PCAS 15 (2013/2014)

Supervised Project Report

(ANTA604)

Heavy metal concentrations in feathers of the Adélie Penguin and the South-Polar Skua from Cape Royds, Ross Island.

Stephanie de Hamel

67130698

Post-Graduate Certificate in Antarctic studies

Gateway Antarctica, University if Canterbury

2013/2014

Word count: 6681

Abstract:

Using chemical analysis to detect traces of heavy metals is a popular technique in the science community. In this report, ICP-MS was used to analyse a sample of feathers from both Adélie Penguins and South-polar Skuas from Cape Royds, Ross Island. These two Antarctic bird species are important parts of the southern ocean ecosystem and food web, and understanding the heavy metal accumulation in these predators gives insight into the whole system of the Ross Sea. The results from this paper show that there was a significant difference in the concentrations of Al, Hg, As and Mn between the Adélie feathers and the Skua feathers (P<0.05). The higher trophic feeding level of the Skua explains the bioaccumulation of the Hg and As, but these two metals are also highly toxic to organisms in high levels. Aluminium levels were significantly higher in the Adélies and this is attributed to unsuccessful washing of the feathers and the fact that the Adélies spend more time on the ground were the Aluminium is able to stick to their feathers. Manganese is not as toxic as the other metals and is of less worry, but again, this was seen in higher levels in the Adélies and again could be attributed to possible higher levels in the soil of Cape Royds. Other metal results are compared to baseline data set in other papers in Antarctica and around the world for seabirds.

Contents

Abstract: 2

Introduction: 4

Cape Royds: *4*

Bird species: *5*

Heavy metal contaminants: *7*

Research Questions and Hypotheses: *8*

Methods: 8

Results: 9

Discussion: 10

Methodological limitations and comments: *10*

Heavy metal concentrations: *11*

The future of this research: *16*

Conclusion: 17

Acknowledgments: *17*

References: 18

Appendix: *21*

Introduction:

Antarctica is often seen as the last pristine environment on earth with little human activity before the early 1900s when seal and whale hunting as well as exploration of the continent became popular. The International geophysical year (IGY) in 1958-59 allowed scientists to visit the continent for a collaborative global research effort and during this year, bought over 5000 people to 55 stations around both the continent and the sub-Antarctic islands (Bargagi 2008). Since then, human influence on the continent has been increasing with tourism and science allowing an increasing number of people to visit. The Antarctic protocol on environmental protection was set in place to ensure that the environment is protected and human activity is regulated in both the terrestrial and the marine environment in order to ensure that these are not degraded or damaged in irreversible ways. Antarctica is surrounded by many natural barriers that keep it isolated, for example the circumpolar current, atmospheric circulation and its distance from other land masses, and these have protected it from a lot of direct pollution that effects other continents (Bargagi 2008). As the southern hemisphere grows in both its population size and its industrial scale, it is likely that polluting effects will spill over into Antarctica. Unfortunately it has already been shown to have happened with several anthropogenic contaminants being found in the environment through both long range transport and direct transport from human settlement on the continent (Bargagli 2008, Jerez *et al* 2011, Szefer *et al* 1993b)

Cape Royds:

Cape Royds (166°09'56"E, 77°33'20"S) is located on Ross Island on an ice free area on the coast line that is approximately 8km long *(Image 1).* This area is marked by the Antarctic treaty as an Antarctic specially protected area (ASPA) due to the fact that it holds the most southerly Adélie penguin rookery in Antarctic and also is the location of Shackleton's historic hut (ATCM 2005). Cape Royds is a popular penguin study area for scientists from the two closest stations (New Zealand and America) and is a common stopover point to see the penguins for tourist vessels coming ashore on Ross Island (ATCM 2005). The ASPA allows visitor numbers to be limited each season to keep the human influence to a minimum. In the past, this system did not exist and the areas was home to both the American station's waste dumping site and Shackleton's hut which lies just 170m to the north of the main penguin roosting area (and is still located there) as well as a small permanent depot just within the penguin nesting area (ATCM 2005). The marine area just beyond the cape is also protected as it was shown it was a significant penguin feeding ground that the birds forage in.

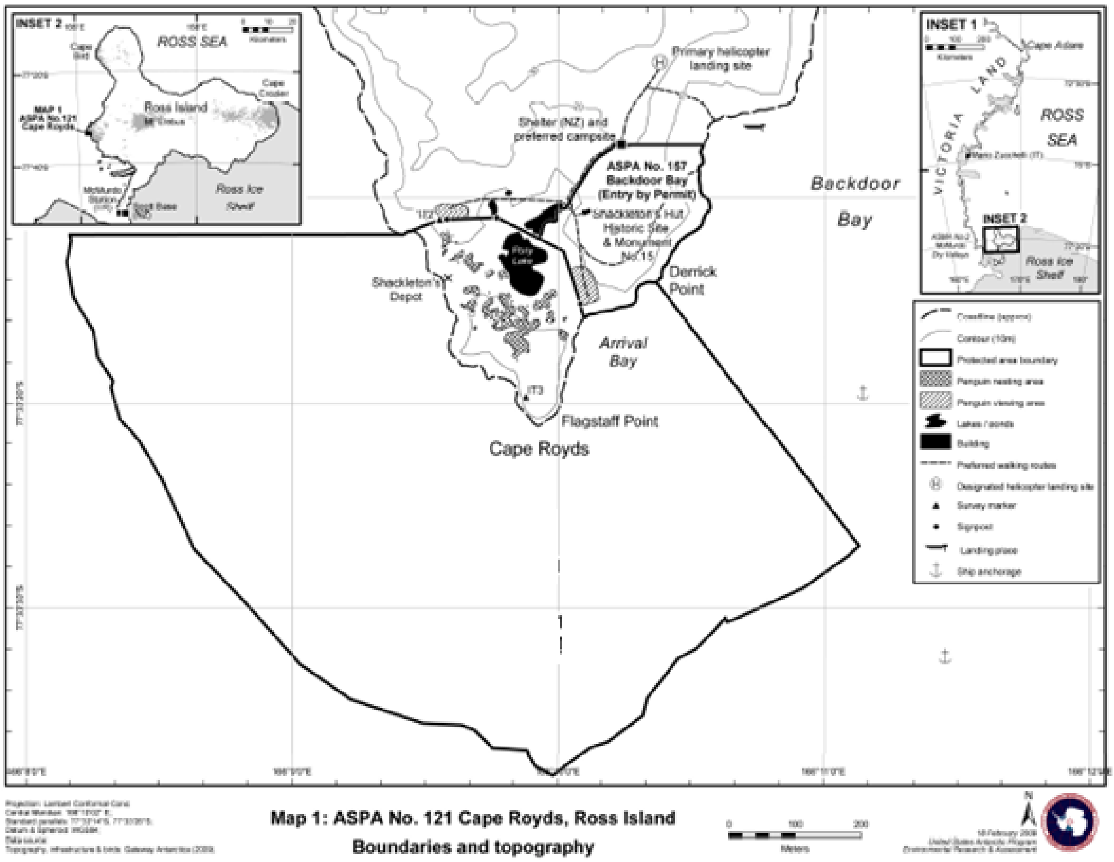

Image 1: Cape Royds and its location on Ross Island. Penguin areas located in grey stripes. The feathers were collected around the hut area located on the map. Taken from the management plan for ASPA No. 121, Cape Royds, Ross Island.

Bird species:

The two species of birds that breed at Cape Royds are the Adélie penguin *(Pygoscelis adeliae)* and the South Polar Skua (*Stercorarius maccormicki*) *(Image 2, 3 & 4).* These two bird species are commonly seen around the fringe of continental Antarctica and the Sub Antarctic islands (Eklund 1961, Ainley *et al* 1986, Ainley *et al* 2004). The Adélie penguin has a long life span of around 10 years and roost in large rookeries on snow free land. The most southerly of these rookeries is located at Cape Royds, where the samples for this study were taken from, and between 2,500 and 4,500 pairs nest there depending on the extent of the sea ice (Ainey *et al* 2004). The penguins feed mainly on Krill, Antarctic silverfish, squid and a few other small fish species and do not travel very far from the breeding and nesting ground to feed. (Ancora *et al* 2002, Cherel, 2008). The South Pole Skua is a carnivorous scavenger who preys mainly on Antarctic silverfish *(Pleuragramma antarcticum*) as well as the eggs of Adélie penguins and the young penguins themselves, and will usually try to eat anything they can including rubbish, seal placenta and their own young (Trillmich 1978, Young 1963). Because the penguins are a major source of food for the Skua during the nesting season, the breeding grounds for these two species are often very close in distance reflecting the tight predator-prey coupling (Eklund 1961). Skuas have been found as far afoot as New Zealand before (In four cases showed in C. R Eklund's 1961 paper on the distribution and life history studies of the south-polar Skua) but most commonly have a distribution south of the Antarctic convergence and usually do not travel great distances for their food sources, especially during the Adélie breeding season where they travel in small half day trips out to forage at sea (Young and Millar 1999).


Image 2 and 3: The Adélie penguin (Pygoscelis adeliae) and the South Polar Skua (Stercorarius maccormicki. Adélie picture is the authors own, and Skua picture taken from Google images.

Image 4: South-polar Skua flying over nesting Adélie penguins at Cape Royds penguin rookery, Ross Island. Photo taken from USAP photo gallery. (Google images)

Heavy metal contaminants:

Since science has started to understand how anthropogenic substances move around the world, there has been increase in the focus of research into the effect that these substances and other human-made pollution may have on the natural environment and the animals living in it. Seabirds have been used widely as vectors for monitoring the bioaccumulation of contaminants in the environment as they tend to be the top of food chains and are easily accessible and widespread around the world (Bortolotti 2010). The bulk of research on seabirds from Antarctica is done in the Antarctic Peninsula area and research there has found that there is in fact levels of contaminants in the tissues of animals similar to those seen in other polluted areas of the world (Jerez et al 2011).

Bioaccumulating metals are of great importance to look into for this sort of research as these metals often multiply in concentration as they move up the food chain potentially causing detrimental toxic effects to top-of-the-chain predators. The southern ocean is a known areas of great nutritional upwelling and this (as well as run-offs from the terrestrial environment) causes surges of nutrients and metals to enter the ecosystem. Of greatest importance to monitor is those heavy metals entering the system through anthropogenic factors. The human presence around McMurdo Sound is ever increasing and the use of metals and technological equipment and the associated waste may be having serious implications into the ecosystem. Heavy metals that cause severe toxic effects such as mercury and lead are especially important not only to ensure the health of local wildlife but also the health of the humans that live at the bases (Bhattachaya et al 2007, Furness et al 1986). Waste dumps and sewage run off could be introducing heavy metals in great quantities into the water ways.

Since Antarctica is relatively untouched through direct anthropogenic impacts, it is important that baseline data for both the Adélie penguin and the South-polar Skua are set so that effects and changes in the future can be better assessed. The feathers gathered for this report and the analysis done on them should provide input into a baseline data set for the birds living at Cape Royds, although it should be mentioned that there is always differences between concentrations in these animals through influencing life history traits such as age, foraging and breeding cycle. Feathers are a non-invasive way to obtain animal material from birds but most research looking at the metal concentrations has been focussed on internal organs such as the liver or the excretion of the birds as these two show a much higher uptake of most metals that the bird is exposed too. Jerez et al (2011) looked at feathers of penguins around the Antarctic Peninsula and the metal concentration levels seen in them, and since Jerez et al (2011) has the largest range of metals tested for, it provides a useful set of data for us to compare this papers results too.

Research Questions and Hypothesis:

The samples collected were from a previous year's season (2009) and were left over from other experiments. The feathers will be used to address the central research question; *Are the trace metal concentrations found in bird feathers from Antarctica any higher than previous reports of these species and/or higher than other analogous areas around the world?* As well as addressing the question *Are trace metal concentrations higher in Skuas compared to Adélies from the same region?* It is hypothesised that the feathers will be of lower concentrations compared to other samples taken around the world due to Antarctica's relatively pristine environment but may be increased compared to any previous results taken on the continent due to increased human presence. The second hypotheses is that the Skua feathers will contain higher levels of metal concentrations than the Adélies due to the diet that they ingest.

Methods:

The feathers had been previously collected during another season and were on hand for our use. A small sample set of around 3g of Adélie feathers were taken from each sample container (approximately 10 feathers). These were placed in a tin container and covered in pure water. The feathers were then mixed around gently using tweezers so as to cover the feathers and remove any dirt that was stuck on them. They were allowed to sit in the water for approximately 10 minutes and then stirred again to remove more dirt. When no more obvious dirt was dropping off the feathers, they were removed one by one and placed onto a dry paper towel to soak up excess water. When all feathers from one set had been removed, they were then placed into a tube using tweezers, sealed and labelled. This was done to three penguin feather sets and then these were put aside. The Skua feathers followed a similar method. A subset of around 10 feathers was removed from the original sample. These were then placed in a tin container of pure water and mixed around gently to remove any excess dirt that was on the feathers. These were then removed using tweezers and placed on a paper towel to dry. Once dried, these were then placed in a single tube. The Skua feathers were too large to fit into the tube and seal it, so the tube was left without its lid on and instead placed in a plastic zip lock bag to prevent the feathers from being contaminated or lost during the next stage. This next stage involved drying the feathers at a temperature of 35 C° for 24 hours. This low temperature was used to avoid destroying any trace chemicals in the samples.

Each tube of feathers was then weighed in order to get the total weight of the feathers that was taken from the original sample. From these weights, it was determined that 1.5g from each of the penguin feather samples would be taken, and 2 Skua feathers of 0.4g each would be taken. A sample of feathers around these weights was then transferred into a new tube set including a repeat set of the Skua feathers and a repeat set of one of the penguin feather sets. The Skua feathers proved difficult to fit into the tube, so they were hygienically broken in half and then placed into the tubes. The remainder was discarded properly. This provided us with 6 tubes of feather material, and along with this, a certified reference material (CRM) for human hair was also added into a tube, as well as two blank sets for both the Adélie and the Skua feathers.

These nine sample tubes were then divided into two groups. One with all the penguin feathers, the CRM and the blank for the penguin feathers, and the second with the Skua feathers and the blank for the Skua feathers. The first group had 2ml of concentrated nitric acid pipetted into each tube and following that, 0.5ml of HCl solution was also added into these tubes. These were then shaken around and left to sit for an hour in 85 C° to digest. The second group had double the solution added to it as it was suspected that the Skua feathers would not dissolve as easily. The solution added was therefore 4ml of nitric acid and 1ml of HCl and these were also shaken around and left to sit for 1 hour at 85 C°. After cooling, a 0.1% cysteine solution was added to the tubes to make the solution up to 5.4ml. This was added to ensure that the mercury was stabilised in the solution. The tubes were then analysed by inductively coupled plasma-mass spectrometry (ICP-MS) for a range of metals including aluminium (Al), antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), vanadium (V) and zinc (Zn).

The results were collected, put into an excel spreadsheet and converted to ug/g to compare and analyse. Statistical analysis for significant differences was done using SPSS performing a one way ANOVA test to produce results.

Results:

The European reference material was used to assess whether the analysis was working accurately. The results from the seven analytes used (As, Cd, Cu, Hg, Pb, Se and Zn) showed varying results. To assess accuracy, a margin of 25% was given (75-125%). Zn, As and Hg all showed results below or above this range. Cu, Cd and Pb all fell within the 25% range with Cd being the closet to 100% similar (Table 1). Se was not assessed during these trials as the ICP-MS did not test for this.

Material:	Cu	Zn	As	Cd	Se	Hg	Pb
Reference Material value (mg/kg)	33	209	0.044	0.125	3.24	0.365	2.14
Measured value (mg/kg)	25.551	130.31	0.0648	0.1361	-	0.2427	1.6621
Percentage similarity	77.427%	62.348%	147.28%	108.89%	-	66.488%	77.666%

Table 1: Table showing the comparative results of the reference material used during the testing.

The raw results showed that Al, V, Cr, Fe, Mn, Fe, Co and Pb were overall higher in the Adélie feathers than the Skua feathers. The metals Ni, Cu, Zn, As, Cd, Sb and Hg were on average higher in the Skua feathers (Table 3 in the appendix). The Skua and the Adélie feathers were compared using a One-way ANOVA in SPSS. The metals Cd, Cr, Co, Cu, Fe, Ni, Pb, Sb, V, and Zn all returned a statistical difference of greater than 0.05 ($p>0.05$) and therefore were not classed as significant differences (Table 2 in appendix). Al, Mn, As and Hg all returned statistically significant results of $p\leq0.05$. Al showed a significance of 0.044, Mn showed a significance of 0.042, As showed a significance of 0.020 and finally Hg showed a significance of 0.007 (Table 2 in appendix). Hg therefore had the highest difference between the Adélie and the Skua feathers with the Skua results much higher than the penguin.

Discussion:

Methodological limitations and comments:

The feathers collected and used for this testing were collected at Cape Royds next to Shackleton's hut. The feathers were in clumps and were from last season's moult. This leads us to a few problems in our sampling. The feathers might not have been from one individual bird and the penguin(s) and Skua(s) in question are of unknown age. Age is an important factor in the assessment of bioaccumulation of heavy metals as it can give insight into the rate of accumulation into the body and into the feathers and this is discussed below (Bortolotti 2010). The mixed feathers were assessed together in the analysis which may have led to other problems. As well as not knowing the age, we may have mixed multiple individuals feathers together to analyse. This does lead to an upside though in that we may have accidentally analysed a subset of the population and therefore got a good estimate of the overall population's trace metal concentrations. The feathers were also collected in 2009 and were possibly from the previous seasons moult, meaning that the data that we have obtained may in fact be around 6 years old and may not reflect the current state of the environment or the birds living there.

The results themselves may be unreliable to assess. The CRM results returned were not all within the ranges acceptable and therefore the results that were acquired through the analysis are not trustworthy and any should be taken with caution. During this report, the results are discussed as they have been recorded.

G. R. Bortolotti (2010) discussed the pros and cons of using feathers for chemical analysis. Feathers provide a good sample for scientist to use as it is not invasive and does not kill the animal being worked on. Bortolotti states that chemical analysis on the feathers "creates artifacts by ignoring the physiology of the feathers ", and goes on to say that "feathers are merely receptacles, and deposition of chemicals is time dependent" throwing a spanner into the works of feathers as an effective tool for chemical analysis. He continues on to discuss the difference in chemical make up between the different types of feathers on the bird as well as the difference in chemicals within the same feather from the shaft of the feather to the tip. As our feather types were unknown moulted types that were analysed as an entire feather, again this proves problematic.

The other issue that may have contributed to our results was the inefficient washing technique used to clean the feathers before analysis. Adélie feathers are small and fluffy while the Skua feathers were long and rigid meaning that the Adélie feathers were rather difficult to wash. The feathers were just washed around in pure water for a few minutes to remove excess dirt, but the high levels of Al and Mn, both of which are found in soil, leads me to believe that the Adélie feathers were not cleaned of the soil properly especially since the levels of Mn seen in the Adélie feathers are over 3000 times higher than those seen by in Antarctica by Szefer et al (1993a), Jerez et al (2011) and Honda et al (1987), and that the levels of Al seen were over 6000 times what Jerez et al (2011) found in the Adélie feathers.

Heavy metal concentrations:

The raw results showed that on average, Adélies showed higher concentrations of Al, V, Cr, Fe, Pb, Mn, Co and Sb, while higher results were seen in Skuas for Ni, Cu, As, Cd and Hg. Since the Skua's are at a higher trophic level than the Adélie penguins and directly feed on them, the heavy metals that are not higher in the Skuas are likely not due to bioaccumulation through the food chain. These heavy metal concentrations are more likely due to the environment that they nest in and the poor removal of soil and waste from the feathers. Comparing to past research on the feathers backs this possibility up. The results were gained for some of these metals were magnitudes higher than the previous results found for these feather types around Antarctica, For example, Fe for Adélies in our sample averaged 651.73ug/g while Jerez et al (2011) found a range between 23.37 and 59.74ug/g, and our Pb levels showed an average of 6.9171 while Jerez et al (2011) found between 0.14 and 0.64ug/g. Jerez et al 2011 found levels of metals in the order of Zn > Fe > Al > Cu > Se > Cr > Mn > Ni > Pb > As > Cd, while our results showed Al> Fe > Zn > Mn > Cu > Pb > V > Cr > Ni > Hg > Co > As > Cd > Sb. There is some differences here in the ordering and this will be discussed below.

Mercury (Hg) levels were significantly higher in Skua feathers than Adélie feathers. The raw data showed that the Skuas had an average Hg level of 1.47ug/g while the Adélies showed an average of 0.59ug/g. Mercury is a metal that has had great scientific effort put into the research for its bioaccumulation as it tends to pass through the food chain of animals, in this case, the southern ocean food web, as it is taken up by the fat tissues in animals and when said animal is preyed upon the Hg is taken up by the predator. Because of this, predators often have over 10 times more Hg in their tissues than the trophic level below them (Furness et al 1986, Hutchinson & Meema 1988). It therefore makes sense that the Skua has a higher level of Hg than the penguin as the Skua feeds at trophic levels higher than the Adélies. The Hg levels in the feathers could have also been affected by the time that the feathers were moulted in relation to the entire moult cycle. Furness et al (1986) showed that feathers moulted earlier in the moulting season often contain higher levels of Hg in them compare to the feathers moulted later in the season. Unfortunately, the timing of the moult for these samples is not known. Hg can be damaging in high levels in the tissues of animals and it is important that the results are not at toxic level (Braune 1987, Burger & Gochfeld 1997). Ancora et al (2002) found that the Hg levels were expressed at the highest levels in the feathers of the Adélies compared to other tissues so it is possible to say that the levels that we see here may not be representative of all the tissues of each animal. Previous studies have also shown that the levels of metal such as Hg and Pb in feathers are more related to the concentrations seen in the blood of the bird (Burger & Gochfeld 1990; Monteiro & Furness 2001, Seco Pon et al 2011). Hg bonds to feathers mostly during the formation of the feathers where it binds to the matrix and during its life, is not able to leech out of the feather, this causes the levels in the feathers to express around 60-70% of the total body concentration (Honda et al 1986). Death due to Hg poisoning is often seen at levels of more than 40ug/g and industrially polluted areas usually contaminate at around 17ug/g and using the knowledge of the amount feathers hold, we can say that anything higher than 10ug/g seen in the feathers should warrant worry (Scheuhammer 1987). Our results for Adélies showed levels of less than 1ug/g so is not near the levels where this will become toxic to the animals, and the levels seen in the Skuas were around 1ug/g which is lower than the levels that Bargagli (2008) found In their Skua feathers (of around 2ug/g) which is similar to those levels seen in birds of the Northern hemisphere. It is therefore possible to say that the levels of Hg in the system are low, and warrant no serious concern.

Antimony (Sb) is a naturally occurring metal that also has many anthropogenic uses although it is not known to have any biological function. Sb in high dosages can be toxic and expresses similar damaging effects to As. Sb is found in rock types, including Basalt rocks and clays, both of which are commonly seen on the Antarctic continent as well as in the ocean (Filella et al 2002). Sb, to my knowledge, has not been assessed in the feathers of Skuas or Adelies in the Antarctic and this data can thereby work as a baseline for future research. High concentrations of Sb are usually directly associated with a smelting plant, but since there is no such activity on the Antarctic continent is concluded that Sb has not entered the system this way (Filella et al 2002). There is no evidence for Sb bioaccumulation in an ecosystem through a food web (even in a directly contaminated food source) so this gives evidence to the fact that our levels of Sb in Adélies that were higher than those seen in the Skua (although not to a significant level) could be factual (Ainsworth et al 1990). Tissue samples for Sb usually show results of less than 1ug/g, and indeed, ours are much lower than this and even ocean algae shows levels of Sb higher than those seen in the feathers from our results (Fergusson 1990, Fiella et al 2002). It is therefore concluded that these levels seen are not of a dangerous range and in fact are much lower than those seen around the world and have probably been recorded from attached soil to the feathers.

Lead (Pb) has been a chemical that has been focussed on extensively in Antarctic research. Since human base establishment, lead has been an increasing worry for environmental contamination especially in somewhere such as Antarctica. Scheuhammer (1987) noted that females accumulate Pb at much higher rates than males of the same species and this could be a problem for our sampling as the genders of the feathers were not known. The results seen in this paper are not of significant difference between the Skuas and the Adélie penguins showing that it is likely that there is little influence from the nearby McMurdo station in influencing the Pb levels in Skuas who are known to forage for food there.

Arsenic (As) is a bioaccumulating metal that can have toxic effects at high levels (Pande 2010). It can enter the biological system through both natural and human activities. Natural processes including rock weathering and erosion and anthropogenic uses including mining, sewage, wood preservation and fertilizer can cause As to enter either the earth’s atmosphere or as a terrestrial deposition (Scheuhammer 1987, Sarkar 2002). Since it is a bioaccumulating substance, we expect it to be higher in the Skua who feeds at a higher trophic level and indeed this is what has been recorded in our results producing significant differences between the Adélies and the Skua feathers. As found by

Jerez et al (2011) was over 300 times lower than the results that we gained. This could be due to inappropriate handling of the samples, but may also point to a larger issue and should be investigated further using more appropriate techniques especially since there were significant differences seen.

Aluminium (Al) is efficiently removed by bird's excretion systems and only a small amount is stored in the body. Significant differences were found between the Skua and the Adélie for Al, with the Adélie having larger concentrations in the feathers. Excessive amounts of Al do not directly affect the bird but can alter the homeostasis of other elements in the body (especially calcium) and cause malfunction, but overall has a low potential toxicity (Scheuhammer 1987). Bone shows the greatest concentration in birds for Al and levels above 10ug/g are very high and indicate and elevated intake of Al. Since our results were in the 100s and 1000s of ug/g it points to a problem in the experiment rather than high levels of Al in the birds (Scheuhammer 1987). Al is often found in the soils and dust around Antarctica and it is instead proposed that the excessive high levels of Al found in Adélies are because of inefficient washing of the samples especially since the harder to wash Adélie feathers were the ones showing the elevated levels.

Manganese (Mn) levels showed a significant difference between Skuas and Adélies. Mn is associated with the making of iron and steel and is also found in natural levels in the soils and rocks in Antarctica. The levels seen in the Adélies were significantly higher than the levels seen in the Skua feathers with the Skuas averaging 13.803ug/g and the Adélies averaging 36.861ug/g. Burger & Gochfeld (1993) showed that the levels of Mn differ significantly in the age groups of birds, and since the age of the feathers is unknown, this could have altered the results if the Adélie feathers were from chicks rather than adults. The levels seen by Jerez et al (2011) are over 3000 times lower than the levels seen in our samples with the average of their Adélie feather levels being 0.9333ug/g. Because of the massive difference seen between the results here and Jerez et al (2011) it is proposed that similar to Al, these samples have been contaminated during the analysis. Since Mn is found in the soils of Antarctica, it is assumed that the contamination has entered the sampling through inefficient washing before the analysis took place.

Zinc (Zn) and Copper (Cu) results were both very similar to those seen by Jerez et al (2011) with Zn showing almost identical results and Cu showing only slightly higher (25% higher). This indicates that the readings for these metals were likely accurate, and therefore the insignificance found between the Skua and the Adélie results is also likely correct. The levels of Cu here are slightly higher than those seen around the world in places such as China and South America. Cu is an important metal in the formation of feathers and coastal marine birds often have higher levels of Cu than terrestrial based birds, that combined with the fact that Krill (A major food source in the southern ocean) contain large quantities of Cu, the concentration of Cu are not of a potential threatening level, and could in fact be a good metal for using as an indicator for changes in the krill abundance in the southern ocean (Jerez et al 2011). Similarly, Zn levels are again higher than other seabirds around the world but Jerez et al (2011) suggested that these levels seen are instead an adaptive reaction to elevated Cd and Hg levels that can be found in the southern ocean ecosystem since Zn is known to reduce the toxicity of these (Jerez et al 2011, Norheim 1987, Underwood et al 1977)

Nickel (Ni) and chromium (Cr) both produced lower results in this report compared to the results seen in Adélie feathers by Jerez et al (2011). Since these two are lower, it is not likely that they were altered by the possible soil attachment on the Adélie feathers and that the insignificance between the two feather types may be correct. Ni is introduced to the environment through landfill run-off, incineration, coal combustion and fuel burning, and Ni levels in ocean water and much lower than those seen in water run offs, suggesting that the low levels seen are representative of lack of directed sewage deposition onto the land and surrounding ocean. Cr is most often used by humans as a metal alloy for steels, as well as the leather tanning industry but most of the industrial Cr release is through waste incineration (Sarkar 2002). The low levels of Cr seen here indicate that Cr is not an effective atmospheric traveller and has not reached dangerous concentrations in the Antarctic ecosystem.

Cadmium (Cd) is another metal that has a lot of scientific interest. Cd is found naturally in the rock and soil systems, and in volcanic rock systems such as Antarctica. Anthropogenic uses include planting, fertilizers and tobacco and is a by-product of fossil fuel burning (Sarkar 2002). Atmospherically, Cd is released through incineration of waste and household items and particles are known to travel long distances and contaminate waters and sols far from emission release areas (Steinhagen-Schneider 1986). Cd accumulation has had a lot of research in Antarctica and its high bioavailability of well documented in this system (Jerez et al 2011). Krill, a keystone species in the southern ocean food web, are known to have high levels of Cd in their system and higher bird species of the Antarctic often reflect this in their tissues (Barbante et al 2000). The levels here were not of significance between the Skua and the Adélies but the Cd levels are 400 times higher than those seen by Jerez et al (2011) and similar to many of the metals here, may be because of the lack of efficient cleaning. The long biological half-life (20 years in humans) is of concern and the age of the animals of who the feathers were taken is essential to know in order to assess whether the Cd concentrations are of importance (Sarkar 2002).

Cobalt (Co) and Vanadium (V), have not been assessed in Adélie or Skua feathers before but the levels seen were similar to what has been seen previously in the muscles of penguins (Szefer et al 1993b). The results were insignificant between the two species so therefore lends itself to be a baseline data set. Although there has been little data published on these two metals, results from Ansara-Ross et al (2013) on owl species found that V had a level of 0.268ug/ g and our results showed levels on average of 1.4705ug/g for Adélies and 0.9676ug/g for Skuas. Co levels shown in other birds of prey species are around 0.1ug/g while our levels showed 0.2315 and 0.4774ug/g for Skuas and Adélie respectively (Dauwe et al 2003). Dauwe et al (2003) also found that there were significant differences between the type of feather used and the resulting Co levels and without knowing the feather types for the samples we used, we are unable to compare these further.

Finally, iron (Fe) levels seen in our results were magnitudes higher than previously seen. Since Fe is a common element in rocks and soils, especially volcanic ones, it is assumed like the other elements that the incredibly high concentrations seen here are because of inefficient washing. Although the differences were insignificant, the levels seen in the Skua feathers were slightly lower, and were closer to the levels seen by Jerez et al (2011). This again gives evidence to the fact that these levels are due to soil contamination.

The future of this research:

There is little data for the metal concentrations in the bird populations around McMurdo Sound. Most of the research has been done in the Antarctic Peninsula and more attention needs to be paid to areas such as Cape Royds in order to establish baseline data or to discovery excess metal concentrations. Metals that are related strongly to anthropogenic inputs should be studied intensely and more emphasis should be placed on those metal which have had little research done on them in this area such as Co, Sb and V. The handling of the samples was detrimental to some of the results and if this testing is repeated, more care should be taken to ensure this does not happen again. Finally, results would show a much better picture of the concentrations if individual penguins or skuas were sampled and a variety of tissues was sampled so that the demographic data could also be factored in to the results.

Conclusion:

Concluding this report, we are able to say that the levels of heavy metals in the feathers if these two bird species (Adélie penguin and the South-polar Skua) are overall not higher than levels in other areas of the world. Cr, Ni, Cu, Zn and Pb are the metals known to travel atmospherically from the southern hemisphere to Antarctica and since the levels seen in these were of no significance, we can conclude that at the moment, this is not causing excess metal build up in the local bird wildlife, but increases in industrialism and population could increase the potential contamination in Antarctica (Jerez et al 2011, Bargagli 2008). In fact, the metals that bio-accumulate through the system and are not greatly affected by inefficient washing before testing, are at lower levels than seen in the Northern hemisphere and lower then levels seen on the Antarctic peninsula. This answers our original question, *Are the trace metal concentrations found in bird feathers from Antarctica any higher than previous reports of these species or and higher than other analogous areas around the world?*

Secondly, the metals that are known to bio-accumulate did in fact show up in higher concentrations in the higher trophic level species, the South-polar Skua an the metals that did not show up higher in the Skua are suspected to be more associated to the environment in which the feathers were collected and the inefficient removal of excess soil before testing. This therefore answers the second of the research questions outlined at the start of this report *Are trace metal concentrations higher in Skuas compared to Adélies from the same region?*

Acknowledgments:

Thank you to Sally Gaw for her supervision and guidance throughout this report, the Chemistry department for the use of their facilities, the Gateway Antarctica team for the opportunity to work on this project and Phil Emnet for the collection and allowed use of the feathers.

References:

ATCM (2005) Management plan for Antarctic specially protected area (ASPA) No. 121, Cape Royds, Ross Island. Retrieved from http://www.nsf.gov/geo/plr/antarct/aca/nsf01151/aca2_spa121.pdf

Ainley, D.G., Morrell, S.H. & Wood R. C. 1986. South Polar skua breeding colonies in the Ross Sea region, Antarctica. Notornis 33(3): 155–63.

Ainley, D.G., Ribic, C.A., Ballard, G., Heath, S., Gaffney, I., Karl, B.J., Barton, K.J., Wilson, P.R. & Webb, S. 2004. Geographic structure of Adélie penguin populations: overlap in colony-specific foraging areas. Ecological Monographs 74(1):159–78.

Ainsworth, N., Cooke, J.A., Johnson, M.S., 1990. Distribution of antimony in contaminated grassland: 2. Small mammals and invertebrates. Environ. Pollut. 65, 79–87.

Ancora, S., Volpi, V., Olmastroni, S., Focardi, S., & Leonzio, C. (2002). Assumption and elimination of trace elements in Adélie penguins from Antarctica: a preliminary study. Marine Environmental Research, 54(3), 341-344.

Ansara-Ross, T. M., Ross, M. J., & Wepener, V. (2013). The use of feathers in monitoring bioaccumulation of metals and metalloids in the South African endangered African grass-owl (Tyto capensis). *Ecotoxicology*, *22*(6), 1072-1083.

Barbante, C., Cozzi, G., Capodaglio, G., Cescon, P., 2000. Trace element determination in a candidate reference material (Antarctic krill) by ICP-sector field MS. Journal of Analytical Atomic Spectrometry 15, 377e382

Bargagli, R. (2008). Environmental contamination in Antarctic ecosystems.Science of the total environment, 400(1), 212-226.

Bhattacharya, P., Welch, A. H., Stollenwerk, K. G., McLaughlin, M. J., Bundschuh, J., & Panaullah, G. (2007). Arsenic in the environment: biology and chemistry. Science of the Total Environment, 379(2), 109-120.

Braune, B. M. (1987). Comparison of total mercury levels in relation to diet and molt for nine species of marine birds. Archives of Environmental Contamination and Toxicology, 16(2), 217-224.

Burger, J., & Gochfeld, M. (1993). Heavy metal and selenium levels in feathers of young egrets and herons from Hong Kong and Szechuan, China. Archives of environmental contamination and toxicology, 25(3), 322-327.

Burger, J., & Gochfeld, M. (1997). Risk, mercury levels, and birds: relating adverse laboratory effects to field biomonitoring. Environmental Research, 75(2), 160-172.

Burger, J., Gochfeld, M., 1990. Tissue levels of lead in experimentally exposed Herring Gull (Larus argentatus) chicks. Journal of Toxicology and Environmental Health 29, 219e233.

Cherel, Y. (2008). Isotopic niches of emperor and Adélie penguins in Adélie Land, Antarctica. *Marine Biology*, *154*(5), 813-821.

Dauwe, T., Bervoets, L., Pinxten, R., Blust, R., & Eens, M. (2003). Variation of heavy metals within and among feathers of birds of prey: effects of molt and external contamination. *Environmental Pollution*, *124*(3), 429-436.

Eklund, C. R. (1961). Distribution and life history studies of the south-polar skua. Bird-banding, 187-223.

Fergusson, J.E., 1990. The Heavy Elements: Chemistry, Environmental Impact and Health Effects. Pergamon, Oxford, 614 pp.

Filella, M., Belzile, N., & Chen, Y. W. (2002). Antimony in the environment: a review focused on natural waters: I. Occurrence. *Earth-Science Reviews*, *57*(1), 125-176.

Furness, R. W., Muirhead, S. J., & Woodburn, M. (1986). Using bird feathers to measure mercury in the environment: relationships between mercury content and moult. Marine Pollution Bulletin, 17(1), 27-30.

Honda, K., Yamamoto, Y., Hidaka, H., & Tatsukawa, R. (1986). Heavy metal accumulations in Adelie penguin, Pygoscelis adeliae, and their variations with the reproductive processes. *Memoirs of National Institute of Polar Research. Special issue*, *40*, 443-453.

Honda, K., Yamamoto, Y., & Tatsukawa, R. (1987). Distribution of heavy metals in Antarctic marine ecosystem. In *Proc NIPR Symp Polar Biol* (Vol. 1, pp. 184-197).

Hutchinson, T. C., & Meema, K. M. (1988). Lead, mercury, cadmium and arsenic in the environment.

Jerez, S., Motas, M., Palacios, M. J., Valera, F., Cuervo, J. J., & Barbosa, A. (2011). Concentration of trace elements in feathers of three Antarctic penguins: geographical and interspecific differences. Environmental Pollution, 159(10), 2412-2419.

Monteiro, L.R., Furness, R.W., 2001. Kinetics, dose-response, and excretion of methylmercury in free-living adult Corýs Shearwaters. Environmental Science and Technology 35, 739e746.

Norheim, G. (1987). Levels and interactions of heavy metals in sea birds from Svalbard and the Antarctic. *Environmental Pollution*, *47*(2), 83-94.

Pande, S. P., & Deshpande, L. S. (2010). Arsenic in Aquatic Environment. Daya Publishing House.

Sarkar, B. (2002). Heavy metals in the environment. CRC Press

Scheuhammer, A. M. (1987). The chronic toxicity of aluminium, cadmium, mercury, and lead in birds: a review. Environmental Pollution, 46(4), 263-295

Seco Pon, J. P., Beltrame, O., Marcovecchio, J., Favero, M., & Gandini, P. (2011). Trace metals (Cd, Cr, Cu, Fe, Ni, Pb, and Zn) in feathers of Black-browed Albatross< i> Thalassarche melanophrys</i> attending the Patagonian Shelf. *Marine environmental research*, *72*(1), 40-45.

Steinhagen-Schneider, G. (1986). Cadmium and copper levels in seals, penguins and skuas from the Weddell Sea in 1982/1983. Polar Biology, 5(3), 139-143.

Szefer, P., Czarnowski, W., Pempkowiak, J., & Holm, E. (1993a). Mercury and major essential elements in seals, penguins, and other representative fauna of the Antarctic. Archives of environmental contamination and toxicology, 25(4), 422-427.

Szefer, P., Pempkowiak, J., Skwarzec, B., Bojanowski, R., & Holm, E. (1993b). Concentration of selected metals in penguins and other representative fauna of the Antarctica. Science of the total environment, 138(1), 281-288.

Trillmich, F. (1978). Feeding territories and breeding success of South Polar Skuas. The Auk, 95(1)

Underwood, E.J., Patty, P.C., Robertson, W.B., (1977). Evidence of heavy metal accumulation in sooty terns. Science of Total Environment 14,

Young, E. C. (1963). Feeding habits of the south polar skua Catharacta maccormicki. Ibis, 105(3), 301-318.

Young, EC and Millar, CD (1999) Skua (Catharacta sp.) foraging behaviour at the Cape Crozier Adelie Penguin (Pygoscelis adelia) colony, Ross Island, Antarctica, and implications for breeding. Notornis, vol. 46, pp. 287-297.

Appendix:

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
27 Al	Between Groups	936678.746	1	936678.746	8.390	.044
	Within Groups	446564.673	4	111641.168		
	Total	1383243.419	5			
51 V	Between Groups	.337	1	.337	1.134	.347
	Within Groups	1.190	4	.297		
	Total	1.527	5			
53 Cr	Between Groups	1.077	1	1.077	.629	.472
	Within Groups	6.854	4	1.714		
	Total	7.931	5			
54 Fe	Between Groups	267566.899	1	267566.899	6.603	.062
	Within Groups	162096.872	4	40524.218		
	Total	429663.772	5			
55 Mn	Between Groups	708.851	1	708.851	8.684	.042
	Within Groups	326.494	4	81.623		
	Total	1035.344	5			
57 Fe	Between Groups	652716.378	1	652716.378	6.767	.060
	Within Groups	385835.154	4	96458.789		
	Total	1038551.532	5			
59 Co	Between Groups	.081	1	.081	2.348	.200
	Within Groups	.137	4	.034		
	Total	.218	5			
60 Ni	Between Groups	.354	1	.354	2.548	.186
	Within Groups	.555	4	.139		
	Total	.909	5			
63 Cu	Between Groups	1.001	1	1.001	.227	.658
	Within Groups	17.604	4	4.401		
	Total	18.605	5			
66 Zn	Between Groups	4911.862	1	4911.862	147.983	.000
	Within Groups	132.768	4	33.192		
	Total	5044.630	5			
75 As	Between Groups	.169	1	.169	13.937	.020
	Within Groups	.049	4	.012		
	Total	.218	5			

111 Cd	Between Groups	.005	1	.005	6.134	.068
	Within Groups	.003	4	.001		
	Total	.009	5			
121 Sb	Between Groups	.004	1	.004	6.804	.060
	Within Groups	.003	4	.001		
	Total	.007	5			
201 Hg	Between Groups	1.006	1	1.006	25.829	.007
	Within Groups	.156	4	.039		
	Total	1.162	5			
208 Pb	Between Groups	16.946	1	16.946	1.367	.307
	Within Groups	49.595	4	12.399		
	Total	66.541	5			

Table 2: One-Way ANOVA results from SPSS for comparisons of the Adélie feather and the Skua feathers. Significance was considered if P<0.05. Significant results are coloured in green.

	Al	V	Cr	Fe	Mn	Fe	Co
Adélie 1	1674.878138	2.245391	0.575222	936.6496	49.47929	1452.617	0.714688
Adélie 2	768.8268525	1.030969	0.134088	381.0507	24.03942	597.1538	0.399414
Adélie 3	1375.690584	0.933167	0.130835	584.8215	36.00108	921.0906	0.265622
Adélie 4	1436.195644	1.672526	3.274043	704.4075	37.92331	1114.651	0.529716
Skua 1	489.5300438	0.785185	0.11587	189.6438	13.09235	297.7872	0.114445
Skua 2	461.9493566	1.150098	0.143729	217.8851	14.51464	345.6303	0.348491
CRM	10.52852519	0.006958	0.371357	9.72363	0.493057	15.81359	0.086902

	Ni	Cu	Zn	As	Cd	Sb	Hg	Pb
Adélie	0.751579	18.50298	68.6812	0.337947	0.203963	0.131944	0.573873	10.22912
Adélie	0.721491	17.99478	74.39007	0.173005	0.170815	0.081477	0.802048	6.759068
Adélie	0.50093	13.17027	63.59913	0.238513	0.20383	0.062598	0.487574	1.815119
Adélie	0.793747	16.20661	74.5365	0.320675	0.14695	0.087311	0.530883	8.864976
Skua 1	1.708776	17.02793	136.0252	0.747998	0.267314	0.027761	1.24719	1.257238
Skua 2	0.705012	17.64223	125.9685	0.499181	0.220582	0.037869	1.687455	5.446785

CRM	0.591604	25.55089	130.3065	0.064805	0.136112	0.070251	0.242681	1.662061

Table 3 (In 2 parts): The final results from the analysis. Results shown in ug/g of the element in each of the samples. 4 Repeats of Adélie feathers were done, and 2 repeats of Skua feathers. CRM results included for reference,