	53.32	83.6	12.43	275.8	329.4	3.372
2/01/23 6:00	-0.055	58.01	122.7	18.38	278.8	331.1	2.735
2/01/23 7:00	-0.471	67.56	207.9	30.66	274.5	334.5	2.53
2/01/23 8:00	-0.536	69.88	322.5	48.6	257.6	338.3	2.779
2/01/23 9:00	-1.818	75.57	250.4	38.01	281.2	342.1	4.401
2/01/23 10:00	-2.364	77.97	563.1	91.7	271.1	365.3	-
2/01/23 11:00	-2.454	77.3	484.9	78.52	279.7	371.5	10.66

Time stamp	Air temp	Relative humidity	Incoming SW radiation	Outgoing SW radiation	Incoming LW radiation	Outgoing LW radiation	Soil temp
	°C	%	W/m2	W/m2	W/m2	W/m2	°C
2/01/23 12:00	-2.519	76.23	601.4	99.3	278.7	386.8	11.87
2/01/23 13:00	-3.088	76.32	574	98.9	256.2	377.3	9.22
2/01/23 14:00	-2.724	75.59	715.4	126	258.3	388.1	8.88
2/01/23 15:00	-2.697	75.52	530.4	86.9	264.1	381.8	9.67
2/01/23 16:00	-2.27	70.82	482.2	82	252.2	379.7	9.79
2/01/23 17:00	-0.54	51.38	380.5	67.84	221.7	355.7	5.808
2/01/23 18:00	0.29	51.37	565.1	104.8	210.9	370.4	8.67
2/01/23 19:00	-0.137	57.66	503.2	91	214.6	374.2	11.21
2/01/23 20:00	-2.091	71.57	380	65.96	265.4	366.9	10.75
2/01/23 21:00	-2.651	75.63	243.7	38.6	257.8	346.7	-
2/01/23 22:00	-2.16	74.36	420.5	66.53	268.8	360.9	-
2/01/23 23:00	-2.413	75.51	331.2	50.48	265	355.5	8.64
3/01/23 0:00	-2.782	74.85	150.5	26.73	216.4	338.4	5.302
3/01/23 1:00	-2.911	66.44	205.6	16.71	201.9	324.7	1.622
3/01/23 2:00	-3.169	61.7	87.3	8.47	205.5	313.5	0.409
3/01/23 3:00	-3.626	60.35	39.2	5.394	196.3	307.5	-0.271
3/01/23 4:00	-4.062	67.68	41.19	5.597	196.8	305	-0.701
3/01/23 5:00	-4.177	71.17	44.42	5.843	197	303.1	-1.292
3/01/23 6:00	-3.885	69.07	154.6	15.2	198.6	304.9	-1.024
3/01/23 7:00	-3.261	67	302.5	39.09	201.4	316.3	3.061
3/01/23 8:00	-3.019	65.04	360.1	53.45	202	324.3	5.359
3/01/23 9:00	-2.561	63.52	421.5	68.91	204	335	7.308
3/01/23 10:00	-2.153	65.12	484.3	84.4	205.3	345.6	8.8
3/01/23 11:00	-2.547	70.38	540.1	98.8	206.1	356.8	9.11
3/01/23 12:00	-2.217	71.31	585.4	112	207.3	371.8	9.37
3/01/23 13:00	-1.707	72.05	620.4	121.6	207.9	384.4	10.2
3/01/23 14:00	-1.792	72.57	639.2	126.7	208.4	389.9	10.38
3/01/23 15:00	-1.764	71.8	640.3	127.2	208.4	391.4	9.64
3/01/23 16:00	-1.437	67.73	625.4	124.8	208.8	391	9.46
3/01/23 17:00	-1.214	69.12	595.2	115.9	209	389.4	10.08
3/01/23 18:00	-1.456	71.74	549.5	104	208.7	382.2	10.09
3/01/23 19:00	-1.716	73.61	478.4	87	209.1	370.8	9.25
3/01/23 20:00	-2.089	76.03	375.7	66.29	210.1	354.7	6.796
3/01/23 21:00	-2.309	76.82	376.6	61.15	205.3	346.5	5.902
3/01/23 22:00	-2.591	74.17	318.9	47.21	203.7	335.4	3.545
3/01/23 23:00	-2.777	67.63	265.4	34.95	200.7	326	0.635
4/01/23 0:00	-2.02	56.42	166.5	26.03	199.3	321.8	-0.128
4/01/23 1:00	-2.233	54.53	199.5	14.71	199.2	316	-0.565
4/01/23 2:00	-3.189	65.04	69.24	4.783	196.2	306.9	-1.067
4/01/23 3:00	-3.101	59.31	35.91	4.821	197.4	304.4	-1.3
4/01/23 4:00	-3.021	59.57	36.54	4.896	197.2	303.5	-1.263
4/01/23 5:00	-3.185	56.84	39.68	5.33	196.4	302.3	-1.339

Time stamp	Air temp	Relative humidity	Incoming SW radiation	Outgoing SW radiation	Incoming LW radiation	Outgoing LW radiation	Soil temp
	°C	%	W/m2	W/m2	W/m2	W/m2	°C
4/01/23 6:00	-2.803	56.15	145.3	15.42	199.8	305.5	-0.852
4/01/23 7:00	-2.343	56.57	300.3	39.05	204.5	316.8	1.93
4/01/23 8:00	-2.454	58.85	366	54.13	203.9	323.9	3.598
4/01/23 9:00	-1.536	53.25	426.8	69.7	205.4	335.4	5.663
4/01/23 10:00	-0.972	52.52	488.8	85.6	206.8	347.4	-
4/01/23 11:00	-1.392	60.86	529.7	96.5	207.8	354.8	7.624
4/01/23 12:00	-1.836	64.55	563.3	105.6	208.6	355.8	5.516
4/01/23 13:00	-1.166	62.2	616.7	117	211.9	369.1	6.361
4/01/23 14:00	-1.046	63.97	601.5	115.1	213	373.6	6.9
4/01/23 15:00	-0.768	61.98	593.9	115.2	215	376.1	7.183
4/01/23 16:00	0.049	55.1	628.4	123.4	215.4	388.5	8.95
4/01/23 17:00	0.018	60.98	632.8	120.6	223	397.4	9.55
4/01/23 18:00	-0.698	69	561.8	101.4	236	387.6	7.234
4/01/23 19:00	-1.192	73.63	522.5	93.8	216.5	381.1	7.928
4/01/23 20:00	-1.357	73.92	435.7	77.61	212.2	374.1	8.91
4/01/23 21:00	-1.745	76.49	394.8	64.71	212.7	364.8	8.18
4/01/23 22:00	-1.916	76.41	323.7	49.6	210.7	356.6	9.15
4/01/23 23:00	-1.925	77.76	310.5	44.12	216.4	352.7	9.65
5/01/23 0:00	-2.094	79.14	248.3	39.79	229.8	350.8	6.792
5/01/23 1:00	-2.227	78.4	249.5	24.31	223.5	341.9	5.219
5/01/23 2:00	-2.607	77.8	115.9	13.26	217.3	328	4.156
5/01/23 3:00	-3.285	81.9	97.1	14.4	219.4	323	3.23
5/01/23 4:00	-3.227	81.6	105.5	15.51	222.2	322.1	2.979
5/01/23 5:00	-3.225	81	101.1	14.6	216.1	320.1	3.02
5/01/23 6:00	-3.148	80.9	125.9	15.23	210.1	317.9	2.427
5/01/23 7:00	-3.155	81	152.9	21.59	216.6	321.7	3.507
5/01/23 8:00	-2.774	79.23	243.6	35.98	220.4	329.9	5.108
5/01/23 9:00	-2.728	79.35	252.9	38.39	211.1	332.9	-
5/01/23 10:00	-2.891	80.7	314.3	51.12	222.4	341.9	-
5/01/23 11:00	-2.598	81.8	327	54.69	223.8	348.7	7.404
5/01/23 12:00	-2.358	81.4	370.1	61.89	251.1	358.7	7.721
5/01/23 13:00	-1.68	77.82	428.9	70.85	274.8	371.6	8.75
5/01/23 14:00	-1.221	76.82	412	67.11	289	375.3	8.88
5/01/23 15:00	-1.554	79.02	380.7	62.71	277	370.7	6.466
5/01/23 16:00	-1.175	77.43	499.2	84.6	282.2	379.2	6.795
5/01/23 17:00	-0.74	74.55	581.3	104.4	254.2	392.4	8.63
5/01/23 18:00	-1.003	74.68	481.6	82	268	383.6	7.54
5/01/23 19:00	-0.596	72.4	550.6	94.6	272.2	390.5	9.43
5/01/23 20:00	-0.476	71.73	421.9	71.11	281.9	388.5	11.21
5/01/23 21:00	-1.295	75.93	212.1	34.17	281.1	363.2	6.68
5/01/23 22:00	-1.614	76.64	143.6	22.61	283.7	350.4	4.608
5/01/23 23:00	-1.772	77.49	111.4	17.47	285.7	343	3.547

Time stamp	Air temp	Relative humidity	Incoming SW radiation	Outgoing SW radiation	Incoming LW radiation	Outgoing LW radiation	Soil temp
	°C	%	W/m2	W/m2	W/m2	W/m2	°C
6/01/23 0:00	-1.92	75.52	71.89	11.09	289	336.1	2.641
6/01/23 1:00	-1.909	70.92	73.81	11.4	282.9	332.8	2.554
6/01/23 2:00	-1.857	71.12	82.4	12.65	280.1	331.7	2.82
6/01/23 3:00	-2.65	82.5	65.32	10.1	257.9	325.1	3.073
6/01/23 4:00	-3.689	86.6	48.26	6.733	206.3	313.7	1.639
6/01/23 5:00	-4.182	88.8	89.2	12.29	212.8	311.9	0.69
6/01/23 6:00	-4.526	89.7	105	14.54	217.9	311.4	0.45
6/01/23 7:00	-4.668	88.2	177.6	23.57	217.4	314.2	1.203
6/01/23 8:00	-4.633	87.7	262.5	37.57	209.8	319.7	3.041
6/01/23 9:00	-4.257	85.7	331.1	50.79	226.3	331.3	6.301
6/01/23 10:00	-4.186	85.3	324.2	52.14	255.8	341.1	6.273
6/01/23 11:00	-4.072	85.5	364	60.52	248.4	346.9	-
6/01/23 12:00	-3.299	82.7	560	100.5	231.8	368.9	9.12
6/01/23 13:00	-1.448	77.23	737.8	132.6	249.8	402.9	12.99
6/01/23 14:00	-1.317	76.78	628.1	115.4	250.4	403.1	-
6/01/23 15:00	-0.837	75.03	642.6	124.8	226.5	410.5	15.69
6/01/23 16:00	-1.017	75.91	493.1	87.7	247.1	396.1	-
6/01/23 17:00	-1.41	78.6	430.2	72.25	264	386.7	-
6/01/23 18:00	-1.712	79.47	286.4	46.21	289	375	10.41
6/01/23 19:00	-1.913	80	180	28.47	297.9	361.3	7.959
6/01/23 20:00	-1.852	79.19	183.5	29	294.8	357.3	6.047
6/01/23 21:00	-1.898	80.2	204.1	32.75	270.1	353.4	3.94
6/01/23 22:00	-2.26	82.2	176.6	28.43	256.9	346.7	2.642
6/01/23 23:00	-2.401	83.6	141.7	22.76	256.1	341.3	2.372
7/01/23 0:00	-2.615	84.2	143.7	22.89	239.3	336.5	1.29
7/01/23 1:00	-2.859	84.3	85.8	13.4	236.8	328.2	0.65
7/01/23 2:00	-3.117	84.5	54.91	8.37	249.9	321.8	-0.003
7/01/23 3:00	-2.857	83.3	58.09	9.16	286.3	325.4	0.762
7/01/23 4:00	-2.958	83	43.45	6.839	291.5	324	0.658
7/01/23 5:00	-3.25	84.3	28.79	4.486	295.5	321.3	0.949
7/01/23 6:00	-3.651	85.4	39.73	5.915	294.4	319	0.753
7/01/23 7:00	-4.137	87.6	77.87	11.46	290.9	318.6	0.305
7/01/23 8:00	-3.918	83.5	111.5	16.74	288.2	319.7	1.311
7/01/23 9:00	-4.336	82.1	136.7	20.69	283.4	319.7	1.469
7/01/23 10:00	-5.368	85.4	105.7	15.98	287.5	319.2	0.661
7/01/23 11:00	-5.248	84.3	167.6	25.88	288.1	324.8	1.654
7/01/23 12:00	-4.797	83.9	162.7	25.11	288.6	328.5	2.253
7/01/23 13:00	-4.273	78.59	234	36.27	289.5	335.2	3.452
7/01/23 14:00	-4.283	79.61	211.2	32.66	288.8	336.2	3.726
7/01/23 15:00	-3.945	78.85	249.5	39.2	290.2	343.1	3.829
7/01/23 16:00	-3.689	75.99	306.9	49.72	289.4	346.9	4.449
7/01/23 17:00	-3.518	74.84	360.3	59.74	288.9	356	5.891

Time stamp	Air temp	Relative humidity	Incoming SW radiation	Outgoing SW radiation	Incoming LW radiation	Outgoing LW radiation	Soil temp
	°C	%	W/m2	W/m2	W/m2	W/m2	°C
7/01/23 20:00	-2.639	74.22	568.8	99	259.3	375.9	5.928
7/01/23 21:00	-3.503	77.72	427.2	70.72	253.8	352.7	2.19
7/01/23 22:00	-3.724	77.48	365.4	57.77	266.2	346.8	1.689
7/01/23 23:00	-4.231	79.21	166.5	25.73	283.5	332.8	0.523
8/01/23 0:00	-4.595	79.7	87.9	13.82	279.8	322.8	-0.512
8/01/23 1:00	-4.749	79.12	55.16	8.59	282.5	318.5	-1.171
8/01/23 2:00	-4.863	78.02	44.39	6.9	282.2	315.8	-0.828
8/01/23 3:00	-4.911	78.22	41.77	6.432	282.6	313.9	-1.113
8/01/23 4:00	-4.955	79.14	46.22	7.076	281.3	312.6	-1.312
8/01/23 5:00	-4.995	77.39	47.29	7.194	281.4	312.2	-1.261
8/01/23 6:00	-5.031	79.12	50.16	7.559	282.6	312.9	-0.577
8/01/23 7:00	-5.135	79.45	59.54	8.96	282	313	-0.45
8/01/23 8:00	-5.115	78.78	77.43	11.56	281.5	314.4	-0.215
8/01/23 9:00	-5.17	78.6	91.1	13.55	282.1	315.6	-0.062
8/01/23 10:00	-5.25	78.56	109.3	16.24	281.9	316.6	0.239
8/01/23 11:00	-5.174	76.13	149.5	22.32	281.5	320.7	0.885
8/01/23 12:00	-4.985	74.08	158.7	23.58	282	322.5	1.341
8/01/23 13:00	-4.89	73.6	184.5	27.48	282	325.1	1.742
8/01/23 14:00	-4.626	73.1	238.6	35.82	281.5	329.6	2.303
8/01/23 15:00	-4.559	75.78	228.8	34.03	281.2	330.8	2.351
8/01/23 16:00	-4.745	79.16	202.1	29.91	281.6	328.3	1.73
8/01/23 17:00	-4.97	80.3	172.6	25.39	281.6	324.1	0.779
8/01/23 18:00	-4.773	78.05	170.6	25.24	281.8	323.9	0.751
8/01/23 19:00	-4.696	78	161.8	24.12	281.3	324.1	1.046
8/01/23 20:00	-4.729	78.74	147.9	22.1	280	322.1	0.601
8/01/23 21:00	-4.647	77.01	127.6	19.19	278.7	319.2	0.06
8/01/23 22:00	-4.646	77.6	120.6	18.34	277.8	317.3	-0.311
8/01/23 23:00	-4.712	77.18	102	15.68	276.8	316	-0.479
9/01/23 0:00	-4.815	77.34	95.7	14.94	270.2	314.5	-0.666
9/01/23 1:00	-4.965	79.16	86.6	13.45	258.5	312	-1.054
9/01/23 2:00	-5.03	73.32	72.54	11.24	265.2	311	-1.101
9/01/23 3:00	-5.476	74.6	64.67	10.08	272.7	310.2	-1.168
9/01/23 4:00	-5.378	72.4	66.1	10.31	277.5	311	-0.964
9/01/23 5:00	-5.415	73.3	85.2	13.26	274.7	311.2	-1.024
9/01/23 6:00	-5.661	73.7	107.9	16.78	272.5	311.5	-1.035
9/01/23 7:00	-5.474	71.95	140.7	21.92	272.3	315.8	-0.013
9/01/23 8:00	-5.102	71.92	156.9	24.16	279.5	319.8	0.842
9/01/23 9:00	-4.745	70.75	225.1	35.47	271.7	326.6	2.515
9/01/23 10:00	-4.527	70.42	298.8	48.65	249.5	333.4	3.635
9/01/23 11:00	-3.937	69.56	465.1	81.3	233.3	350.3	-
9/01/23 12:00	-3.872	70.68	381.3	64.48	251.5	356.4	10.24
9/01/23 13:00	-3.514	70.83	508	89.8	255.9	365.6	10.1

Time stamp	Air temp	Relative humidity	Incoming SW radiation	Outgoing SW radiation	Incoming LW radiation	Outgoing LW radiation	Soil temp
	°C	%	W/m2	W/m2	W/m2	W/m2	°C
9/01/23 14:00	-3.255	70.12	667.9	128	212.7	378.2	9.34
9/01/23 15:00	-3.175	70.09	629.1	123.9	204.1	376.9	-
9/01/23 16:00	-2.902	70.03	616.3	123.6	205.7	389.2	14.02
9/01/23 17:00	-2.51	70.02	587.3	115.4	207.6	390.9	-
9/01/23 18:00	-2.539	69.87	538.6	103.2	205.3	383.8	9.94
9/01/23 19:00	-2.226	69.54	484.4	90.5	205.8	380.4	-
9/01/23 20:00	-2.147	71.93	429	76.48	217.1	372.2	9.45
9/01/23 21:00	-2.24	76.12	307.4	50.45	236.4	355.3	5.941
9/01/23 22:00	-2.321	76.84	156	25	250.6	339.9	3.088
9/01/23 23:00	-1.967	74.1	182.5	27.43	256.6	336.6	2.352
10/01/23 0:00	-2.5	72.09	84	13.31	237.6	325.5	0.368
10/01/23 1:00	-2.795	70.41	77.96	12.54	248.4	322.2	-0.011
10/01/23 2:00	-2.952	71.16	69.81	11.11	238.1	319.6	0.043
10/01/23 3:00	-3.755	73.91	49.54	6.999	207	311.3	-1.312
10/01/23 4:00	-4.324	76.35	37.96	5.104	196.2	305.6	-2.55
10/01/23 5:00	-4.54	76.38	41.08	5.418	196.5	303.2	-2.878
10/01/23 6:00	-4.073	70.95	101.9	10.88	196.9	303.9	-2.887
10/01/23 7:00	-3.706	72.77	287.7	35.74	200.4	316.2	-1.822
10/01/23 8:00	-3.662	72.57	343.6	49.83	201.6	326	-0.858
10/01/23 9:00	-3.402	74.35	404.2	65.07	203.6	337.2	-0.123
10/01/23 10:00	-3.355	75.86	466.5	80.5	205.1	349.1	2.001
10/01/23 11:00	-3.795	75.62	524.6	94.9	205.2	359.4	3.226
10/01/23 12:00	-3.267	73.57	572.4	107.6	206.3	367.8	5.044
10/01/23 13:00	-3.075	73.16	605.7	117	207.1	373.9	5.575
10/01/23 14:00	-2.902	73.73	621.3	122.3	207.8	380.1	6.694
10/01/23 15:00	-2.266	75.08	626.9	126.5	208.6	386.6	8.71

‘ – ‘ = No data

Appendix 13: ANOVA and Tukey's HSD results

Water heavy metal comparisons

Tukey's HSD comparisons and ANOVA from heavy metal concentrations in samples taken from the northern colony stream (P1 to P5) and the control stream (C1 to C5) at Cape Bird, Ross Island. Results in bold represent a statistically significant *p*-value of <0.05. ANOVA comparison is between the northern colony stream and the control stream.

Sites	Arsenic	Cadmium	Lead
P1-P3	**<0.001**	**0.022**	**<0.001**
P1-P5	**0.001**	**<0.001**	**<0.001**
P3-P5	0.997	0.057	0.611
C1-C3	0.999	1.000	0.978
C1-C5	0.999	1.000	0.974
C3-C5	1.000	1.000	1.000
P1-C1	0.996	0.997	0.987
P3-C3	**<0.001**	**0.004**	**<0.001**
P5-C5	**<0.001**	**<0.001**	**<0.001**
ANOVA	**<0.001**	**<0.001**	**<0.001**

Water nutrient comparisons

Tukey's HSD comparisons and ANOVA of nutrient concentrations from samples taken from the northern colony stream (P1 to P5) and the control stream (C1 to C5) at Cape Bird, Ross Island. Results in bold represent a statistically significant *p*-value of <0.05. ANOVA comparison is between the northern colony stream and the control stream.

Sites	Nitrate	Phosphate	Ammonium
P1-P2	0.998	**0.039**	1.000
P1-P3	**0.001**	**<0.001**	**<0.001**
P1-P4	**<0.001**	**<0.001**	**<0.001**
P1-P5	**0.002**	**<0.001**	**<0.001**
P2-P3	**0.019**	**<0.001**	**<0.001**
P2-P4	**<0.001**	**<0.001**	**<0.001**
P2-P5	**0.029**	**<0.001**	**<0.001**
P3-P4	0.289	1.000	0.817
P3-P5	1.000	1.000	0.987
P4-P5	0.215	0.980	1.000
C1-C2	1.000	1.000	1.000
C1-C3	1.000	1.000	1.000
C1-C4	1.000	1.000	1.000
C1-C5	1.000	1.000	1.000
C2-C3	1.000	1.000	1.000
C2-C4	1.000	1.000	1.000
C2-C5	1.000	1.000	1.000
C3-C4	1.000	1.000	1.000
C3-C5	1.000	1.000	1.000
C4-C5	1.000	1.000	1.000
P1-C1	1.000	1.000	0.243
P2-C2	0.896	**0.030**	0.215

Sites	Nitrate	Phosphate	Ammonium
P3-C3	**<0.001**	**<0.001**	**<0.001**
P4-C4	**<0.001**	**<0.001**	**<0.001**
P5-C5	**<0.001**	**<0.001**	**<0.001**
ANOVA	**<0.001**	**<0.001**	**<0.001**

Water heavy metal and nutrient load comparisons

ANOVA of heavy metal and nutrient loads from samples taken from northern colony stream site P3 and control stream site, at Cape Bird, Ross Island. Results in bold represent a statistically significant *p*-value of <0.05.

Sites	Arsenic	Cadmium	Lead	Ammonium	Nitrate	Phosphate
P3-C3	**0.013**	**0.030**	**0.018**	**0.011**	**<0.001**	**0.003**

Soil heavy metal and nutrient comparisons

Tukey's HSD comparisons and ANOVA of heavy metal and nutrient concentrations in ornithogenic (P4) and non-ornithogenic (P0 and C5) soil samples at Cape Bird, Ross Island. Results in bold represent a statistically significant *p*-value of <0.05.

Sites	Arsenic	Cadmium	Lead	Ammonium	Total Carbon	Total Nitrogen
P0-C5	0.976	0.989	0.458	1.000	1.000	1.000
P4-C5	**0.030**	0.065	**0.029**	**<0.001**	0.103	0.128
P4-P0	0.051	0.091	0.415	**<0.001**	0.055	0.071
ANOVA 1	**0.0106**	**0.027**	**0.031**	**<0.001**	**0.029**	**0.041**
ANOVA 2	**<0.001**	**<0.001**	**0.005**	**<0.001**	**0.003**	**0.005**

ANOVA 1 = Comparisons between all three sites, ANOVA 2 = Comparison of ornithogenic soil (P4) vs non-ornithogenic soils (P0 and C5).